MODELING THERMODYNAMIC AND DIFFUSION PROPERTIES IN CONCENTRATED POLYMER SOLUTIONS

By

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ABSTRACT

MODELING THERMODYNAMIC AND DIFFUSION PROPERTIES
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A methodology for evaluating solvent activities in concentrated polymer solutions is proposed and demonstrated. This method allows the use of any expression for the residual (enthalpic) interaction between polymer and solvent, in conjunction with a Flory-Huggins expression for the combinatorial entropy, and an empirical free volume correction. The new method is applied using several choices for the residual term, including the Analytical Solution of Groups (ASOG) group contribution equations. When adjustable parameters are determined by best fit to data, results predicted by the method generally agree with observed data from 21 isothermal binary polymer-solvent systems better than results given by the Flory-Huggins model. When parameters are determined from a single data point at low solvent concentration and extrapolated to higher concentrations, a version of the new method agrees better with observed data than the Flory-Huggins model and better than the UNIFAC-FV model which uses no binary data.

Transformations of equations used by group contribution models to calculate the residual contribution to the activity coefficient are demonstrated. Using these transformations to allow more convenient analysis of the mathematical properties of the equations, bounds on the range of activity coefficients can be derived from incomplete data without knowledge of the interaction parameter values. The predicted values of activity coefficients are shown to depend on a normalization step implicit in the definition of functional group size.

Three alternative models for prediction of binary diffusivities in concentrated polymer solutions are compared: a complete free volume model, a linearized form of this model, and a constant diffusivity model. A method is presented for determining when the simpler models are appropriate for calculations. The linear model is convenient to use for determining the effects of the solvent activity coefficient on the diffusivity.

A new statistical technique is proposed and demonstrated for determining

whether a nonlinear data fit is systematically in error with observation. Unlike many statistical techniques, the new method is valid regardless of the distribution of the observed variables. It is capable of detecting complex patterns of systematic error not found significant by other statistical methods.

To my wife, Aimee, and to both our families,
who can now celebrate their first Ph.D. recipient.

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A_1, A_2	groups of parameters used in free volume diffusion model
A_{kl}	group interaction parameter for group k with group 1
a	coefficient of quadratic term
a_{kl}	temperature-independent part of the group interaction parameter for group k with group 1
a_{1exptl}	solvent activity
a_{1pred}	experimental solvent activity
a_{1S}	predicted solvent activity
a_1	entropic, combinatorial, or size interaction part of the solvent activity
B_{kl}	transformed group interaction parameter for group k with group 1
b	coefficient of linear term
b_{kl}	temperature-dependent part of the group interaction parameter for group k with group 1
C_{kl}	transformed group interaction parameter for group k with group 1
c	constant term
c_i	size-weighted fraction of component i in solution
D	binary mutual diffusion coefficient
D_0	preexponential constant in temperature-dependent factor of D
D_{01}	preexponential constant in free volume-dependent factor of D_1
D_1	self-diffusion coefficient of solvent
d	statistical degrees of freedom
d_i	difference between ϵ_i and T_i from observation i
e	base of the natural logarithm
E	critical energy per mole needed to overcome attractive forces
g_i	size-weighted ratio of group 2 to group 1 in component i
K_1	free volume coefficient in the linearized diffusivity model
K_{1i}, K_{2i}	WLF free volume parameters of component i
K_2	thermodynamic coefficient in the linearized diffusivity model
k	a nonnegative integer
M_i	molecular weight of component i
m	occurrences of the symbol - in the runs test
n	number of data points observed
n	occurrences of the symbol + in the runs test
n_{ki}	number of functional groups of type k in component i
p	pressure
R	gas law constant
R	random variable used in runs test
R_d	random variable used in sum square rank difference test

r	correlation coefficient
r	observed value of R in runs test
r_s	rank correlation coefficient
R_i^s	size term for component i
S_i	number of size groups found in component i
s	standard error
T	absolute temperature
T_{gi}	glass transition temperature of component i
T_i	temperature from observation i
V_{i*}^i	partial specific volume of component i
V_i^*	specific critical hole free volume of component i required for a jump
V_{FH}	average hole free volume per gram of mixture
v_i	molar volume of component i
w_{iexptl}	weight fraction of component i in solution
w_i	experimental weight fraction of component i in solution
x	independent variable
X_k	group mole fraction of functional group k in solution
x_i	mole fraction of component i in solution
Y	group of terms used in iteration procedure to determine Ω_1^∞ from data not at infinite dilution of solvent
Y_0	initial estimate of Y
Y_n	estimate of Y after n iterations
y	dependent variable
y_{ipred}	value of the dependent variable from observation i
y_i	predicted value of the dependent variable from observation i
Z	normally distributed random variable
z	observed value of z

Greek Letters

α	probability of rejecting the null hypothesis when it is true
ϵ_i	difference between predicted and observed value of the dependent variable from observation i
Γ_{ki}	functional group activity coefficient for group k in solution
Γ_k^*	functional group activity coefficient for group k in pure component i
Γ_k	functional group activity coefficient for group k in solvent
γ	overlap factor for free volume
γ_{1G}	solvent activity coefficient
γ_1^G	enthalpic, residual, or group interaction part of the solvent activity coefficient
$\gamma_1^{G\infty}$	limiting value of the enthalpic, residual, or group interaction part of the solvent activity coefficient at infinite dilution of solvent
γ_1^S	entropic, combinatorial, or size interaction part of the solvent activity coefficient
γ_1^∞	limiting value of solvent activity coefficient at infinite dilution of solvent
η_{1pred}	viscosity of solvent
η_1	predicted viscosity of solvent

λ_{ij}	interaction energy of an i-j pair (of molecules or groups)
μ_R	mean or expected value of R
μ_1	chemical potential of solvent
ν_{ki}	number of functional groups of type k in component i
ξ	ratio of critical molar volume of solvent jumping unit to critical molar volume of polymer jumping unit
ρ_i	density of component i or mass concentration of component i
ϕ_i	volume, size, or segment fraction of component i in solution
χ	Flory-Huggins interaction parameter or reduced chemical potential
Ω_1	solvent weight fraction activity coefficient
Ω_{1exptl}	experimental solvent weight fraction activity coefficient
Ω_1^{∞}	limiting value of solvent weight fraction activity coefficient at infinite dilution of solvent

Subscripts

i	from observation i
i,j	molecular components in solution
k,l,m	functional groups in solution
1	solvent, component 1, or functional group 1
2	polymer, component 2, or functional group 2

Superscripts

exptl	experimentally observed
G	enthalpic, residual, or group interaction part
i	in component i
pred	predicted
S	entropic, combinatorial, or size interaction part
∞	limiting value at infinite dilution of solvent

CHAPTER 1

INTRODUCTION

An understanding of the properties of polymer solutions is important for rational process design. Basic physical properties, such as densities and heat capacities, may often be estimated with reasonable accuracy from pure component properties. This is generally untrue for thermodynamic equilibrium properties, such as activities, and mass transfer properties, such as binary diffusivities. In addition, thermodynamic and diffusion properties of polymer solutions often show a strong dependence on composition in a nonlinear manner. An understanding of these properties is important in analysis of polymer processing and use, in such topics as devolatization, plasticization, permeability, and adhesion, to name a few.

This dissertation deals with four general topics applicable to thermodynamic equilibria and mass transfer properties in binary solutions. A variable size parameter approach to polymer solution thermodynamics used a single adjustable parameter in the entropy of mixing and could be used with any functional expression for the residual enthalpy of mixing to predict solvent activities in polymer solutions with good accuracy. Normalization and bounding properties of the residual interaction term in solution of groups models for prediction of

activity coefficients were studied. The variable size parameter thermodynamic model was combined with a free volume description of diffusion in concentrated polymer solutions to generate a single model for scaling of binary mutual diffusivities with temperature and concentration above the glass transition temperature. A nonparametric statistical method was developed to test for systematic error in data fitting involving nonlinear parameter estimation.

VARIABLE SIZE PARAMETER METHOD FOR POLYMER SOLUTION THERMODYNAMICS

Polymer solution thermodynamics is characterized by low values of the entropy of mixing. This necessitated a different approach to modeling polymer solution behavior as compared to that of mixtures of similarly sized small molecules. The standard approach was that taken by Flory and Huggins (Flory, 1953) which relied on a statistical approach to model entropy of mixing and used a single interaction parameter to incorporate enthalpy of mixing. Subsequent work has shown the theoretical basis of this model to be incorrect: solutions having little or no enthalpy of mixing typically have positive nonzero values of the interaction parameter. By framing the interaction parameter as a free energy rather than enthalpy parameter, theoretical objection to the model can be avoided.

Recent models for solution thermodynamics of small molecules have incorporated many enhancements to calculation of molecular interactions. These include modeling of molecular segregation (Wilson, 1964), use of a

quasi-chemical approach (Abrams and Prausnitz, 1975), and use of functional group interactions to predict overall solution behavior (Derr and Deal, 1969). Continued use of the Flory-Huggins approach ignores these advances in the modeling of solution interactions: its single interaction parameter makes it more similar to the one-suffix Margules equation.

Nonideal effects in polymer solutions due to changes in solution free volume have also been proposed and studied. Equation of state approaches have been used for this purpose (Flory, 1970; Lacombe and Sanchez, 1976; Liu and Prausnitz, 1979; Scholte, 1982). Such approaches, combined with mixing rules, could make solution behavior predictable from pure component data and a small number of adjustable system parameters. At present, agreement is lacking in fundamental details such as what constitutes a pure component critical pressure or temperature. It is definitely agreed that free volume relationships affect polymer solution thermodynamics and should be included in models. When the Flory-Huggins interaction parameter is interpreted as a free energy parameter, the entropy part may be considered to arise from free volume changes in solution.

Despite its shortcomings, the Flory-Huggins approach is commonly used in practical calculations, mainly due to its simplicity and historical acceptance. One goal of this work was to propose a novel approach to solution thermodynamics, referred to as VSP (Variable Size Parameter). Like Flory-Huggins, VSP contained a single adjustable parameter. This

parameter had a fundamental significance: it was the infinite dilution limit of the solvent activity coefficient taken on a weight fraction basis. The mathematical form of the VSP model relied on an adjustment of the concentration variable in the statistical entropy of mixing expression. The Flory-Huggins model adds an extra term to that expression. The VSP model also allowed any functional form to be used as an added term to incorporate enthalpy of mixing effects, if desired. Comparisons with available binary polymer-solvent data were made. These indicated that the VSP approach, even without an additional enthalpy term, was approximately as accurate as the Flory-Huggins approach in athermal solutions, and generally more accurate in more nonideal (enthalpic) solutions. Comparison with the UNIFAC-FV model (Oishi and Prausnitz, 1978) which incorporates a free volume approach, showed VSP to be more accurate. This may have been due, in part, to the fact that UNIFAC-FV generates predictions without use of binary activity data.

RESIDUAL INTERACTIONS IN GROUP CONTRIBUTION MODELS

A recent trend in solution thermodynamics has been the modeling of molecular interactions by summing the interactions of the various functional groups which compose the molecule in solution. This allows predictions of solution behavior to be made for compounds for which no binary data are available. All that is necessary is binary data for the functional groups which constitute the compounds, which can be derived from known data for other compounds containing the same functional groups.

This concept has been successfully applied in the UNIFAC model (Fredenslund, Jones, and Prausnitz, 1975) and the ASOG model (Derr and Deal, 1969). Both methods predict activity coefficients by summing a size interaction (combinatorial or entropic) contribution and a group interaction (residual or enthalpic) contribution. Databases for functional group interaction parameters have been constructed and updated for both of these models (Kojima and Tochigi, 1979; Gmehling, Rasmussen, and Fredenslund, 1982) and both show good predictive ability.

In these models, residual contributions to the activity coefficient of a given molecular component are calculated by summing activity coefficients of the functional groups which constitute the molecule. Functional group activity coefficients are given by a form of the Wilson equation (Wilson, 1964) written over functional groups in solution rather than molecular species. Another goal of this work was to study some basic properties of the equations as applied by these models. Normalization refers to the effects of choosing a particular size basis for measuring the number of functional groups in a molecule. Such a normalization directly affects the predictions of the model because of the nonlinearity of the Wilson equation. In addition, functional group composition provides additional constraint within a solution which can be used to bound the possible range of activity coefficients from an incomplete set of experimental data.

DIFFUSION IN POLYMER SOLUTIONS ABOVE T_G

The study of diffusion in polymer solutions is complicated by several factors. There exists no single theory capable of describing the phenomena which occur under various conditions: viscoelastic and relaxation-controlled processes, anomalies such as swelling and solvent crazing, and diffusion coefficients which are non-Fickian in a classical sense inasmuch as they are strong functions of penetrant concentration (Vrentas and Duda, 1979). Characterization and modeling of polymer solution diffusion is possible within limits of temperature and concentration where abrupt changes in polymer morphology and physical properties do not occur.

It is possible to scale binary mutual diffusion coefficients in concentrated polymer solutions with temperature and concentration. Models have been developed which assume that solution free volume is the primary factor determining mobility and thus mass transfer in solution (Fujita, 1968; Vrentas and Duda, 1977). This assumption is true above the glass transition temperature T_g, but not so far above T_g that solution free volume becomes large, and activation energy effects become important. It is true from zero solvent concentration up to approximately 80 weight percent solvent, above which the gross mobility of polymer molecules becomes important.

Since the driving force for diffusion is the chemical potential gradient rather than the concentration gradient, nonideal thermodynamic effects

must be considered in modeling binary mutual diffusivities. Another goal of this work was to combine the VSP solution thermodynamics model with the free volume diffusion model to generate a single model for scaling of diffusivity with temperature and concentration in concentrated polymer solutions above T_g. A simplified form of the general free volume model was also derived for use in certain practical calculations, e.g., devolatilization of polymer melts. The process of fitting experimental viscosity data to evaluate free volume parameters was also discussed.

STATISTICS OF NONLINEAR DATA FITTING

In the process of fitting experimental data to an empirical equation or model, it is necessary to choose values of the adjustable parameters which are "best" according to some criterion. Normally, this is accomplished by use of statistical results or procedures designed for this purpose, such as least squares analysis and regression. The criterion typically applied is that the sum of the squared deviations between the actual and predicted values of the dependent variable be minimized over all the points in the data set. Equations for this purpose are commonly used when the model is linear in the parameters to be fit.

When the model is nonlinear in the adjustable parameters, the equations of linear least squares no longer apply to the situation. In this case, it may be possible to linearize the model around a certain point to

permit the approximate use of linear least squares techniques. However, such an approach may be inaccurate, particularly when there are several adjustable parameters which are strongly dependent upon one another.

Even in the case where the model is linear in the adjustable parameters, least squares analysis is optimal only when the error or deviation between actual and predicted values is distributed normally with zero mean. The presence of outlier values in a data set can strongly affect least squares estimation of parameters, making them inaccurate. This is because outliers result from a distribution of error that does not follow a normal law.

In this work, some statistical techniques to overcome these problems have been successfully applied. Nonlinear parameter estimation was done by directly applying the least squares criteria and solving them numerically rather than using the standard linear least squares equations which are algebraic. To test whether a nonlinear model fit data with systematic rather than random error, a novel approach applying nonparametric statistics was used. Test statistics were generated which combined the best properties of both the runs test for randomness and the rank correlation coefficient.

CHAPTER 2

VARIABLE SIZE PARAMETER APPROACH TO THERMODYNAMICS OF CONCENTRATED POLYMER SOLUTIONS

In modeling the behavior of solutions containing both large molecules (polymers) and small molecules (solvents), two types of interaction occur to cause solution nonideality. Energetic (enthalpic or residual) interactions between different types of molecules occur because of changes in secondary bonding within solution as compared to within pure solvent or pure polymer. This type of interaction is not unique to polymer solutions, but occurs in mixtures of ordinary sized molecules as well. Size (entropic or combinatorial) interactions between different molecules occur on statistical grounds as determined by the number of possible configurations that the solution can exhibit. This number decreases substantially when large molecules are present. Size effects are ordinarily not important in mixtures of similarly sized molecules.

In addition to residual and combinatorial interactions, additional interactions may take place, particularly in polymer solutions. These interactions are generally considered to be the cause of noncombinatorial entropy in solution. Three distinct methods of handling noncombinatorial entropy have been used historically in the study of polymer solutions.

The earliest method was given by the Flory-Huggins approach (Flory, 1942; Flory, 1953), which assumed a standard combinatorial entropy of mixing and empirically adjusted an interaction parameter to fit experimental data. The original definition of the interaction parameter term was an enthalpic or residual interaction. Later interpretation of this term (Flory and Krigbaum, 1950) allowed it to take on entropic significance, i.e., noncombinatorial entropy. For this reason, the Flory-Huggins model effectively treats noncombinatorial entropy as if it were an additional enthalpy interaction, since the same term is used for both types of interaction.

A second approach, which has been quite popular recently, is to model solution behavior with an equation of state derived empirically or from statistical thermodynamics. A variety of techniques have been proposed (Flory, 1970; Lacombe and Sanchez, 1976; Oishi and Prausnitz, 1978; Liu and Prausnitz, 1979; Scholte, 1982). In some, the equation of state embodies both entropy and enthalpy effects in such a way that separate terms for these are not used. In others, the equation of state is used to generate an additional correction term to be applied in addition to standard entropy and enthalpy interaction terms. There is presently no single equation of state technique which is predominantly accepted in the same way, for example, that the Flory-Huggins model is accepted for prediction of combinatorial entropy. The general approach used for liquid phase equations of state is corresponding states, but liquid phase equations of state suffer from a lack of consensus on what should

constitute a critical value of temperature and pressure. These parameters are typically derived from a data fit with little physical significance.

The final approach, which is developed in this chapter, is to assume a standard enthalpy or residual interaction term while empirically adjusting a parameter within the combinatorial entropy term to account for the noncombinatorial entropy. This method originally was derived from an analysis of the Analytical Solution of Groups (ASOG) group contribution model for prediction of activity coefficients in solution (Derr and Deal, 1969). In actuality, the ASOG model itself was of significance only in that a form of the athermal Flory-Huggins equation was used within ASOG to generate a size interaction term. However, the ASOG model did yield insight into the modification of this size term, and also suggested the terminology "Variable Size Parameter" which was associated with the new approach. (In 1973, Derr and Deal, the original authors of ASOG, found that their equations were less accurate when applied to polymer solutions than they had been for solutions of similarly sized molecules. By choosing an "effective" value for the size ratio of the molecules, rather than using the actual size ratio, they were able to predict solvent activities in polymer solutions with accuracy comparable to their results for solutions of similarly sized molecules.)

The approach taken here is the converse of the the Flory-Huggins interaction term in which noncombinatorial entropy effects were used to

adjust a residual enthalpy term. In this work, noncombinatorial entropy effects are used to adjust a combinatorial entropy term. Any expression for residual interaction may be used in conjunction with this corrected entropy term.

ORIGINAL VSP SINGLE PARAMETER METHOD

The reprint article which follows describes the derivation of the original VSP method from the ASOG model. This is a simplified version of the complete VSP method in that no residual interaction term is used. Comparisons are made between the new method (referred to as "ASOG-VSP"), the Flory-Huggins equation, and the UNIFAC-FV model by extrapolating data from low solvent concentration to make predictions at higher solvent concentration. Further details of the experimental data and results are given in Appendices A, B, and D. Detailed derivations for the equations proposed in the article are given in Appendix F.

There is one typographical error in the reprint which is significant. In eq 27, the last term in the denominator of the argument of the natural logarithm function should contain w_2 in its numerator, not in its denominator as given. The grouping should equal (e/Ω_1^{∞}) multiplied by w_2, not divided by w_2 as is shown.

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Generalized Correlation for Solvent Activities in Polymer Solutions

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A correlation for solvent activities is developed by applying an athermal form of the ASOG (Analytical Solution of Groups) group-contribution model to polymer solutions. The new model provides a correction which accounts for differences in the free volume between the solvent and polymer and does not require group-contribution calculations. Instead, a closed-form solution containing only one adjustable parameter is derived for the weight fraction solvent activity coefficient as a function of weight fraction composition. The adjustable parameter represents an experimentally measurable infinite dilution weight fraction solvent activity coefficient. The new model is compared with the Flory–Huggins and UNIFAC-FV models for 29 isothermal binary systems, including systems with sizable enthalpy of mixing effects. Calculated activity coefficients of the new model are found to agree within the 10% to experimentally observed values for 120 of 130 data points. This agreement represented a better performance than either the Flory–Huggins or the UNIFAC-FV model.

An understanding of the thermodynamics of polymer–solvent systems is important in many practical applications; processing steps such as polymerization, devolatilization, plasticization, and addition of other additives all require a knowledge of polymer solution thermodyamics. Diffusion phenomena in polymer melts and solutions are often strongly affected by nonideal solution behavior. Proper design of many polymer processes depends greatly upon accurate modeling of thermodynamic parameters such as solvent activities.

This work presents a thermodynamic correlation method for solvent activities in polymer solutions as a function of concentration. The method is developed theoretically from consideration of athermal solutions; however, it shows good agreement with experimental data available for some polymer–solvent systems which have enthalpic interactions. The model is based upon an athermal form of the ASOG (Analytical Solution of Groups) group-contribution model for calculation of activity coefficients in solution and uses weight fractions to describe concentrations. A correction is made to account for the difference in the free volume between the solvent and polymer, as evidenced by their different densities. Since only athermal terms are considered in the model development, group-interaction parameters used in calculating enthalpy effects are not included and the final model reduces to a single equation.

The model shows good agreement with experiment over the entire range of concentrations reported in the literature

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for solvent activities. In nearly all cases considered, performance of the model is approximately equal to the better of either the Flory-Huggins model or the UNIFAC-FV group contribution model proposed by Oishi and Prausnitz (1978). The Flory-Huggins model contains a single adjustable parameter, the interaction parameter, and requires density data for the polymer and solvent if the weight fraction is the concentration variable. UNIFAC-FV requires knowledge of the densities for calculation of the free volume correction. A constant value for a fitting parameter, the degrees of freedom for a solvent molecule, has been determined by modeling a number of data sets. The adjustable parameter in the model proposed here is an experimentally obtainable weight fraction solvent activity coefficient at infinite dilution.

Group-Contribution Models

Group contribution concepts have been successfully used in modeling various physical and chemical phenomena. By reducing a chemical compound to a set of functional groups, it is possible to greatly reduce the amount of information which needs be stored. Thousands of chemical compounds can be represented by a set of only a hundred or so functional groups which make them up. Storing the needed functional group properties of compounds from the known functional group properties provides a more efficient means, in many cases, of determining the desired properties. This is especially true in cases where few experimental data are available for the compound in question. There are often little equilibrium data for polymer–solvent systems over the concentration and temperature ranges for devolatilization. In addition, polymers are distributed in size but basically identical in their functional group composition.

The first group-contribution model for prediction of activity coefficients in solution was the Analytical Solution of Groups (ASOG) model by Derr and Deal (1969). It is capable of separately modeling the effects of molecular size differences with an entropic term from Flory–Huggins theory and the effects of functional group interactions with an enthalpic term from Wilson (1964). Agreement with experiment is found to be good. Variations and extensions of the original ASOG model have been recently elaborated, particularly for hydrocarbon systems (Kojima and Tochigi, 1979; Vera and Vidal, 1984).

Recent work in phase equilibrium has resulted in a more general formulation of the fundamental solution of groups concept. This is the UNIFAC model (Fredenslund et al., 1975). In application, this model is similar to ASOG, but the theoretical framework is quite distinct. UNIFAC is based upon UNIQUAC, the Universal Quasi-Chemical model developed by Abrams and Prausnitz (1975). This model is based upon statistical thermodynamics, particularly the work of Guggenheim (1952) on his quasi-chemical theory of solutions. Like ASOG, UNIFAC/UNIQUAC contains separate entropic (combinatorial) and (residual) terms, which are derived naturally from statistical thermodynamics. Pure component data are used to generate molecular size and surface area terms for each molecule, based upon the number and type of functional groups it contains. These values, along with parameters for the residual interactions between different functional groups, have been updated frequently and presently constitute a data base of 76 basic functional groups (Gmehling et al., 1982).

Both the ASOG and UNIFAC models must be modified to model solution activity in polymer solutions, because of the large differences in the free volume between the polymer and solvent. An extension to the UNIFAC model, called UNIFAC-FV, was proposed by Oishi and Prausnitz (1978). By adding an extra term to the combinatorial and residual terms already given by UNIFAC, the effects of free volume differences between the polymer and solvent were modeled. Results were found to agree with experiment within 10%.

Although the bulk of recent work in the group-concentration thermodynamic models has centered on the UNIFAC model, a comparison of the predictive ability of ASOG and UNIFAC shows that they are approximately equal in accuracy, and both are substantially better than the group-contribution Non-Random-Two-Liquid-Group (NRTLG) and Enthalpic-Wilson-Group (EWG) models (Rizzi and Huber, 1981). The theoretical advantage of UNIFAC is a basis in statistical mechanics, but the ASOG model has the advantage of a simpler mathematical form, particularly for the entropic (combinatorial) activity term. The Flory–Huggins form of the combinatorial term used by ASOG is also preferred over the Staverman form used by UNIFAC because the Staverman potential may lead to physically unrealizable positive combinatorial contributions (Thomas and Eckert, 1984). Although the Flory–Huggins model (Flory, 1953) uses an entropy term similar to that proposed in ASOG, there are no separate terms for enthalpy or free volume effects on activity. Both effects are lumped into the entropy term by the use of the interaction parameter.

Since UNIFAC-FV was successful at extending the UNIFAC model to polymer solutions, the extension of ASOG to polymer solutions was attempted in this work. In the theoretical development proposed here, we considered only systems of chemically similar polymers and solvents, where the group interaction (enthalpic) effects were shown to be negligible. This allowed the derivation of a closed-form solution for the entropic activity coefficient.

ASOG Model

In the ASOG model, the two contributions to the activity coefficient are γ_i^S, the entropic part, and γ_i^G, the enthalpic part. The entropic activity coefficient is given by

$$\ln \gamma_1^S = 1 - R_1 + \ln R_1 \tag{1}$$

where R_1 is the size term for component 1 (solvent). The size term is in turn given by

$$R_1 = \frac{S_1}{S_1 x_1 + S_2 x_2} \tag{2}$$

where the S_1 and S_2 terms are the number of size groups found in the solvent and polymer molecules, respectively, and the x_1 and x_2 terms are the mole fractions of components 1 or 2 within the solution. The definition of the size group used in the original ASOG model (Derr and Deal, 1969) was adopted here: the number of size groups in a molecule is equal to the number of carbon atoms in the molecule. When this definition is used, the ratio of size groups S_2/S_1 for the chemically similar polymer and solvent is the same as the ratio of molecular weights M_2/M_1, where M_1 is the molecular weight of the solvent and M_2 was the number-average molecular weight of the polymer. The reason for using the number-average molecular weight is shown by Misovich (1984) as following mathematically from the mole fraction composition variables used by ASOG combined with the directly proportional dependence of the polymer size term S_2 on the degree of polymerization of the polymer molecule.

The enthalpic activity coefficient is given by ASOG as

$$\ln \gamma_i^G = \sum_k \nu_{k_i} \ln \Gamma_k - \sum_k \nu_{k_i} \ln \Gamma_k^\circ \tag{3}$$

Table I. Entropic and Enthalpic Activity Coefficients for the Toluene-Poly(styrene) System Given by ASOG

wt fract toluene	entropic ln γ_1^S	enthalpic ln γ_1^G
0.000	-5.72	0.006507
0.001	-5.12	0.006506
0.01	-3.51	0.006501
0.1	-1.40	0.005547
0.5	-0.20	0.002758
0.9	-0.005546	0.000217
0.99	-0.000050	0.000003

where r_k is the number of functional groups of type k in the solvent molecule, Γ_k is the group activity coefficient for group k in solution, and Γ_k° is the standard group activity coefficient for group k in pure solvent. Both Γ_k and Γ_k° are defined as

$$\ln \Gamma_k = -\ln \sum_l x_l A_{lk} + 1 - \sum_l \frac{x_l A_{lk}}{\sum_m x_m A_{lm}} \qquad (4)$$

where x_l is the mole fraction of group l and A_{lk} is a group interaction parameter for group k with group l (enthalpic interaction). A_{lk} values have been tabulated for various functional groups (Palmer, 1975; Rizzi and Huber, 1984).

The group mole fractions, x_k, used for calculating Γ_k are defined on the functional group composition of the entire solution, whereas those used for calculating Γ_k° are defined only upon the functional group composition of the solvent. For systems of chemically similar polymers and solvents, the group mole fractions were approximately equal whether defined on the entire solution or only upon the solvent molecule. This resulted in approximately equal values of Γ_k and Γ_k°, giving ln γ_1^G equal to 0 in eq 3. On the other hand, the entropic contribution was expected to be large, due to the size differences between the polymer and solvent molecules.

A comparison was made between the entropic and enthalpic activity coefficients calculated by the ASOG model for toluene–poly(styrene), representing a typical system without large enthalpic interactions. The results are shown in Table I. The logarithms of entropic activity coefficients were from 2 to 4 orders of magnitude larger than the logarithms of enthalpic activity coefficients at nearly all concentrations of solvent. These results provide justification for neglecting the enthalpic activity coefficient in modeling polymer–solvent systems which are similar chemically. In the subsequent theoretical development presented in this paper, only the entropic activity coefficient will be considered in calculating solvent activities.

Modification of ASOG for Polymer Solutions

The size group concept in ASOG applied to polymer solutions assumes that the free volume of polymer and solvent are equal. This is generally not true; if it were, the densities of chemically similar polymer–solvent pairs would be equal. To show that this assumption results in substantial error, the infinite dilution weight fraction solvent activity coefficient Ω_1^∞ was calculated according to the ASOG model. Equations 1 and 2 above, combined with the assumption

$$S_1 \ll S_2 \qquad (5)$$

resulted in an infinite dilution mole fraction activity coefficient (the value of γ_1^S as x_1 goes to zero)

$$\gamma_1^\infty = e\frac{S_1}{S_2} \qquad (6)$$

where e is the base of the natural logarithm, approximately 2.718.

Table II. Typical Infinite Dilution Weight Fraction Activity Coefficients for Chemically Similar Systems

solv–polym	temp, °C	Ω_1^∞	ref
toluene–poly(styrene)	124	3.93–5.50	a
	148	3.96–4.95	a
	150	5.22	c
	173	3.72–4.56	a
	175	5.29	c
	200	5.34	c
benzene–poly(styrene)	124	3.93–5.33	a
	148	3.80–4.86	a
	150	4.72–5.36	b
	173	3.67–4.26	a
ethylbenzene–poly(styrene)	150	4.96	c
	175	5.47	c
	200	5.67	c

[a] Covitz and King, 1972; polymer molecular weight 3600–1 780 000. [b] Galin and Rupprecht, 1978; linear and branched polymer. [c] Newman and Prausnitz, 1972; polymer molecular weight 97 000.

At infinite dilution of the solvent in pure polymer, the mole fraction and weight fraction activity coefficients are related by

$$\Omega_1^\infty = \gamma_1^\infty \frac{M_2}{M_1} \qquad (7)$$

Substituting eq 6 into eq 7 gives the desired result.

$$\Omega_1^\infty = e\frac{S_1}{S_2}\frac{M_2}{M_1} \qquad (8)$$

Since for chemically similar polymer–solvent systems ASOG gives S_2/S_1 equal to M_2/M_1, the size group ratio and molecular weight ratio cancel, leaving the result

$$\Omega_1^\infty = e \qquad (9)$$

This result is in substantial disagreement with much data, since for most chemically similar polymer–solvent systems, the experimentally observed activity coefficient is much larger than e, as shown in Table II. When the ASOG model was applied directly to polymer solutions by Derr and Deal (1973), they also noted that the predictions of solvent activity were generally too low. They chose an "effective" S_2 for the polymer molecule but proposed no general procedure for making such a choice.

The proposed correction to the ASOG model, referred to as ASOG–variable size parameter (ASOG-VSP), assumes that the form of eq 8 is correct but that the assumption of equal free volumes of solvent and polymer

$$\frac{S_2}{S_1} = \frac{M_2}{M_1} \qquad (10)$$

is incorrect. To produce a correct value for the ratio S_2/S_1, eq 8 is rearranged with Ω_1^∞ considered as a known parameter for the polymer–solvent system. The resulting equation allows the size parameter ratio to vary in a standard way for solvent–polymer systems.

$$\frac{S_2}{S_1} = \frac{e}{\Omega_1^\infty}\frac{M_2}{M_1} \qquad (11)$$

The independent composition variable used in the ASOG model is the mole fraction. The mole fraction is generally not a useful variable for modeling polymer–solvent systems, because the molecular weight of the components differs by several orders of magnitude in most cases. To make the ASOG-VSP results more practical for modeling polymer solutions, a transformation from mole

fraction to weight fraction was made. The identities

$$x_1 = \frac{\frac{M_2}{M_1}w_1}{\frac{M_2}{M_1}w_1 + w_2} \quad (12)$$

$$x_2 = \frac{w_2}{\frac{M_2}{M_1}w_1 + w_2} \quad (13)$$

were applied to eq 2 for the ASOG size term R_1 along with eq 11, giving R_1 as a function of solvent weight fraction w_1.

$$R_1 = \frac{w_1 + \frac{M_1}{M_2}(1 - w_1)}{w_1 + \frac{e}{\Omega_1^\infty}(1 - w_1)} \quad (14)$$

Since the weight fraction was being used as the concentration variable, the activity coefficient was put on the same basis. This was done by transforming from the mole fraction activity coefficient, γ_1, to the weight fraction activity coefficient, Ω_1.

$$\Omega_1 = \frac{\gamma_1}{w_1 + \frac{M_1}{M_2}(1 - w_1)} \quad (15)$$

The final step involved using the size term from eq 14 to compute the entropic activity coefficient in eq 1 and then finding Ω_1 from eq 15.

$$\Omega_1 = \frac{\exp\left[\frac{\frac{e}{\Omega_1^\infty}(1 - w_1)}{w_1 + \frac{e}{\Omega_1^\infty}(1 - w_1)}\right]}{w_1 + \frac{e}{\Omega_1^\infty}(1 - w_1)} \quad (16)$$

In deriving this result, the assumption

$$\frac{e}{\Omega_1^\infty} \gg \frac{M_1}{M_2} \quad (17)$$

was made, allowing the molecular weight ratio term to be ignored. This result is thus restricted to polymers of high molecular weight compared to the solvent and to solutions where Ω_1^∞ is not very large.

The result (eq 16) is a closed-form solution, giving the weight fraction solvent activity coefficient, Ω_1, as a function of the solvent weight fraction w_1. The only adjustable parameter which appears in the equation is the infinite dilution weight fraction solvent activity coefficient, Ω_1^∞. This parameter can be obtained from a single physical measurement of equilibrium solubility of a trace of solvent in pure polymer.

It was also possible, of course, to correlate Ω_1^∞ as a function of w_1 based upon a single measurement of solvent activity at conditions other than infinite dilution of solvent in pure polymer. This can be done by solving eq 16 for Ω_1^∞, given values of Ω_1^{expt} and w_1^{expt}. Due to the nonlinearity of the right-hand side of eq 16, a closed-form solution of Ω_1^∞ in terms of Ω_1^{expt} and w_1^{expt} was not possible. A solution is possible by trial and error, or by the following iteration procedure. Define

$$Y = w_1^{expt} + \frac{e}{\Omega_1^\infty}(1 - w_1^{expt}) \quad (18)$$

and substitute Y into eq 16.

$$\Omega_1^{expt} = \frac{\exp\left(\frac{Y - w_1^{expt}}{Y}\right)}{Y} \quad (19)$$

Rearranging this gives

$$Y = \exp\left(1 - \frac{w_1^{expt}}{Y} - \ln \Omega_1^{expt}\right) \quad (20)$$

Take an initial approximation

$$Y_0 = \exp(1 - \ln \Omega_1^{expt}) \quad (21)$$

and define

$$Y_n = \exp\left(1 - \frac{w_1^{expt}}{Y_{n-1}} - \ln \Omega_1^{expt}\right) \quad (22)$$

When a convergent value is found for Y_n, calculate Ω_1^∞ by rearrangement of eq 18.

$$\Omega_1^\infty = \frac{e(1 - w_1^{expt})}{Y - w_1^{expt}} \quad (23)$$

This procedure converges quickly and allows eq 16 to be used even when an infinite dilution activity coefficient is not known.

Comparison To Flory-Huggins Model

The Flory–Huggins model for polymer solution activity coefficients in concentrated solutions (Flory, 1953) relates solvent activity, a_1, to solvent volume fraction, ϕ_1, polymer volume fraction, ϕ_2, and the interaction parameter χ by the equation

$$\ln a_1 = \ln \phi_1 + \phi_2 + \chi\phi_2^2 \quad (24)$$

As mentioned previously, the ASOG entropy term (eq 1) is similar in form to eq 24. If the size fraction R_1 given by eq 2 is equated with the volume fraction ϕ_1 in eq 24, eq 1 and 24 become identical when χ is taken as 0. The interaction parameter χ derived from experimental data in the athermal systems is generally small and positive. Since enthalpy effects do not play a role in athermal systems, χ represents the contribution of the free volume effects on the activity predicted by eq 24.

Since the enthalpy term in ASOG was neglected in the ASOG-VSP model, the difference between the Flory–Huggins model and the ASOG-VSP model lies in the treatment of the free volume contribution to activity. ASOG-VSP corrects the molecular size ratio for free volume effects so that the ASOG entropy term correctly predicts infinite dilution behavior. Flory–Huggins uses the interaction parameter to modify the entropic activity term which wholly constitutes eq 24. Both models do lump enthalpy effects with free volume effects: Flory–Huggins via the χ parameter and ASOG-VSP via the size ratio parameter, since ASOG group interactions were neglected.

It is generally accepted that the interaction parameter can be a strong function of concentration, especially in systems with large enthalpic interactions. The ASOG-VSP

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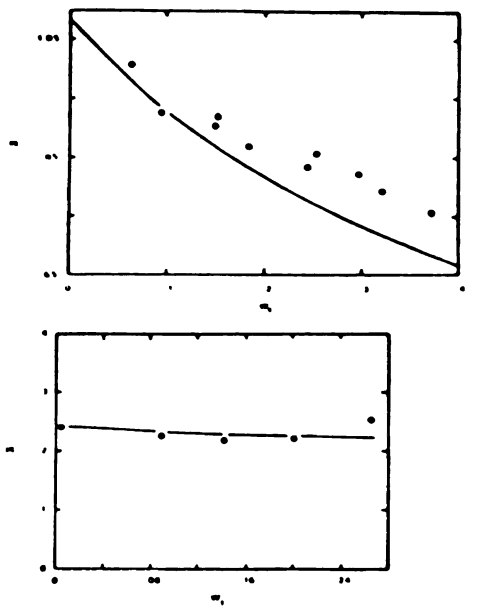

Figure 1. Concentration dependence of the interaction parameter. (a, top) Benzene-poly(isobutylene) at 25 °C, (b, bottom) benzene-poly(ethylene oxide) at 70 °C. Data points are denoted by closed circles and the solid line gives eq 27.

model could be applied to predicting the variation of χ with concentration. To do this, the transformations

$$\phi_1 = \frac{\frac{\rho_2}{\rho_1}w_1}{\frac{\rho_2}{\rho_1}w_1 + w_2} \tag{25}$$

$$\phi_2 = \frac{w_2}{\frac{\rho_2}{\rho_1}w_1 + w_2} \tag{26}$$

were made within eq 24, and eq 16 and 24 were combined to express χ in terms of the independent variable w_1, the ASOG-VSP parameter Ω_1^*, and the ratio of polymer density to solvent density ρ_2/ρ_1.

$$\chi = \frac{\frac{e}{\Omega_1^*}w_2}{w_1 + \frac{e}{\Omega_1^*}w_2}\left(\frac{\rho_2}{\rho_1}\frac{w_1}{w_2} + 1\right)^2 - \left(\frac{\rho_2}{\rho_1}\frac{w_1}{w_2} + 1\right) + \left(\frac{\rho_2}{\rho_1}\frac{w_1}{w_2} + 1\right)^2 \ln\left(\frac{w_1 + \frac{\rho_1}{\rho_2}w_2}{w_1 + \frac{e}{\Omega_1^*}w_2}\right) \tag{27}$$

Strict applications of Flory–Huggins requires χ to be constant, yet the temperature and composition dependence of χ can be substantial even in athermal systems (Scholte, 1971). Equation 27 gives a functional form for the dependence of χ upon the weight fraction predicted by the ASOG-VSP model at constant temperature. Figure 1 compares the concentration dependence of χ based upon eq 27 to χ values generated from experimental activity measurements for benzene–poly(isobutylene) and benzene–poly(ethylene oxide).

The behavior of the interaction parameter as a function of concentration predicted by eq 27 depends strongly upon the particular value of Ω_1^*. Athermal polymer–solvent systems typically have Ω_1^* values in the range 4–6, and the curve corresponding to such a system shows that χ remains fairly constant, decreasing slightly with increasing concentration. The experimental data for benzene–poly(isobutylene) show a general decrease, a bit more steeply than predicted but still very small in magnitude. On the other hand, the curve corresponding to a system with enthalpic interaction, with Ω_1^* equal to 8.5, decreases rather sharply with increasing concentration. The experimental data for benzene–poly(isobutylene) follow the same pattern, although not quite as sharply as predicted.

The results in Figure 1 indicate that the Flory–Huggins model and ASOG-VSP model agree fairly closely in their predictions for low weight fractions in athermal systems, since χ is roughly constant. For systems with enthalpic interactions, the ASOG-VSP and Flory–Huggins models predict different behavior, and ASOG-VSP correctly predicts the downward trend of the experimental data. ASOG-VSP predicts that χ decreases with concentration for a range of physically reasonable values of e/Ω_1^* and ρ_2/ρ_1. The rate of decrease is least for athermal systems and becomes larger as Ω_1^* increases or decreases, i.e., in systems with either positive or negative enthalpy effects.

Experimental data do exist which do not show a decrease in χ with concentration, possibly because of scatter in the data. χ values are particularly sensitive to activity measurements at higher solvent concentrations. This is because eq 24, when rearranged to solve for χ, requires division by ϕ_2^2. For this reason, the relative accuracy of the Flory–Huggins and ASOG-VSP models can be better assessed by comparing their predicted activity coefficients (eq 16 and 24).

Both the ASOG-VSP and Flory–Huggins models have a fairly simple mathematical form, with a single adjustable parameter. However, the calculation of this parameter requires only the measurement of one activity for ASOG-VSP, whereas the Flory–Huggins χ parameter is derived from an activity and two densities. The sparseness and uncertainty of much of the experimental data relating to polymer solutions under devolatilization conditions increases the utility of a model with a more easily obtained adjustable parameter. Since it is also necessary to vary χ as a function of concentration to correctly model many systems, the ASOG-VSP model is also superior in that its adjustable parameter is a function of only the system components and temperature, not of concentration.

Comparison To UNIFAC-FV Model

The ASOG-VSP model, in the form presented here, is less general in its theoretical basis than the UNIFAC-FV model. The enthalpic or group interaction terms included in the original UNIFAC model, and hence incorporated into UNIFAC-FV, are analogous to the terms which were ignored during the derivation of ASOG-VSP. The free volume correction made in ASOG-VSP is more empirical in nature than the free volume correction in UNIFAC-FV, based upon the equation-of-state theory proposed by Flory (1970).

The UNIFAC-FV model contains adjustable parameters representing a proportionality factor used in defining the reduced volume and a number of external degrees of freedom per solvent molecule. Constant values are recommended for these parameters in most cases (Oishi and Prausnitz,1978; Prausnitz, 1982). It is difficult to deter-

Table III. Comparison of ASOG-VSP, Flory-Huggins, and UNIFAC-FV Models for Solvent-Polymer Systems

solv-polym	temp, °C	correlat pt	Ω_1^*	wt fract range	no. of pts	av % error ASOG-VSP	av % error Flory-Huggins	av % error UNIFAC-FV	ref
toluene-poly(styrene)	25[a]	0.111	4.68	0.156-0.918	10	2.5	1.5	4.1	a
	60	0.102	4.77	0.179-0.261	2	1.5	0.6	1.9	a
	80	0.246	5.10	0.458-0.671	2	1.1	0.2	2.4	a
methyl ethyl ketone-poly(styrene)	25[a]	0.091	8.69	0.215-0.298	3	2.1	8.4	9.4	a
benzene-poly(isobutylene)	10	0.225	10.04	0.157-0.454	2	2.2	18.2	2.9	b
	25	0.043	8.47	0.063-0.371	10	2.9	13.2	2.3	b
cyclohexane-poly(isobutylene)	25	0.128	4.91	0.165-0.569	7	2.1	1.7	3.9	c
n-pentane-poly(isobutylene)	25	0.028	8.58	0.072-0.584	8	2.0	5.2	7.4	d
trimopropylbenzene-poly(styrene)	165	0.029	12.43	0.065-0.086	2	2.9	15.7	27.5	e
	175	0.020	11.52	0.037-0.065	2	16.3	20.5	22.4	e
carbon disulfide-poly(styrene)	115	0.014	3.75	0.024-0.040	2	0.8	1.3	30.7	e
	140	0.008	3.95	0.011-0.029	3	18.3	18.8	36.9	e
methanol-poly(methyl methacrylate)	120	0.002	16.56	0.006-0.009	2	1.3	2.6	37.6	e
	130	0.002	11.85	0.005-0.008	2	9.9	8.6	66.6	e
toluene-poly(methyl methacrylate)	130	0.016	12.06	0.059-0.112	2	30.3	49.2	8.3	e
	160	0.005	13.36	0.014-0.036	4	24.6	33.6	29.8	e
toluene-poly(vinyl acetate)	35	0.084	9.29	0.117-0.195	3	3.3	8.0	24.8	f
	40	0.051	8.85	0.076-0.171	6	3.3	5.5	25.7	f
	47.5	0.052	8.31	0.071-0.107	2	6.5	0.3	26.9	f
chloroform-poly(vinyl acetate)	35	0.163	1.65	0.231-0.464	6	7.9	9.2	16.1	f
	45	0.093	1.49	0.121-0.499	15	3.4	4.6	14.7	f
benzene-poly(ethylene oxide)	70	0.061	5.06	0.067-0.388	6	2.7	4.1	10.1	g
	70	0.050	4.61	0.089-0.265	4	0.7	1.0	8.3	g
	75.1	0.052	4.48	0.081-0.145	3	0.7	0.3	8.9	g
	88.1	0.026	4.50	0.050-0.090	3	0.7	1.1	10.3	g
	102	0.020	4.51	0.021-0.118	10	1.9	2.1	12.0	g
	125.4	0.010	4.35	0.017-0.032	3	1.3	1.4	12.4	g
	125.7	0.011	4.25	0.017-0.033	3	1.8	1.9	10.1	g
	150.4	0.007	4.38	0.011-0.022	3	3.9	4.0	13.1	g

[a] Hawn et al. (1950). [b] Eichinger and Flory (1968a). [c] Eichinger and Flory (1968b). [d] Eichinger and Flory (1968c). [e] Liu (1980). [f] Ju (1981). [g] Chang and Bonner (1975). [h] Indicates some experimental points were deleted as outliers. [i] Point used to determine Ω_1^* (ASOG-VSP) and χ (Flory-Huggins).

mine whether these parameters, particularly the external degrees of freedom parameter, are correct for a particular polymer–solvent system without checking the predictions of UNIFAC-FV against experimental data for that system.

If such activity data are available, the ASOG-VSP model is much simpler from a computational standpoint. In particular, infinite dilution activity coefficient data are typically available for many polymer–solvent systems even in the absence of other thermodynamic data for the system, and it is such data which can directly provide a value for the one adjustable parameter, Ω_1^*, in ASOG-VSP. For example, inverse-phase gas chromatography has been used by Newman and Prausnitz (1972), Galin and Rupprecht (1978), Gündüz and Dincer (1980), and DiPaola-Baranyi (1981) to measure infinite dilution activity coefficients for many solvents in poly(styrene), various methacrylate polymers, and some copolymers. Other methods for measuring this coefficient are head space analysis and quartz spring or microbalance sorption experiments.

One major advantage of the UNIFAC-FV model is that it does not require activity coefficient data for polymer–solvent systems. In this sense, UNIFAC-FV is predictive while ASOG-VSP is correlative, using a single binary datum to generate activity as a function of concentration. On the other hand, UNIFAC-FV does require pure component density data for both the solvent and polymer. The same comments which were made in regard to the need for such data in using the Flory–Huggins model also apply to UNIFAC-FV.

Comparison of ASOG-VSP, UNIFAC-FV, and Flory–Huggins Models with Experimental Data

Experimental data for 130 points in 29 sets of isothermal polymer–solvent activities were used to test the predictions of the ASOG-VSP, UNIFAC-FV, and Flory–Huggins models. Of the 29 sets, 2 showed negative enthalpic interactions ($\Omega_1^* < 2.0$), 14 showed roughly athermal behavior ($3.5 < \Omega_1^* < 5.5$) and 13 showed positive enthalpic interactions ($\Omega_1^* > 8.0$). Table III gives the details of the sets studied.

For each set, the lowest concentration data point was chosen for correlation of Ω_1^* by eq 18–23. This Ω_1^* was then used to predict the activity using the ASOG-VSP model. The Flory–Huggins χ was calculated from Ω_1^* and used as a constant value in the Flory–Huggins equation. The UNIFAC-FV model was applied according to Oishi and Prausnitz (1978), using their recommended values for the free volume parameters and the Gmehling et al. (1982) values for the group interaction and size parameters. Density data for solvents and polymers were obtained from Timmermans (1950), Brandup and Immergut (1975), and Mark et al. (1972). In some cases, liquid density data below the normal boiling point were extrapolated to estimate liquid densities at higher temperatures.

The ability of any of the models to fit the data depends on the value of Ω_1^*. Tables IV–VI give typical results for three data sets: one each exhibiting negative, positive, and athermal behavior. Table VII summarizes the accuracy of the three models on the given data sets. The performance of the Flory–Huggins model and ASOG-VSP model was roughly equal on athermal systems, with both models accurate within 5% of the experimental activity for about 90% of the data points. In systems showing marked positive or negative deviations from athermal behavior, the ASOG-VSP model predicted activity within 5% of experiment for over 70% of the data, while the Flory–Huggins model was as accurate less than 30% of the time. The UNIFAC-FV model generally performed more poorly than ASOG-VSP and Flory–Huggins, as might be expected since it utilizes no binary data in its predictions. It is possible that performance of UNIFAC-FV could have been

Table IV. Comparison of Calculated and Experimental Activities for Chloroform–Poly(vinyl acetate) at 45 °C. Ω_1^∞ = 1.49 and χ = -0.392 Determined at w_1 = 0.093

		solv activ coeff and % error					
wt. fract solv	exptl	ASOG-VSP		Flory-Huggins		UNIFAC-FV	
0.121	1.408	1.473	4.6	1.489	5.8	1.207	-14.3
0.139	1.405	1.469	4.6	1.488	5.9	1.204	-14.3
0.164	1.416	1.463	3.3	1.485	4.8	1.200	-15.3
0.198	1.366	1.455	6.5	1.480	8.3	1.195	-12.5
0.206	1.452	1.453	0.0	1.478	1.8	1.195	17.8
0.227	1.400	1.448	3.5	1.475	5.3	1.192	14.8
0.247	1.380	1.443	4.6	1.471	6.6	1.190	-13.7
0.276	1.382	1.434	3.8	1.464	5.9	1.187	-14.1
0.295	1.380	1.429	3.6	1.459	5.7	1.186	-14.1
0.325	1.365	1.420	4.0	1.451	6.3	1.183	-13.3
0.355	1.351	1.410	4.4	1.441	6.7	1.181	-12.6
0.427	1.389	1.383	-0.4	1.415	1.9	1.177	-15.3
0.461	1.378	1.369	-0.6	1.400	1.6	1.175	-14.8
0.478	1.395	1.362	-2.3	1.391	-0.1	1.174	-15.8
0.499	1.416	1.353	-4.5	1.382	-2.4	1.172	-17.2
av % error		3.4		4.6		14.7	

Table V. Comparison of Calculated and Experimental Activities for Benzene–Poly(ethylene oxide) at 75.1 °C. Ω_1^∞ = 4.48 and χ = 0.210 Determined at w_1 = 0.052

		solv activ coeff and % error					
wt fract solv	exptl	ASOG-VSP		Flory-Huggins		UNIFAC-FV	
0.081	3.755	3.749	-0.2	3.764	0.2	3.416	-9.0
0.108	3.561	3.543	-0.5	3.559	-0.0	3.247	-8.8
0.145	3.332	3.289	-1.3	3.307	-0.7	3.038	-8.8
Av % error		0.7		0.3		8.9	

Table VI. Comparison of Calculated and Experimental Activities for Benzene–Poly(isobutylene) at 25 °C. Ω_1^∞ = 8.47 and χ = 1.09 Determined at w_1 = 0.043

		solv activ coeff and % error					
wt fract solv	exptl	ASOG-VSP		Flory-Huggins		UNIFAC-FV	
0.063	6.409	6.274	-2.1	6.871	7.2	6.016	-6.1
0.094	5.468	5.520	1.0	6.224	13.8	5.452	-0.3
0.150	4.608	4.506	-2.2	5.251	14.0	4.620	0.3
0.152	4.636	4.484	-3.3	5.229	12.8	4.601	-0.8
0.184	4.127	4.032	-2.3	4.752	15.1	4.199	1.8
0.245	3.484	3.370	-3.3	4.001	14.8	3.572	2.5
0.254	3.452	3.294	-4.6	3.911	13.3	3.497	1.3
0.297	3.070	2.946	-4.0	3.485	13.5	3.144	2.4
0.321	2.873	2.779	-3.3	3.275	14.0	2.970	3.4
0.373	2.541	2.472	-2.7	2.881	13.4	2.642	4.0
av % error		2.9		13.2		2.3	

Table VII. Accuracy of the ASOG-VSP, Flory-Huggins, and UNIFAC-FV Models on the Data Tested

model	$\Omega_1^\infty < 2$	$3.5 < \Omega_1^\infty < 5.5$	$\Omega_1^\infty > 8$	all data
% of Data Points for Which Model Was Accurate Within 5%				
ASOG-VSP	71	90	71	80
Flory–Huggins	29	89	21	54
UNIFAC-FV	0	28	25	22
% of Data Points for Which Model Was Accurate Within 10%				
ASOG-VSP	100	97	83	92
Flory–Huggins	86	95	56	79
UNIFAC-FV	0	59	50	46

improved if the value of the parameter used in calculating the free volume correction had been adjusted; however, no definitive guidelines for doing so are given by the authors of UNIFAC-FV.

Conclusions

The ASOG-VSP model was successful in predicting solvent activities in the polymer–solvent systems reviewed. Performance was equal to the Flory–Huggins model, superior to the UNIFAC-FV model in athermal systems, and superior to both of these models in systems with significant enthalpic interactions. ASOG-VSP also had an advantage over these models in not requiring density data for applications of the model and is much simpler than UNIFAC-FV from a computational standpoint. However, ASOG-VSP does require a single value of activity or an infinite dilution activity coefficient as a parameter, which UNIFAC-FV does not.

The results presented here can be extended to multicomponent polymer–solvent systems. A theoretical derivation for systems with enthalpic interactions between polymer and solvent molecules by including the ASOG group-interaction parameters is also possible, as is extension to modeling of temperature dependence of activity. We are continuing work on these topics and on the application of the results presented here to diffusion in polymer melts.

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Registry No. Toluene, 108-88-3; poly(styrene), 9003-53-6; benzene, 71-43-2; ethylbenzene, 100-41-4; methyl ethyl ketone, 78-93-3; poly(isobutylene), 9003-27-4; cyclohexane, 110-82-7; pentane, 109-66-0; triisopropylbenzene, 27322-34-5; carbon disulfide, 75-15-0; methanol, 67-56-1; poly(methyl methacrylate), 9011-14-7; poly(vinyl acetate), 9003-20-7; chloroform, 67-66-3; poly(ethylene oxide), 25322-68-3.

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VSP METHOD USED WITH RESIDUAL INTERACTION TERMS

The manuscript which follows describes the derivation of the complete VSP method which includes an additional residual interaction term. Comparisons are made between the new method and the Flory-Huggins equation by fitting complete data sets to the adjustable parameters in each model. The new method is applied with three residual terms: one which describes no residual interaction (equivalent to the original VSP single parameter method); one which uses a term similar to the Flory-Huggins interaction term; and one which uses the ASOG-KT group contribution model to generate an interaction term from a parameter database without use of any adjustable parameters for residual interaction. Further details of the experimental data and results are given in Appendices A, C, and E. Detailed derivations for the equations proposed in the article are given in Appendix G.

Prediction of Solvent Activities in Polymer Solutions Using an Empirical Free Volume Correction

ABSTRACT

A recent correlation for solvent activities in polymer solutions is extended in scope to provide a methodology for modeling nonideal effects in polymer solutions. This new method allows the use of any expression for the residual (enthalpic) interaction between polymer and solvent in conjunction with a standard (Flory-Huggins) expression for the combinatorial entropy. An empirical free volume correction uses the infinite dilution weight fraction activity coefficient of the solvent as an adjustable parameter. The new method is applied using one residual term given by the Analytical Solution of Groups (ASOG) technique, one similar to the Flory-Huggins interaction term, and one which yields no residual interaction. The results of these three models are compared to one another and to the Flory-Huggins model for 21 isothermal binary polymer-solvent systems. When adjustable parameters are determined by best fit to the data, each of the models applying the new method results in a standard error of less than five percent for at least 16 of the systems studied. This represented a better performance than the Flory-Huggins model.

INTRODUCTION

An understanding of the thermodynamics of polymer solutions is important in practical applications such as polymerization, devolatilization, and the incorporation of plasticizers and other additives. Diffusion phenomena in polymer melts and solutions are strongly affected by nonideal solution behavior, since chemical potential rather than concentration provides the driving force for diffusion. Proper design and engineering of many polymer processes depend greatly upon accurate modeling of thermodynamic parameters such as solvent activities.

This work was an extension of previous work by the authors for correlating solvent activities in polymer solutions (Misovich et al, 1985). In that paper, an empirical free volume correction is derived from an athermal form of the Flory-Huggins combinatorial entropy (Flory, 1953) suggested by the Analytical Solution of Groups (ASOG) group contribution model for calculation of activity coefficients in solution (Derr and Deal, 1969). The technique generally performs better than the classical Flory-Huggins equation in extrapolating solvent activity data from low solvent concentrations to higher concentrations. One deficiency of the approach is that phase separation cannot be predicted, i.e., $da_1/dw_1 > 0$ is always the case.

In this paper, the empirical free volume correction was modified to allow the explicit inclusion of an expression for residual (enthalpic) interaction between polymer and solvent. A general scheme was given to

accomplish this, and three specific cases were analyzed and compared. One case used the ASOG expression for residual interaction, while a second used an interaction parameter approach similar to the Flory-Huggins equation. The third case assumed that there was no residual interaction term, and reduced to the generalized correlation previously cited (Misovich et al, 1985).

The results in this paper were based upon a best fit of the adjustable parameters in each model using a least squares evaluation of all the data, not by extrapolation from a single data point. In each of the three cases, the infinite dilution weight fraction solvent activity coefficient Ω_1^{∞} is an adjustable binary parameter. A residual interaction parameter is a second adjustable binary parameter in the second case. The classical Flory-Huggins equation was also fit to the data for comparison. In general, regardless of which residual interaction expression was used, the new method fits the data with less error than the Flory-Huggins equation.

GENERALIZED THERMODYNAMIC MODELING

Nonideal interactions between molecules in solution are generally classified in one of two categories. Interactions resulting from differences in the size or shape of molecules are classified as entropic, while interactions resulting from differences in energy are classified as enthalpic. The complete expression for solvent activity a_1 is typically derived by multiplying concentration (mole fraction) x_1,

a size or entropy activity coefficient, γ_1^S, and a enthalpy or group interaction activity coefficient, γ_1^G, or by adding their logarithms as shown in eq 1a. It is also common to lump the concentration with one of the activity coefficients (usually the entropic coefficient) to give eq 1b.

$$\ln a_1 = \ln x_1 + \ln \gamma_1^S + \ln \gamma_1^G \tag{1a}$$

$$\ln a_1 = \ln a_1^S + \ln \gamma_1^G \tag{1b}$$

A statistical approach allows entropic interactions to be handled combinatorially, as is done by the athermal Flory-Huggins equation (Flory, 1953), giving for the entropic contribution to activity, a_1^S

$$\ln a_1^S = \ln (x_1 \gamma_1^S) = 1 - \phi_1 + \ln \phi_1 \tag{2}$$

where x_1 is the mole fraction, γ_1^S is the entropic activity coefficient, and ϕ_1 is the volume or segment fraction of component 1 (solvent). Staverman (1950) has also given an expression for combinatorial entropy which includes surface area variables as well as volume variables.

The modeling of enthalpic interactions generally involves the use of some type of binary interaction parameters. For similarly sized molecules, the entropic term is often considered small and the activity coefficient model consists wholly of the enthalpic term. In cases where both effects must be considered, the enthalpic or group interaction contribution to the activity coefficient, γ_1^G, is taken as the residual remaining after the combinatorial entropic term is removed from the

total activity coefficient. In the Flory-Huggins equation, this term is given by

$$\gamma_1^G - \chi\phi_2^2 \qquad (3)$$

where χ is the adjustable interaction parameter.

Several models for solution thermodynamics incorporate both types of effects. Analytical Solution of Groups, or ASOG, (Derr and Deal, 1969) uses a Flory-Huggins combinatorial entropy along with a residual enthalpy similar to Wilson (1964). Universal Quasi-Chemical, or UNIQUAC (Abrams and Prausnitz, 1975) and UNIFAC (Fredenslund et al, 1975) are similar, but use a Staverman combinatorial entropy, and use surface area fraction rather than mole fraction as the independent variable.

ASOG and UNIFAC also differ from UNIQUAC in that a group-contribution concept is used to analyze a solution in terms of interactions between functional groups rather than molecules. In both models, a database of functional group interaction parameters has been built. This allows prediction of residual interactions without use of binary data for the molecular components. All necessary binary data for functional groups is available from the database.

Group-contribution models can be particularly useful in describing polymer solutions. Although polymer molecules are distributed in molecular weight, they are identical in their functional group composition regardless of their size.

Predictions of classical Flory-Huggins theory and the group-contribution models show deficiencies when compared to actual data for concentrated polymer solutions. The interaction parameter in the Flory-Huggins equation, χ, does not correlate directly to the enthalpic interaction between molecules. This is evidenced by the fact that significantly nonzero values of χ are required for accurate fit of data for systems with little enthalpic interaction, like polystyrene-toluene. The presently accepted interpretation of χ is that of a free energy interaction parameter incorporating both entropic and enthalpic effects. When functional group interaction parameters (which are derived from small molecules in ASOG and UNIFAC databases) are used to predict solvent activities in polymer solutions, the results are significantly poorer than those found for solutions of small molecules. Again, this seems to be due to the existence of a noncombinatorial entropy effect.

Free volume differences contribute to such nonideal interactions. Chemically similar polymers and solvents still differ in their free volume, as evidenced by the difference in densities between polystyrene and toluene. To account for such effects, Flory (1970) proposes an equation of state approach for analysis of polymer solution properties in terms of pure component properties. This is adapted to the UNIFAC model by Oishi and Prausnitz (1978); the resulting UNIFAC-FV model is more accurate than UNIFAC in fitting activity data from polymer solutions. Other equations of state for polymer solutions have also been proposed (Lacombe and Sanchez, 1976; Liu and Prausnitz, 1979;

Scholte, 1982).

Derr and Deal (1973) note that the ASOG model is not accurate when applied to polymer solutions. By choosing an "effective" size parameter for the polymer molecule, they are able to improve predictions. A technique for choosing size parameters, referred to as Variable Size Parameter (VSP), results in a correlation for solvent activities in polymer solutions which shows good accuracy (Misovich et al, 1985). However, it is deficient in that residual interactions are not properly modeled. That drawback was eliminated in this paper.

VARIABLE SIZE PARAMETER

The following discussion reviews the development of the VSP technique. An expression similar to the combinatorial entropy given by eq 2 is used in the ASOG model, shown in eq 4, with the volume fraction ϕ_1 replaced by the size ratio R_1 defined in eq 5.

$$\ln \gamma_1^S = 1 - R_1 + \ln R_1 \qquad (4)$$

$$R_1 = S_1 / (S_1 x_1 + S_2 x_2) \qquad (5)$$

where S_i is the size parameter of component i, and x_i is the mole fraction of component i. The size parameter is intended to correlate with the molar volume of a component, and is calculated by counting the number of atoms other than hydrogen in the molecule, with a few exceptional cases such as H_2O.

At infinite dilution of component 1 (pure polymer limit), and taking $S_1 \ll S_2$ because of the size disparity of the molecules, eqs 4 and 5 yield a mole fraction activity coefficient

$$\gamma_1^{\infty} = e \frac{S_1}{S_2} \tag{6}$$

Mole fraction concentration variables are seldom used for polymer solutions because the difference in component molecular weights makes them impractical. Weight fraction w_1 is typically used, and weight fraction activity coefficients Ω_1 are defined by

$$a_1 = \Omega_1 w_1 \tag{7}$$

If the ratio of polymer size parameter to solvent size parameter, S_2/S_1, is assumed equal to the ratio of molecular weights, eq 6 can be rewritten in terms of weight fraction activity coefficient at infinite dilution.

$$\Omega_1^{\infty} = e \tag{8}$$

Experimental values of Ω_1^{∞} range from 1.5 for chloroform in poly(vinyl acetate) (Ju, 1981) to over 100 for water in polystyrene (Gunduz and Dincer, 1980). Much of the discrepancy can be attributed to residual interactions which are not accounted for in eq 4. However, data for toluene in polystyrene yield Ω_1^{∞} values between 3.7 and 5.5 (Covitz and King, 1972; Newman and Prausnitz, 1972), yet little residual interaction is expected for this system. The discrepancy in this case can be explained only in terms of the noncombinatorial entropy. The data for

other chemically similar systems show a similar pattern.

Originally (Misovich et al, 1985), an empirical correction was proposed for the size ratio R_1 in eq 5.

$$R_1 = \frac{w_1}{w_1 + (e/\Omega_1^{\infty})w_2} \tag{9}$$

This results in a correct value of weight fraction activity coefficient at infinite dilution when used in eqs 4 and 7. Reasonably accurate results are obtained for the variation of activity coefficient with concentration for most systems for which data are available. However, the approach lacks theoretical correctness for systems with residual interactions since a term like the one given by eq 3 is not employed in addition to eq 4. Also, the parameter Ω_1^{∞} describes the complete activity coefficient containing residual effects as well as combinatorial and noncombinatorial entropy effects. Hence, including Ω_1^{∞} in the size ratio R_1 incorrectly places residual effects in an entropic factor.

REVISED VARIABLE SIZE PARAMETER APPROACH

A more correct treatment of the size ratio given by eq 9 was made by canceling the effect of residual interactions from Ω_1^{∞}. This was accomplished by placing the infinite dilution value of the residual activity coefficient, $\gamma_1^{G\infty}$, in the numerator of the ratio e/Ω_1^{∞}.

$$R_1 = \frac{w_1}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2} \tag{10}$$

Eq 1 can then be used in an appropriate manner to calculate solvent activity. The first term on the right side of eq 1 will account for size and free volume interactions between molecules according to eqs 4, 5, and 10. The second term on the right side of eq 1b will account for residual interactions. Any functional expression may be used to generate the term γ_1^G, e.g., the Flory-Huggins interaction parameter term (eq 2) could be used. The factor $\gamma_1^{G\infty}$ in eq 10 has the value given by the expression for γ_1^G with w_1 taken as zero, i.e.,

$$\gamma_1^G = f(w_1) \tag{11}$$

implies that

$$\gamma_1^{G\infty} = f(0) \tag{12}$$

The set of eqs 1, 4, 10, 11, and 12 constitute a method for correlating solvent activities in polymer solutions as a function of concentration. The order in which the steps are applied is crucial. First, choose an expression for residual interaction (eq 11) and solve for its infinite dilution value (eq 12). Then determine the empirical size ratio, R_1, for the chosen concentration using a known value of Ω_1^{∞} (eq 10) and use it to calculate the size and free volume component of solvent activity, a_1^S (eq 4). Determine the residual activity coefficient, γ_1^G (eq 11), for the chosen concentration, and sum the entropic and residual terms in eq 1 to produce solvent activity.

This approach includes free volume effects with the entropy term a_1^S; a separate term is not written for these effects. Other approaches have variously modeled these effects as part of the entropy term as done here, or with a term separate from entropy and enthalpy, or as part of both entropy and enthalpy terms. These variations make direct comparison of various free volume terms difficult except in the context of overall activity predictions.

APPLICATION WITH VARIOUS RESIDUAL TERMS

Three examples using various residual terms will be presented here. We believe the technique should be useable with other choices for the residual term. In all cases, the general procedure outlined above was followed. The first residual term to be considered was no residual interaction.

$$\gamma_1^G - \gamma_1^{G\infty} - 1 \tag{13a}$$

or

$$\ln \gamma_1^G - \ln \gamma_1^{G\infty} - 0 \tag{13b}$$

The second residual term was given by a Flory-Huggins type expression analogous to eq 3, replacing ϕ_2 by R_2.

$$\ln \gamma_1^G - \chi^* R_2^2 \tag{14a}$$

$$\gamma_1^{G\infty} - \exp(\chi^*) \tag{14b}$$

where χ^* is an interaction parameter based on size ratio rather than volume fraction. The third residual term was given by the ASOG model equations.

$$\ln \gamma_1^G = \sum_k \nu_{k1} (\ln \Gamma_k - \ln \Gamma_k^*) \tag{15a}$$

$$\ln \Gamma_k = - \ln \sum_l X_l A_{kl} + 1 - \sum_l \frac{X_l A_{lk}}{\sum_m X_m A_{lm}} \tag{15b}$$

$$\ln \Gamma_k^* = \ln \Gamma_k (x_1 = 1) \tag{15c}$$

$$X_k = \sum_i x_i \nu_{ki} \Big/ \sum_j \sum_l x_j \nu_{lj} \tag{15d}$$

$$\ln \gamma_1^{G\infty} = \ln \gamma_1^G (x_1 = 0) \tag{15e}$$

In these equations, x_i is the mole fraction of molecular component i, ν_{ki} is the number of functional groups of type k in component i, X_l is the group mole fraction for group type l, Γ_k is the group activity coefficient for group type k in solution, and Γ_k^* is the group activity coefficient for group type k in pure component 1. Indices i and j represent molecular components, while indices k, l, and m represent functional groups. The set of eqs 15a-15d are analogous to the Wilson equation (Wilson, 1964) taken over functional groups rather than molecular components, weighted over the functional group composition of a molecule, and normalized for the relative occurrence of different functional groups in the solution as compared to a pure component.

When eqs 13 were used, no residual interaction was modeled. The result reduced to the previously described expression (Misovich et al, 1985)

for Ω_1 as a function of concentration with Ω_1^∞ as a single parameter.

$$\Omega_1 = \frac{\exp\left((e/\Omega_1^\infty)w_2 \,/\, [w_1 + (e/\Omega_1^\infty)w_2] \right)}{w_1 + (e/\Omega_1^\infty)w_2} \qquad (16)$$

This expression contained a single adjustable parameter, Ω_1^∞, which was selected to minimize the residual error in $\ln \Omega_1$ compared to experiment. A numerical minimization technique was necessary.

The residual interaction given by eq 14 also allowed an expression to be written for Ω_1. In this expression, $\gamma_1^{G\infty}$ was used in place of $\exp(\chi^*)$, which gave

$$\Omega_1 = \frac{\exp\left[\dfrac{(e\gamma_1^{G\infty}/\Omega_1^\infty)w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^\infty)w_2}\left[1 + \dfrac{(e\gamma_1^{G\infty}/\Omega_1^\infty)w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^\infty)w_2} \ln \Omega_1^\infty\right]\right]}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^\infty)w_2} \qquad (17)$$

Both $\gamma_1^{G\infty}$ and Ω_1^∞ were taken as adjustable parameters. They were chosen in the same way as described for eq 16.

When the ASOG model given by eqs 15 was used for residual interaction, constants from Kojima and Tochigi (1979) were used. (This version of ASOG is called ASOG-KT.) Only Ω_1^∞ was taken as an adjustable parameter, because $\gamma_1^{G\infty}$ is given by eq 15e as a function of the ASOG-KT constants only; hence, $\gamma_1^{G\infty}$ is itself a constant for a given polymer-solvent system and temperature.

FITTING OF MODEL PARAMETERS

Experimental data for 116 points in 21 sets of isothermal polymer-solvent activities were used to test the VSP approach with each of the three residual expressions. The classical Flory-Huggins model, eqs 1-3, was also applied for comparison. For each data set and each equation, the best fit of adjustable parameters was made to minimize the sum of squares residual of ln a_1, i.e., to minimize the relative error in a_1. An example of the technique is given as Appendix A. The parameters adjusted were Ω_1^{∞} (VSP with eq 13 and VSP with eqs 15), Ω_1^{∞} and $\gamma_1^{G\infty}$ (VSP with eqs 14), and χ (Flory-Huggins). Table 1 contains all values of the adjustable parameters which were derived from experimental data. In addition, the value of $\gamma_1^{G\infty}$ given by eq 15e from the ASOG-KT parameter database is given for comparison.

Table 1 shows a remarkable consistency in Ω_1^{∞} values in the VSP results using different residual expressions. This indicates the physical significance of the parameter, as distinguished from a mere data fit. As long as there is a reasonable model for the enthalpic term, the VSP method yields similar values for Ω_1^{∞}. In Figure 1, the values of Ω_1^{∞} given using eqs 13 have been arbitrarily taken as x-coordinates, and the values given using eqs 14 and 15 are plotted as y-coordinates. The plot shows little scatter from the line x = y. Values of Ω_1^{∞} given using eq 13 exceeded those given using the other equations when $\gamma_1^{G\infty}$ was greater than unity (positive enthalpic deviations from Raoult's Law); the opposite was true when $\gamma_1^{G\infty}$ was less than unity.

Comparison of the value of $\gamma_1^{G\infty}$ between eqs 14 and 15 showed that some data sets agreed well, while others had no apparent correlation, as Figure 2 indicates. In particular, there were three data sets where eq 14 predicted a best fit value of $\gamma_1^{G\infty}$ of unity or less while eq 15 predicted a value substantially larger than unity. The apparent disagreement was due to the nature of the calculation of $\gamma_1^{G\infty}$ in the VSP model with eqs 14 and 15. In eq 14, $\gamma_1^{G\infty}$ was an adjustable parameter, while in eq 15, it was not adjustable but was given as a function of the ASOG-KT constants. Noting this distinction, the results from eq 15 would generally have been considered preferable as they had a more fundamental basis in a solution model than the parameter fitting results from eq 14. The general agreement between parameters derived from numerical fit and those estimated from the ASOG-KT database was encouraging in many cases.

In Figure 3, the size factors defined as (e/Ω_1^{∞}) in eq 13, and as $(e\gamma_1^{G\infty}/\Omega_1^{\infty})$ in eqs 14 and 15 were compared. Again, there is a sizable amount of scatter in the plot. Of the total of 63 data fits (21 sets with three models), only in eight cases was a size factor greater than unity predicted by any model. In no case did all three models predict a size factor greater than unity for a given data set. These results are consistent with the observation of Derr and Deal (1973) that the "effective size factor" must be less than the actual size ratio of the molecules; in our models, size factors less than unity indicated they were less than the actual weight ratio.

Table 1. Parameter Values Determined by Data Fit.

Solvent-Polymer Temp, °C	wt frac range	no. of pts	Ω_1^∞ VSP with eqs 13	14	15	$\gamma_1^{G\infty}$ VSP with eq 14	χ Flory-Huggins	$\gamma_1^{G\infty}$ VSP with eq 15e (not data fit)
toluene-poly(styrene)[a]								
25	0.111-0.918	11	4.95	4.56	4.94	1.73	0.34	1.01
60	0.102-0.261	3	4.85	4.63	4.84	1.59	0.29	1.01
80	0.246-0.671	3	5.17	4.72	5.15	1.58	0.32	1.00
methyl ethyl ketone-poly(styrene)[a]								
25	0.091-0.298	4	8.93	8.23	7.77	1.65	0.71	1.88
benzene-poly(isobutylene)[b]								
10	0.225-0.454	3	10.66	7.96	6.70	1.92	0.84	1.82
25	0.044-0.373	11	8.79	8.18	7.35	1.73	0.92	1.71
cyclohexane-poly(isobutylene)[c]								
25	0.128-0.569	8	4.97	4.90	4.94	1.25	0.39	1.06
n-pentane-poly(isobutylene)[d]								
25	0.029-0.584	9	8.76	8.33	8.76	1.64	0.68	1.00
triisopropylbenzene-poly(styrene)[e]								
165	0.030-0.086	3	12.34	12.25	12.05	1.22	1.00	1.07
175	0.020-0.066	3	10.61	9.84	10.51	2.66	0.92	1.06
carbon disulfide-poly(styrene)[e]								
115	0.014-0.041	3	3.73	3.73	3.70	1.00	0.41	3.61
140	0.008-0.029	4	3.48	3.48	3.48	1.00	0.34	4.15
methanol-poly(methyl methacrylate)[e]								
120	0.003-0.009	3	16.65	16.33	16.23	2.71	1.28	2.97
130	0.003-0.008	3	12.73	10.79	12.56	0.19	1.01	2.84
toluene-poly(methyl methacrylate)[e]								
130	0.017-0.112	3	9.68	9.68	9.69	1.00	0.79	0.97
160	0.006-0.037	5	10.95	10.95	11.07	1.00	0.95	0.90
toluene-poly(vinyl acetate)[f]								
35	0.084-0.195	4	9.71	8.41	8.26	2.06	0.78	1.40
40	0.051-0.171	7	9.26	8.35	8.26	2.06	0.77	1.38
47	0.052-0.107	3	8.87	7.63	8.18	3.09	0.76	1.35
chloroform-poly(vinyl acetate)[f]								
35	0.163-0.464	7	1.49	1.49	1.62	1.00	-0.41	0.41
45	0.093-0.499	16	1.44	1.40	1.48	0.67	-0.46	0.45

References: [a]Bawn et al (1950). [b]Eichinger and Flory (1968a). [c]Eichinger and Flory (1968b). [d]Eichinger and Flory (1968c). [e]Liu (1980). [f]Ju (1981).

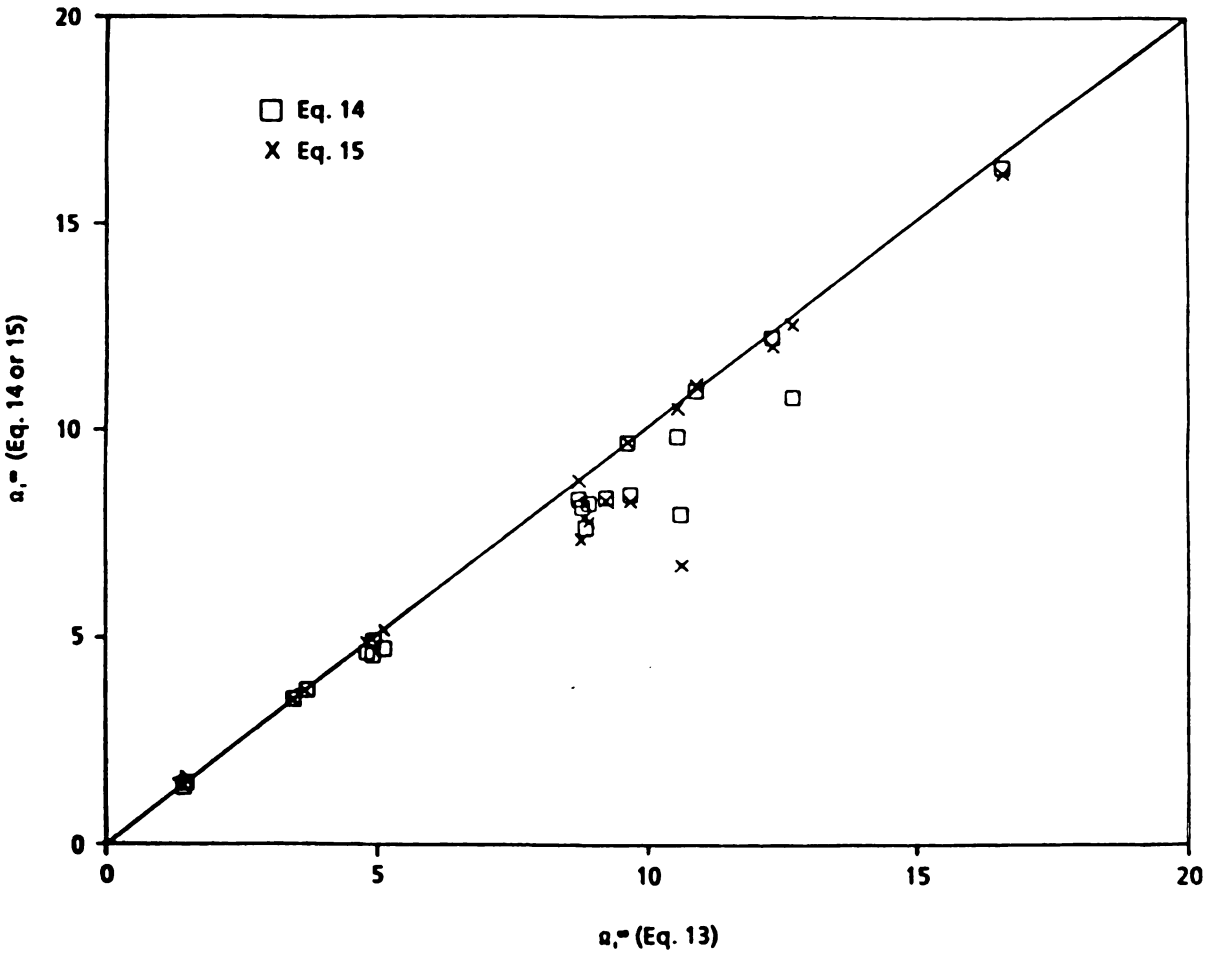

Figure 1. Comparison of Infinite Dilution Activity Coefficients from Different Residual Terms. Squares, eq 14; crosses, eq 15.

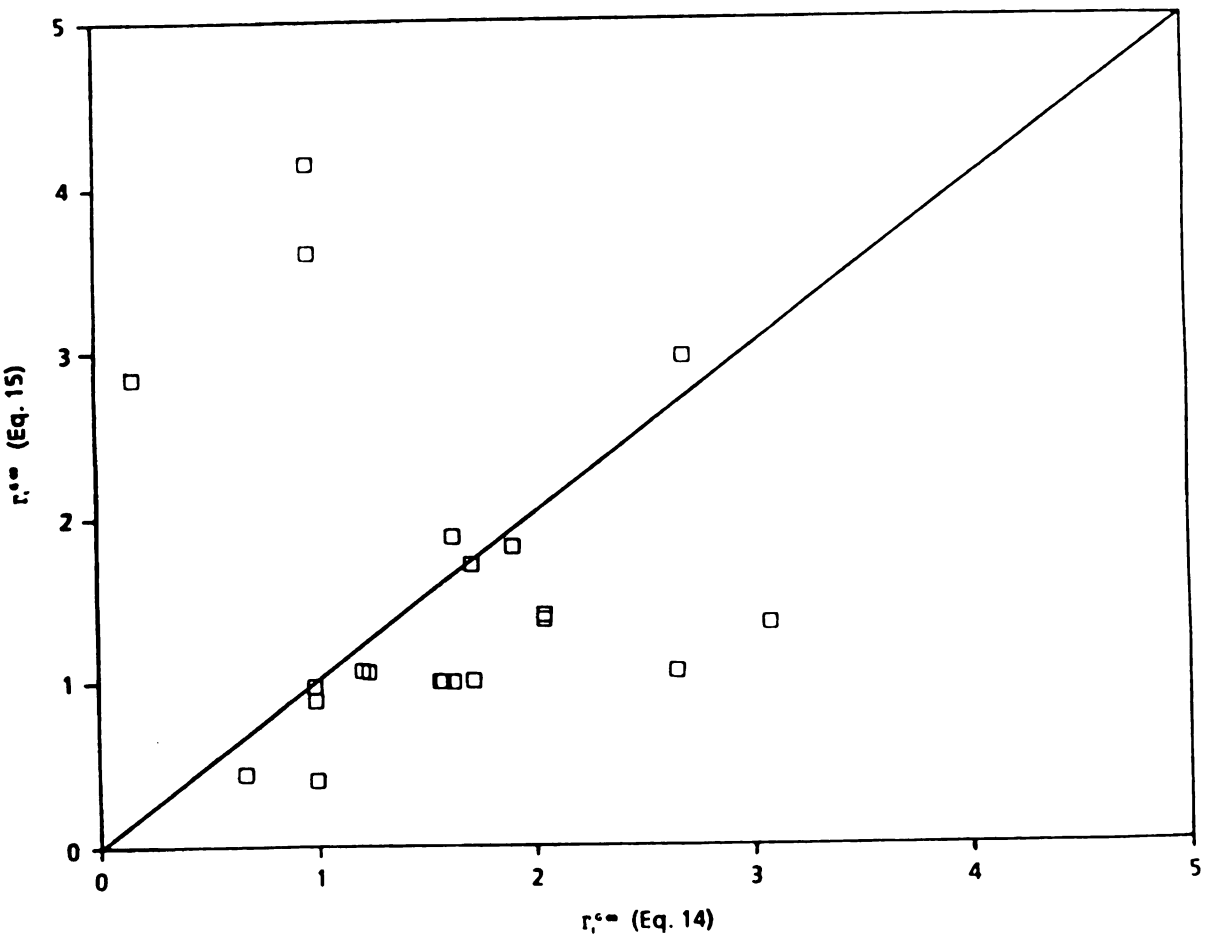

Figure 2. Comparison of Infinite Dilution Residual Coefficients from Different Residual Terms.

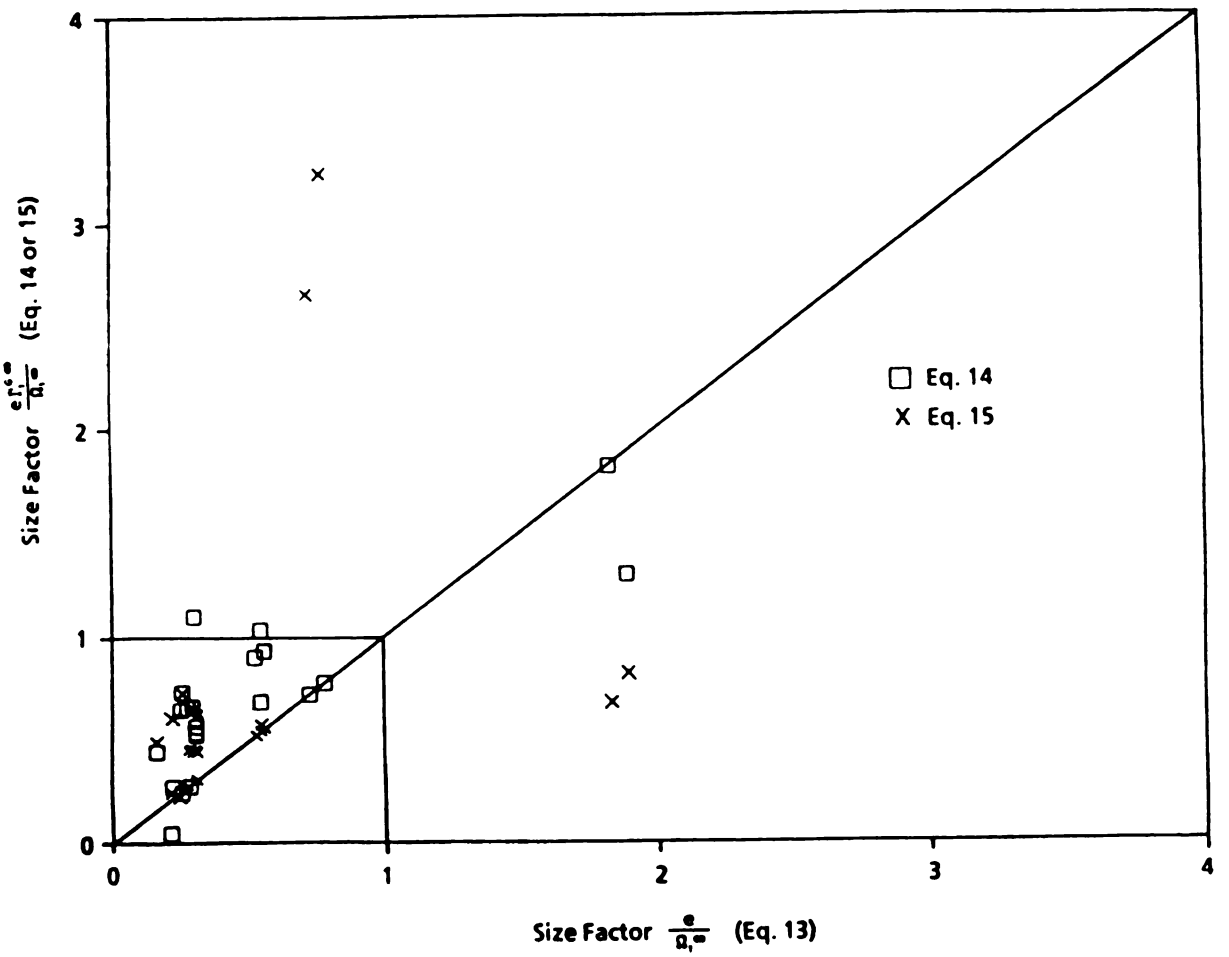

Figure 3. Comparison of Size Factors from Different Residual Terms. Squares, eq 14; crosses, eq 15.

Disagreement among the models on the parameter values did not appear to be random. Rather, certain systems seemed prone to good agreement or poor agreement on certain parameters, as can be seen from examination of Table 1. The systems benzene-poly(isobutylene), methyl ethyl ketone-poly(styrene), and toluene-poly(vinyl acetate) had large relative deviations among Ω_1^{∞} values; the first two also had small relative deviations among $\gamma_1^{G\infty}$ values. The opposite was true for the system carbon disulfide-poly(styrene). Finally, the systems toluene-poly(methyl methacrylate) and cyclohexane-poly(isobutylene) showed small relative deviations in both parameter values. The other systems showed either intermediate levels of deviation among parameters or showed different trends at different temperatures.

COMPARISON WITH SOLVENT ACTIVITIES IN POLYMER SOLUTIONS

Some specific results which illustrate the accuracy and flexibility of the method are given in Figures 4 through 6. Solvent weight fraction activity coefficient Ω_1 was plotted versus solvent weight fraction for a given polymer-solvent system at a given temperature. Experimental points were shown along with lines or curves representing the best fit results of certain models.

In Figure 4, data for benzene-poly(isobutylene) at 25°C is shown, along with the VSP model using eq 13 and the Flory-Huggins model. (Both of these models contain one adjustable parameter.) The VSP predictions were more accurate in this case, particularly at the extremes of

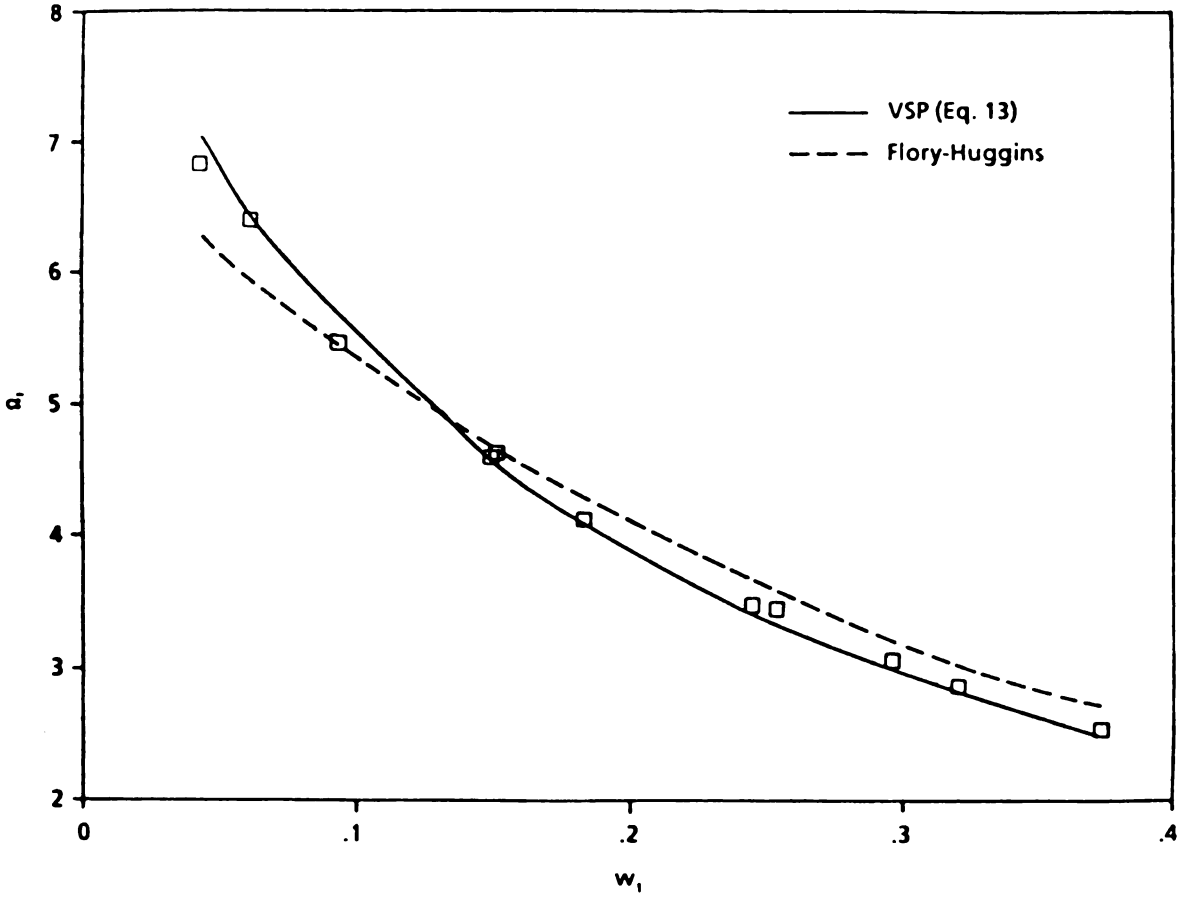

Figure 4. Solvent Activity Coefficient as a Function of Concentration, Benzene-Poly(isobutylene) at 25°C. Curves, equations; squares, experiment.

concentration that were used. Some investigators prefer to express activity results as a variation of the interaction parameter χ with concentration, often referred to as "reduced residual chemical potential." The curve in Figure 4 labeled "Flory-Huggins" would represent a constant χ value. The experimental data would show χ decreasing with concentration because the slope of the data is more steeply negative than the "Flory-Huggins" curve. The curve representing VSP with eq 13 also correctly showed this decrease.

Figure 5 compares VSP using eq 15 with Flory-Huggins for the system toluene-poly(methyl methacrylate) at 160°C. Neither model performed well on this data set, although VSP with eq 15 did correctly model the fact that χ decreases with concentration, although not the magnitude of decrease. In Figure 6, data for the system toluene-poly(styrene) at 60°C showed a very slight increase in χ with concentration, and this was correctly modeled by VSP with eq 14, since it predicted a less steeply negative slope than the Flory-Huggins model. The examples in Figures 4 through 6 show that the VSP method is capable of modeling systems in which χ either decreases or increases with solvent concentration.

For each data set and equation, a standard error was defined by

$$s = \left[\frac{\Sigma \left(\ln a_1^{\text{pred}} - \ln a_1^{\text{exptl}}\right)^2}{(n - d)} \right]^{1/2} \qquad (18)$$

where the sum was over all n points in the data set, and where d was the number of adjustable parameters (degrees of freedom) in the model used.

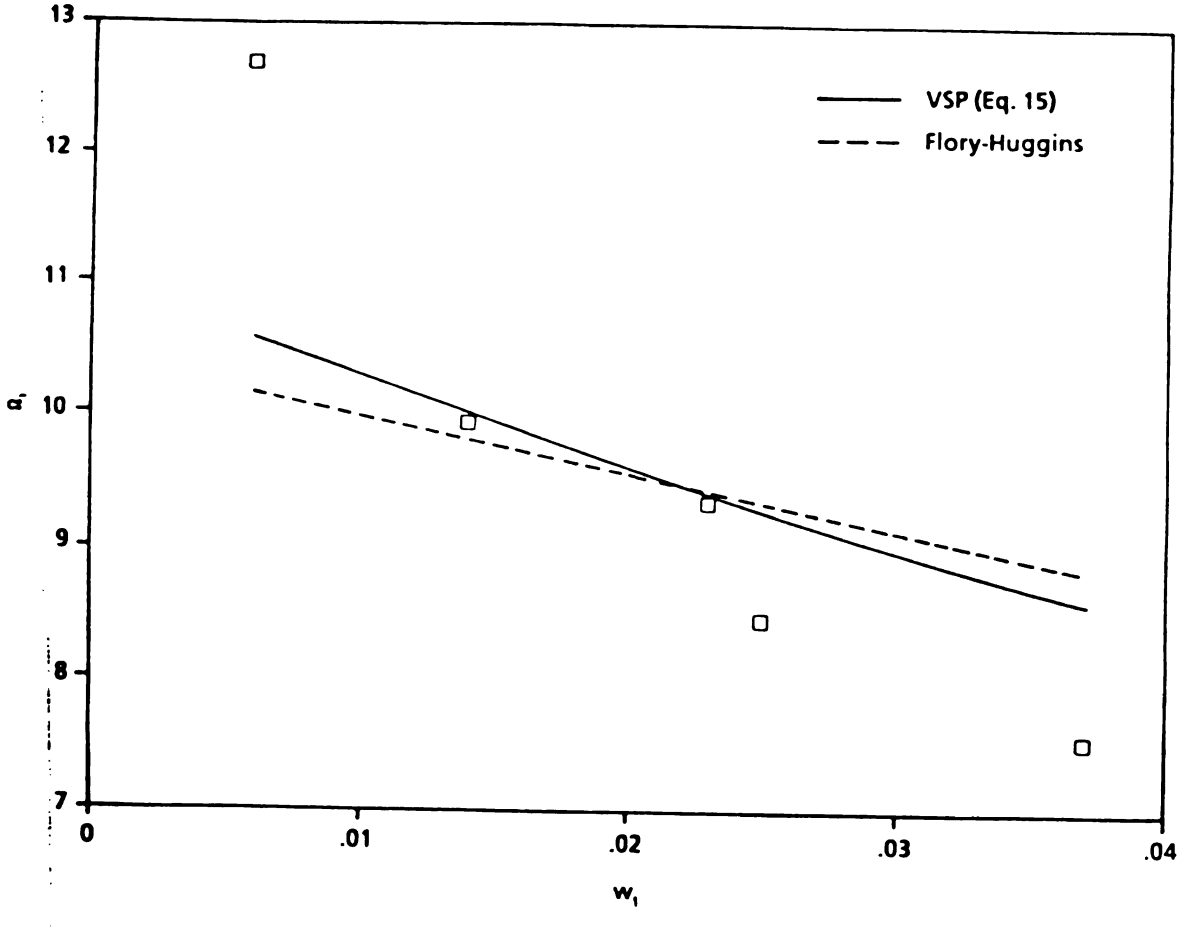

Figure 5. Solvent Activity Coefficient as a Function of Concentration, Toluene-Poly(methyl methacrylate) at 160°C. Lines, equations; squares, experiment.

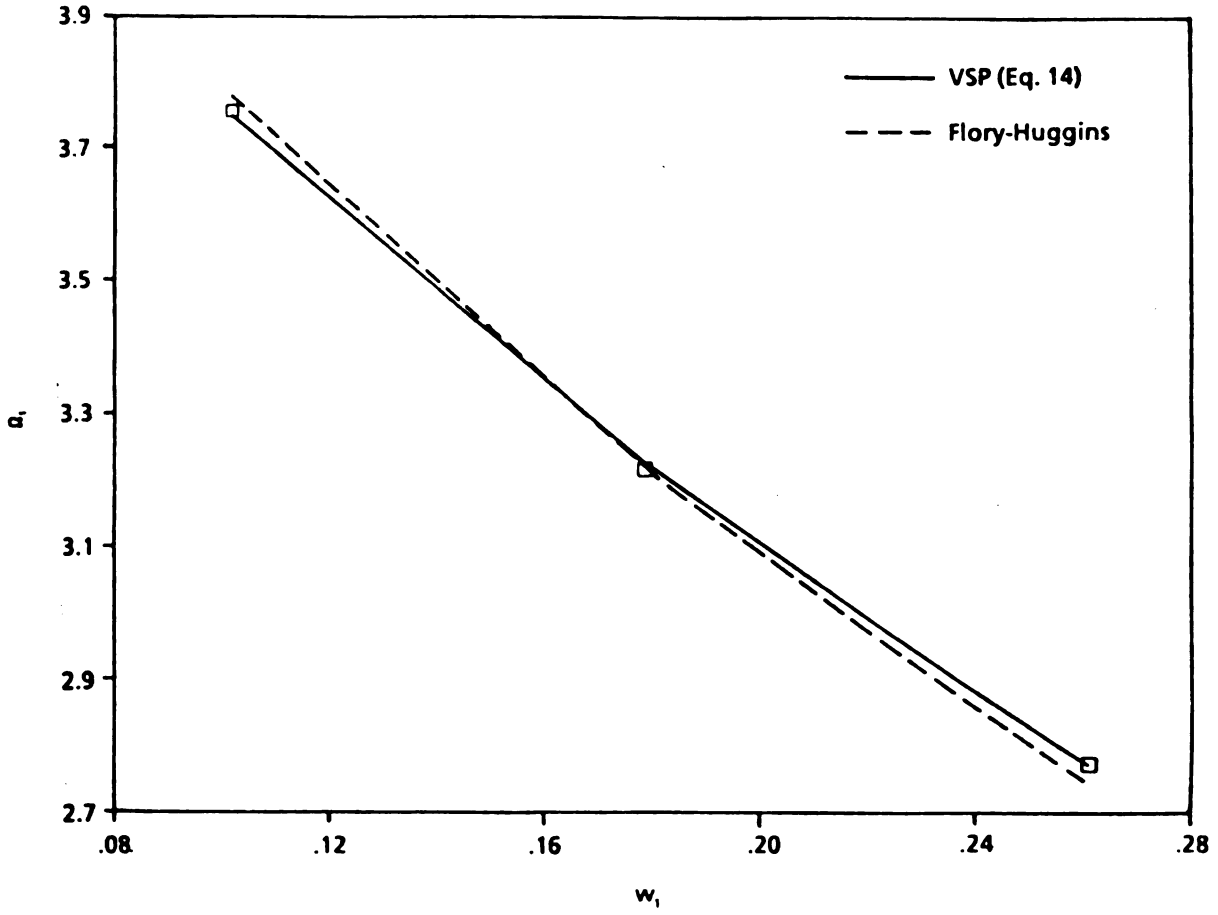

Figure 6. Solvent Activity Coefficient as a Function of Concentration, Toluene-Poly(styrene) at 60°C. Lines, equations; squares, experiment.

For the VSP model with eqs 14, d = 2; for all the other models, d = 1. Hence, in cases where the VSP model with eqs 14 produced the same standard error as the other models, it must have resulted in a smaller deviation from experiment on the average. The standard error defined by eq 18 in effect penalizes eq 14 because it has more adjustable parameters.

The standard error results are given as Table 2, and were generally quite good for all the models. Even the Flory-Huggins model, when fit to the data, had a standard error of less than five percent in 14 of 21 data sets. The VSP models were somewhat more accurate, with standard errors less than five percent for 16 of 21 data sets using eqs 13 and 15 for the residual term, and 17 of 21 data sets using eq 14. Previous work (Misovich et al, 1985) has shown that the VSP model using eqs 13 is superior to the Flory-Huggins model when data from low concentration is extrapolated to higher concentrations. The same results were found here in a best fit of all data, for all the models using the VSP method regardless of the residual expression used.

Because of the generally good performance of all the models, it was not clear that any given model was significantly better or poorer than the others for a particular system in many cases, outside of the general trend noted in the previous paragraph.

(VSP, eq 14) > (VSP, eq 13) = (VSP, eq 15) > (Flory-Huggins)

Table 2. Comparison of Models with Experiment.

Solvent-Polymer Temp, °C	wt frac range	no. of pts	Std % error VSP 13	with eqs 14	15	Flory-Huggins
toluene-poly(styrene)						
25	0.111-0.918	11	2.1	1.1	2.0	1.6
60	0.102-0.261	3	1.3	0.4	1.3	0.8
80	0.246-0.671	3	1.0	0.1	1.0	0.6
methyl ethyl ketone-poly(styrene)						
25	0.091-0.298	4	1.9	0.6	1.6	2.4
benzene-poly(isobutylene)						
10	0.225-0.454	3	2.1	0.8	2.3	2.6
25	0.044-0.373	11	2.6	1.2	4.4	5.2
cyclohexane-poly(isobutylene)						
25	0.128-0.569	8	2.4	2.6	2.4	2.4
n-pentane-poly(isobutylene)						
25	0.029-0.584	9	2.2	0.9	2.2	2.2
triisopropylbenzene-poly(styrene)						
165	0.030-0.086	3	2.9	4.1	2.9	5.4
175	0.020-0.066	3	15.4	21.4	15.4	15.1
carbon disulfide-poly(styrene)						
115	0.014-0.041	3	0.5	0.6	0.7	0.7
140	0.008-0.029	4	13.8	16.9	13.8	13.9
methanol-poly(methyl methacrylate)						
120	0.003-0.009	3	1.4	1.4	1.0	1.0
130	0.003-0.008	3	6.9	0.6	6.2	6.2
toluene-poly(methyl methacrylate)						
130	0.017-0.112	3	20.2	28.6	20.2	24.1
160	0.006-0.037	5	12.4	14.3	11.9	14.3
toluene-poly(vinyl acetate)						
35	0.084-0.195	4	2.8	0.3	0.5	0.5
40	0.051-0.171	7	2.9	1.4	1.4	1.4
47	0.052-0.107	3	4.6	2.4	2.7	2.7
chloroform-poly(vinyl acetate)						
35	0.163-0.464	7	3.9	4.3	3.1	4.5
45	0.093-0.499	16	2.7	2.6	3.0	2.6

It was also difficult to define an average error over all the systems tested because the presence of large errors in a few data sets tended to obscure the behavior in the majority of data sets in which standard errors were relatively small. The average error, defined by the arithmetic mean over all 21 data sets, was greatly affected by this. At the same time, the average defined by the geometric mean over all data sets was affected most strongly by the presence of very small errors in a few data sets. Both these averages, as well as the median standard error for the 21 data sets, are given for each model as part of Table 3. VSP with eqs 14 and 15 performed best according to these measurements; VSP with eqs 13 and Flory-Huggins performed worst, but still showed small standard errors on many sets.

Also included in Table 3 are the number of times each model had the lowest (or highest) standard error for a single data set. (The numbers total more than 21 because of ties.) VSP with eqs 14 and 15 again outperformed the other two models. Finally, for each data set in which a given model had the lowest (or highest) standard error, an average amount by which the error in the other models exceeded that of the best model (or the error in the worst model exceeded that of the other models) was calculated. Both absolute (differences in standard errors) and relative (ratios of standard errors) amounts are listed in Table 3. As was the case with arithmetic and geometric means above, the absolute amounts gave greater weight to data sets in which all models had large standard errors, while the relative amounts gave greater weight to data sets in which standard errors were small. On an absolute

Table 3. Comparison of Errors.

	Model			
	VSP eq 13	VSP eq 14	VSP eq 15	Flory-Huggins
Average standard error:				
arithmetic mean	5.0	5.1	4.7	5.2
geometric mean	3.2	1.8	2.8	2.9
median	2.7	1.4	2.4	2.6
Number of data sets where standard error was				
lowest	5	12	8	5
highest	9	6	5	8
In sets with lowest standard error, average amount by which error was larger in other models				
absolute	0.3	0.8	0.5	0.2
relative	1.2	2.7	1.2	1.1
In sets with highest standard error, average amount by which error was smaller in other models				
absolute	0.5	0.9	0.1	0.4
relative	2.0	1.2	1.5	1.5

basis, VSP with eqs 15 was the only model which outperformed the other models by a wider margin when having the lowest error than the other models outperformed it when it had the highest error. On a relative basis, the same was true of only VSP with eqs 14.

By most measurements of average performance, the VSP model using eqs 14 or 15 produced a lower standard error than the VSP model using eq 13 or the Flory-Huggins model. This was attributed to the fact that the Flory-Huggins equation does not correctly model nonideal solution interactions due to free volume differences, while the VSP model using eq 13 does not include a term for nonideal residual interactions. However, due to their simplicity, they were more convenient to use than the more accurate models. Table 2 indicates that their performance was generally in the same order of magnitude of standard error as the more complicated, more accurate VSP models using eqs 14 or 15.

There are, however, certain situations in which behavior in the infinite dilution limit of zero solvent is important, e.g., thermodynamic modeling for polymer devolatilization. In such cases, as Table 1 shows, the choice of model may produce a large difference in the predicted value of infinite dilution parameters. This can be true even when all models perform relatively equally over a larger concentration range as shown by the standard errors in Table 2. For modeling behavior near the pure polymer limit, the VSP models using eqs 14 or 15 would be preferable to the other models tested.

CONCLUSIONS

The VSP method using various residual terms allowed accurate prediction of solvent activities in most of the polymer-solvent systems reviewed. Choosing terms which modeled nonideal residual interactions in solution gave the best results. When all the points in a given experimental data set were fit to determine adjustable parameters, the VSP method generally performed better than the Flory-Huggins model.

Use of the VSP method with residual interaction given by the ASOG-KT equations produced accurate results with only one adjustable parameter representing the infinite dilution solvent activity coefficient on a weight fraction basis. Even better results were sometimes obtained by using a residual term containing an additional adjustable parameter.

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APPENDIX A. EXAMPLE OF VSP METHOD.

The following experimental data are given for toluene(1)-poly(styrene)(2) at 80°C.

w_1	a_1
0.246	0.706
0.458	0.914
0.671	0.984

To fit the Flory-Huggins parameter χ in eqs 1-3, weight fraction data must be converted to volume fraction data. Density data can be used for this transformation.

$$\phi_i = \frac{w_i/\rho_i}{w_1/\rho_1 + w_2/\rho_2} \qquad \text{(A-1)}$$

Densities:
$\rho_1 = 0.8075$
$\rho_2 = 1.068$

w_1	a_1	ϕ_1
0.246	0.706	0.301
0.458	0.914	0.528
0.671	0.984	0.730

The least squares condition results in the following equation which can be directly solved for χ. Subscripts 1i and 2i refer to components 1 and 2, data point i.

$$\chi = \sum_i \left(\phi_{2i}^2 \ln (a_{1i}/\phi_{1i}) - \phi_{2i}^3 \right) / \sum_i \left(\phi_{2i}^4 \right) \qquad \text{(A-2)}$$

$\chi = 0.319$

Applying eqs 1-3 gives these results.

w_1	a_1	a_1^{pred}
0.246	0.706	0.708
0.458	0.914	0.909
0.671	0.984	0.979

To apply VSP using eq 13, it is necessary to minimize the error between the activity calculated using eqs 1, 2, 4, 10, and 13, and the measured activity. Ω_1^{∞} is an adjustable parameter, but the least squares condition cannot be solved directly for it. The simplest way to proceed is to assume a value for Ω_1^{∞}, generate R_1 values from eq 10 (using $\gamma_1^{G\infty} - 1$ as given by eq 13), and calculate the sum of squares residual given by adding $[\ln(a_1/a_1^{pred})]^2$ for each data point. A good initial choice for Ω_1^{∞} comes from the Flory-Huggins model

$$\Omega_1^{\infty} = (\rho_2/\rho_1) \exp (1 + \chi) \qquad \text{(A-3)}$$

using the known density values and χ. The two tables below illustrate the results using this initial Ω_1^{∞} and the best fit value of Ω_1^{∞}.

$\Omega_1^{\infty} = 4.948$ $\quad e/\Omega_1^{\infty} = 0.549$

w_1	a_1	R_1	a_1^{pred}	$[\ln(a_1/a_1^{pred})]^2$
0.246	0.706	0.373	0.698	1.36×10^{-4}
0.458	0.914	0.606	0.899	2.87×10^{-4}
0.671	0.984	0.788	0.974	1.04×10^{-4}
		sum of squared residuals		5.26×10^{-4}

$\Omega_1^{\infty} = 5.166$ $\quad e/\Omega_1^{\infty} = 0.526$

w_1	a_1	R_1	a_1^{pred}	$[\ln(a_1/a_1^{pred})]^2$
0.246	0.706	0.383	0.710	2.45×10^{-5}
0.458	0.914	0.616	0.905	1.09×10^{-4}
0.671	0.984	0.795	0.976	6.91×10^{-5}
		sum of squared residuals		2.03×10^{-4}

To apply VSP using eq 14, two adjustable parameters must be fit to the data, Ω_1^{∞} and $\gamma_1^{G\infty}$. As in the previous case, the simplest way to proceed is to assume values for these parameters, generate R_1 values from eq 10, and calculate the sum of squares residual given by adding $[\ln(a_1/a_1^{pred})]^2$ for each data point. Initial choices for the parameters can be made using the results from the previous case (or eqs A-2 and A-3) for Ω_1^{∞} and setting $\gamma_1^{G\infty}$ equal to unity. The table below illustrates the results using the best fit values. The initial values are identical to the best fit results from the previous case.

$\Omega_1^{\infty} = 4.719$ $\quad \gamma_1^{G\infty} = 1.580$ $\quad e\,\gamma_1^{G\infty}/\Omega_1^{\infty} = 0.526$

w_1	R_1	a_1^S	γ_1^G	a_1^{pred}
0.246	0.264	0.551	1.281	0.706
0.458	0.481	0.809	1.131	0.914
0.671	0.691	0.941	1.044	0.983

w_1	a_1	a_1^{pred}	$[\ln(a_1/a_1^{pred})]^2$
0.246	0.706	0.706	1.69×10^{-8}
0.458	0.914	0.914	2.64×10^{-7}
0.671	0.984	0.983	5.53×10^{-7}
		sum of squared residuals	8.34×10^{-7}

To apply VSP using eq 15, only Ω_1^{∞} must be fit to the data because γ_1^G is given a priori from the ASOG equations. The necessary parameters for use of these equations for the example are given by Kojima and Tochigi (1979). Molecular components toluene and poly(styrene) are defined in

terms of functional groups CH_2 and ArCH as follows.

ν_{ki} = number of functional groups k occuring in molecule or repeat unit i

MW = molecular weight of molecule or repeat unit i

	ν_{ki}		
	CH_2	ArCH	MW
toluene	1.0	6.0	92.0
PS	1.8	6.0	104.0

ASOG-KT gives functional group interaction parameters A_{kl} used in eqs 15 as the sum of a temperature-independent and a temperature-dependent term given by eq A-4. Values of these constants are listed for the groups in this example.

$$A_{kl} = \exp (a_{kl} + b_{kl} / T) \qquad \text{(A-4)}$$

	a_{kl}		b_{kl}	
	CH_2	ArCH	CH_2	ArCH
CH_2	0	-0.7457	0	146.0
ArCH	0.7297	0	-176.8	0

In the example, the temperature is 80°C or 353.16 K, giving interaction parameter values of

	A_{kl}	
	CH_2	ArCH
CH_2	1.000	0.717
ArCH	1.257	1.000

which are used in eqs 15. Consider the calculation of $\ln \Gamma_k^*$ in eq 15c.

Since x_1 equals one in this calculation, eq 15d gives this result for group mole fractions.

$$X_1 = 1.0 / (1.0 + 6.0) = 0.143$$

$$X_2 = 1 - 0.143 = 0.857$$

Applying these group mole fractions in eq 15b gives

$$\ln \Gamma_1^* = - \ln (0.143 \cdot 1 + 0.857 \cdot 0.717) + 1 - \frac{0.143 \cdot 1}{0.143 \cdot 1 + 0.857 \cdot 0.717} - \frac{0.857 \cdot 1.257}{0.143 \cdot 1.257 + 0.857 \cdot 1}$$

$$\ln \Gamma_1^* = 0.037$$

$$\ln \Gamma_2^* = - \ln (0.143 \cdot 1.257 + 0.857 \cdot 1) + 1 - \frac{0.143 \cdot 0.717}{0.143 \cdot 1 + 0.857 \cdot 0.717} - \frac{0.857 \cdot 1}{0.143 \cdot 1.257 + 0.857 \cdot 1}$$

$$\ln \Gamma_2^* = 0.005$$

The same procedure is used to calculate $\ln \Gamma_k$ at any concentration. The only additional step needed is the conversion of component or repeat unit weight fraction to mole fraction.

$$x_1 = 0.246/92 / (0.246/92 + (1-0.246)/104) = 0.269$$

$$x_2 = 1 - 0.269 = 0.731$$

$$X_1 = (0.269 \cdot 1.0 + 0.731 \cdot 1.8) / (0.269 \cdot 7.0 + 0.731 \cdot 7.8) = 0.209$$

$$X_2 = 1 - 0.209 = 0.791$$

$$\ln \Gamma_1 = - \ln (0.209 \cdot 1 + 0.791 \cdot 0.717) + 1 - \frac{0.209 \cdot 1}{0.209 \cdot 1 + 0.791 \cdot 0.717} - \frac{0.791 \cdot 1.257}{0.209 \cdot 1.257 + 0.791 \cdot 1}$$

$$\ln \Gamma_1 = 0.040$$

$$\ln \Gamma_2 = - \ln (0.209 \cdot 1.257 + 0.791 \cdot 1) + 1 - \frac{0.209 \cdot 0.717}{0.209 \cdot 1 + 0.791 \cdot 0.717} - \frac{0.791 \cdot 1}{0.209 \cdot 1.257 + 0.791 \cdot 1}$$

$$\ln \Gamma_2 = 0.004$$

The activity coefficient γ_1^G for this concentration is given by eq 15a.

$$\gamma_1^G = \exp (1.0 \cdot (0.040 - 0.037) + 6.0 \cdot (0.004 - 0.005)) = 1.003$$

Results for all data points as well as pure components 1 and 2 are given in the table.

w_1	x_1	X_1	X_2	$\ln \Gamma_1$	$\ln \Gamma_2$	γ_1^G	
1	1.000	0.143	0.857	0.049	0.002		pure toluene
0	0	0.231	0.769	0.037	0.005	1.005	pure polymer
0.246	0.269	0.209	0.791	0.040	0.004	1.003	
0.458	0.489	0.190	0.810	0.043	0.003	1.001	
0.671	0.697	0.172	0.828	0.045	0.003	1.000	

The adjustable parameter Ω_1^∞ can now be fit to the data. A good initial choice for this parameter is the result from VSP using eq 13 or from eqs A-2 and A-3. The tables below give results for the initial value and best fit value.

$\Omega_1^{\infty} = 5.166$ $\gamma_1^{G\infty} = 1.005$ $e\,\gamma_1^{G\infty} / \Omega_1^{\infty} = 0.529$

w_1	R_1	a_1^S	γ_1^G	a_1^{pred}
0.246	0.382	0.708	1.003	0.710
0.458	0.615	0.904	1.001	0.905
0.671	0.794	0.976	1.000	0.976

w_1	a_1	a_1^{pred}	$[\ln(a_1/a_1^{pred})]^2$
0.246	0.706	0.710	3.38×10^{-5}
0.458	0.914	0.905	9.52×10^{-5}
0.671	0.984	0.976	6.40×10^{-5}
		sum of squared residuals	1.93×10^{-4}

$\Omega_1^{\infty} = 5.152$ $\gamma_1^{G\infty} = 1.005$ $e\,\gamma_1^{G\infty} / \Omega_1^{\infty} = 0.530$

w_1	R_1	a_1^S	γ_1^G	a_1^{pred}
0.246	0.381	0.708	1.003	0.709
0.458	0.615	0.904	1.001	0.905
0.671	0.794	0.976	1.000	0.976

w_1	a_1	a_1^{pred}	$[\ln(a_1/a_1^{pred})]^2$
0.246	0.706	0.709	2.34×10^{-5}
0.458	0.914	0.905	1.03×10^{-4}
0.671	0.984	0.976	6.58×10^{-5}
		sum of squared residuals	1.92×10^{-4}

CHAPTER 3

ANALYSIS OF RESIDUAL TERMS USED IN GROUP CONTRIBUTION MODELS

One of the important advances in modeling of solution behavior has been the isolation of residual (enthalpic or energetic) effects and combinatorial (entropic) effects. The recent approach to both types of interaction has become fairly standardized. In the case of combinatorial effects, some form of combinatorial entropy (such as Flory, 1953 or Staverman, 1950) is used. For residual effects, a local composition model similar to Wilson (1964) is applied. The synthesis of both types of interaction in a single model is typified by UNIQUAC (Abrams and Prausnitz, 1975).

The use of distinct combinatorial and residual terms is commonplace in group contribution models; in fact, the original development of the ASOG model (Derr and Deal, 1969) predates UNIQUAC by several years. The unique feature of group contribution models such as ASOG and UNIFAC (Fredenslund, Jones, and Prausnitz, 1975) is the treatment of summed functional group interactions rather than individual molecular interactions. This makes data reduction possible in terms of functional groups, so that binary molecular data is not required once a functional group interaction database has been tabulated.

The concept of deriving molecular solution properties, e.g., activity coefficients, by summing properly weighted and normalized functional group properties is the basis of the residual interaction terms in ASOG and UNIFAC. The summations used make sense from an intuitive standpoint, and the residual interaction given by a Wilson-like equation has a theoretical basis in local composition and like-unlike pair interaction. However, a careful study of the mathematical properties inherent in the residual terms of group contribution models shows an implicit dependence of the model predictions on the choice of unit used to describe functional group size. This dependence arises from the fact that the summation of functional group activity coefficients is done in a linear fashion, but the Wilson-like equation used to derive these coefficients is nonlinear in all its parameters and variables. In this chapter, this idea is developed and studied in depth for the simplest possible non-trivial case of a binary solution containing at most two distinct functional groups.

One consequence of the detailed study of such systems is that the group contribution model equations for residual interaction can be transformed to make their behavior more explicit in some fashion. Doing so allows the additional constraint of molecular composition (in terms of the different ratios of functional groups present in different molecules) to modify the rather weak constraint on activity coefficients given by a Wilson-like equation. A framework is thus given for determining bounds on activity coefficients without sufficient knowledge to actually fit all the interaction parameters for functional groups in solution.

Derivation of such bounds can also assist in the design of experiments to take the necessary data for fitting interaction parameters.

ANALYSIS OF RESIDUAL TERM IN SOLUTION OF GROUPS MODEL

The manuscript which follows contains the analysis of bounding and normalization properties inherent in typical solution of groups model residual expressions. Transformations of the model which allow more convenient analysis are developed and some typical results are shown for a binary solution containing at most two distinct functional groups. Extension of the technique to multicomponent, multifunctional group solutions should be possible, but is not described here. Details of the derivation of new equations which are presented in this manuscript are given in Appendix H.

Normalization and Bounding Properties Inherent in Solution of Groups Activity Coefficient Models

ABSTRACT

Recent thermodynamic models for activity coefficients such as UNIFAC and ASOG use a form of Wilson's equation to calculate the residual contribution to the activity coefficient. These equations can be transformed to allow more convenient analysis of their mathematical properties. Two important results have been obtained from such an analysis. Bounds on the range of activity coefficients can be derived without knowledge of the interaction parameter values. The predicted values of activity coefficients are shown to depend on a normalization step implicit in the definition of functional group size.

INTRODUCTION

The equation proposed by Wilson [1] for modeling nonideal liquid solutions is a popular and useful tool in the design of chemical processes. Comparisons of the Wilson equation to other activity coefficient correlations such as the Margules and Van Laar equations have shown the Wilson equation to have superior predictive ability for binary systems and particularly for multicomponent systems [2]. Furthermore, the Wilson equation embodies the concept of local composition as distinct from overall solution composition, thus modeling the molecular segregation which occurs in nonideal solutions.

The success of the original Wilson equation has led to its adoption as a basis or component of more sophisticated solution models. Among these are the Nonrandom, Two-liquid (NRTL) equation [3], the Analytical Solution of Groups (ASOG) model [4], the Universal Quasi-chemical (UNIQUAC) model [5], and the UNIQUAC Functional Group Activity Coefficient (UNIFAC) model [6]. These models utilize the form of the Wilson equation because of its theoretical basis and good predictive ability, but allow prediction of anomalous behavior such as phase separation which the original Wilson equation is incapable of modeling.

Of these models, ASOG and UNIFAC include the concept of functional group contribution. This concept allows a solution to be treated as if it were composed not of interacting molecules, but rather of interacting functional groups, and considers the interaction of a molecule to be the

sum of its functional group interactions. By correlating available equilibrium data, a database of functional group interaction parameters can be derived and used to make predictions about substances for which no equilibrium data are available, but which contain only functional groups with parameters in the database. Progress has been made toward constructing such databases for both UNIFAC [6,7] and ASOG [8-11]. Comparison of these two models shows both to have approximately equal predictive ability and accuracy, and to be superior to other models applying the group contribution concept [12].

Both UNIFAC and ASOG consider the activity of a component in solution to be composed of two parts: a size interaction (entropic or combinatorial) and a group interaction (enthalpic or residual). In both models, the group or residual interaction term is given by a form of the multicomponent Wilson equation. The ASOG model uses group mole fraction as the independent variable for residual interaction while the UNIFAC model uses group surface area fraction. The unit of surface area in the UNIFAC model was originally chosen as the surface area of a single methylene (CH_2) group in an infinitely large polymethylene molecule. Skjold-Jorgensen, Rasmussen, and Fredenslund [13] showed that the predictions made by UNIFAC are quite sensitive to the selection of surface area unit size, and indicated that the database could more accurately model solution behavior if the interaction parameters were derived again based on a different normalization of the surface area and segment size parameters.

The ASOG model, since it employs mole fractions rather than surface area fractions, contains a natural normalization of its independent variable in the entity of a single functional group of any type. However, this may be somewhat misleading since functional groups themselves vary in mass and size: for example, is it consistent to assign the same importance to the interaction of a large carboxylic acid (COOH) group as a small methylene (CH_2) group? It is exactly this problem which UNIFAC addresses by using functional group segment size and surface area parameters. Recent revisions of ASOG, such as ASOG-KT [9], have also attempted to address this problem in a somewhat systematic way by assigning to each functional group a weighting factor equal to the number of non-hydrogen atoms it contains, and including some special cases as well. In doing so, ASOG makes explicit the normalization of functional group size.

There are several methodological ideas which are useful in describing and analyzing normalization effects in the calculation of residual contributions to the activity coefficient within the solution of groups framework. The ASOG model is used throughout to illustrate these proposals and comments; however, they are applicable in the most part to UNIFAC and other similar models. The standard equations for residual activity coefficient in the ASOG model are reduced to simpler forms applicable to binary systems containing at most two distinct functional groups. This simple case can be representative of many binary solutions, and was chosen to enable discussion and graphical representation of the effects of changes in system parameters. The

approach taken can be extended to multicomponent solutions containing multiple distinct functional groups.

In addition to facilitating the discussion of size normalization, the approach also allows the behavior of the ASOG model to be analyzed for cases in which insufficient data are available to specify complete sets of interaction parameters for the functional groups. In such cases, conclusions about residual activity coefficients can be derived as bounds rather than single values. These bounds can be made on the concentration dependence of activity for either component of a binary system based on a single measurement.

EFFECTS OF NORMALIZATION ON RESIDUAL ACTIVITY

Consider a binary solution whose molecules contain two distinct functional groups, e.g., ethanol and methanol contain the functional groups CH_3 (or CH_2) and OH. Denote the component mole fractions by x_1 and x_2. In order to apply the ASOG model, it is necessary to define group mole fractions X_1 and X_2 according to

$$X_k = \frac{n_{k1}x_1 + n_{k2}x_2}{(n_{11}+n_{21})x_1 + (n_{12}+n_{22})x_2} \qquad (1)$$

where n_{kj} is proportional to some measure of the number of functional groups of type k found in molecule j. Derr and Deal [4,8] consider this measure to be the number of functional groups, whereas others [9-11] consider it to be the number of functional groups multiplied by an

appropriate weighting factor accounting for relative group sizes.

The use of a size-weighting factor to model group size in ASOG makes the method equivalent to UNIFAC in its definition of the functional group concentration variables denoted here by X_1 and X_2. As studied by Skjold-Jorgensen et al [13], there is an implicit normalization step in the definition of group size. UNIFAC applies this normalization by choosing the methylene (CH_2) group to have unit volume and unit surface area. ASOG does essentially the same thing in a less precise manner by considering the number of non-hydrogen atoms in a group to be its size measurement, with a few explicit exceptions such as water and multiple-substituted carbon atoms (>CH- or >C<).

ASOG gives the residual part of component i activity coefficient for a binary system containing two distinct functional groups by the following equations.

$$\ln \gamma_i^G = n_{1i}(\ln \Gamma_1 - \ln \Gamma_1^i) + n_{2i}(\ln \Gamma_2 - \ln \Gamma_2^i) \qquad (2)$$

$$\ln \Gamma_k = -\ln(X_1A_{k1} + X_2A_{k2}) + 1 - \frac{X_1A_{1k}}{X_1A_{11}+X_2A_{12}} - \frac{X_2A_{2k}}{X_1A_{21}+X_2A_{22}} \qquad (3)$$

$$\ln \Gamma_k^i = \ln \Gamma_k \ (x_i = 1) \qquad (4)$$

In these equations, γ_i^G is the residual (or group interaction, hence the letter G) part of component i activity coefficient, and Γ_k is the functional group activity coefficient for group type k. Γ_k^i is the functional group activity coefficient for group type k, evaluated at the functional group composition of pure component i, and A_{kl} are group

interaction parameters, with $A_{kk} = 1$. Eq 3 is the Wilson equation, applied to functional groups in solution rather than the actual molecular components. Eq 2 gives the logarithm of component i activity coefficient as the sum of its functional group activity coefficients, $\ln \Gamma_1 - \ln \Gamma_1^i$ and $\ln \Gamma_2 - \ln \Gamma_2^i$, relative to a pure component basis. The functional group activity coefficients in pure component i are subtracted from the functional group activity coefficients in solution; if this were not done, activity coefficients would not approach unity in the pure component limit for molecules containing more than one distinct functional group type.

The effect of group size normalization is to change the absolute values of the factors n_{1i} and n_{2i} in eq 2, although not their ratio. (ASOG would give a different ratio than UNIFAC, since each measures a different type of size, but once a method is selected, the unit of size will not affect the ratio.) If eq 3, the Wilson equation for group activity coefficients, were linear in the group interaction parameters A_{kl}, the magnitudes of n_{1i} and n_{2i} would not affect overall predictions of the equation set. The Wilson equations are obviously nonlinear in the group interaction parameters (as well as the composition variables), therefore an activity coefficient result in eq 2 cannot be associated, independent of normalization, with any single set of group interaction parameters A_{12} and A_{21} in eqs 3 and 4.

Since the technique used by both ASOG and UNIFAC is to construct a database of group interaction parameters based upon reduction of

experimental activity data, it is apparent that such a database must depend on the normalization of group size in a nonlinear way. This is the underlying cause behind the discovery by Skjold-Jorgensen et al [13] that varying the group size normalization within UNIFAC results in changes in the group interaction parameter database. Some normalizations produce a database which gives more accurate prediction of concentration and temperature dependence of activity coefficients than other normalizations. The relative merit of different normalization schemes will not be discussed here; the relevant issue in this paper is means of analyzing such effects.

A NORMALIZATION INDEPENDENT EXPRESSION FOR RESIDUAL ACTIVITY COEFFICIENTS

It is possible to derive an expression related to residual activity coefficient which contains no implicit or explicit dependence on the unit of functional group size. The complexity of this expression can be minimized by introduction of a conveniently weighted composition variable, c_i, for the molecular species in a binary solution, defined as follows.

$$c_i = \frac{(n_{1i}+n_{2i})x_i}{(n_{11}+n_{21})x_1 + (n_{12}+n_{22})x_2} \qquad (5)$$

Such composition variables represent size-weighted fractions in that c_i equals the total size (as measured by number of functional groups) of all molecules of component i in solution divided by the total size of

all molecules in solution. Although c_i depends explicitly on the n_{kj} values, it does not depend on the unit of functional group size. Since eq 5 contains one occurrence on an n_{kj} in each term of the numerator and denominator, size effects will cancel in the overall expression.

Following through the calculations for a binary solution containing two distinct functional groups, but using composition variables c_1 and c_2 rather than the actual mole fractions x_1 and x_2, simplified results for group mole fraction can be found. Define group ratios

$$g_i = n_{2i} / n_{1i} \tag{6}$$

giving the size-weighted ratio of group 2 to group 1 in each component molecule, then

$$X_1 = \frac{c_1}{1 + g_1} + \frac{c_2}{1 + g_2} \tag{7}$$

defines the group mole fraction, X_1 in eq 1, in terms of component size-weighted fractions c_1 and c_2.

Group ratios are particularly useful in polymer solutions, because polymer molecules are typically distributed in their molecular weight, hence in their absolute size. This fact can make eqs 1-4 difficult to apply to a solvent molecule in polymer solution since there is no single x_2. Characterization in terms of group ratios is size-independent, thus all polymer molecules of a given type have the same group ratios regardless of their molecular weights. Eq 5 can also be rewritten for

polymer solutions by using weight fraction w_i rather than mole fraction x_i on the right side and adding average molecular weight factors to the equation.

The definition of group ratios also allows eq 2 to be rewritten as

$$\frac{\ln \gamma_i^G}{n_{1i}} = (\ln \Gamma_1 - \ln \Gamma_1^i) + g_i(\ln \Gamma_2 - \ln \Gamma_2^i) \qquad (8)$$

The left side of eq 8 is the normalized residual activity coefficient of component i. (It is termed "normalized" because it contains the term n_{1i}, inversely proportional to the unit chosen for functional group size, in its denominator.) The right side contains no explicit dependence on the n_{kj}, since the group ratio g_i has been substituted. The implicit dependence of Γ_1, Γ_1^i, Γ_2, and Γ_2^i on n_{kj} can be removed by substituting eq 7 into eqs 3 and 4, and using the property that both component size-weighted fractions and group mole fractions sum to unity. The resulting lengthy equation is

$$\frac{\ln \gamma_i^G}{n_{1i}} = \ln \frac{(1 + g_j)(1 + A_{12}g_i)}{(1 + g_j)(1 + A_{12}g_i) + (g_j - g_i)(A_{12} - 1)c_j}$$

$$+ g_i \ln \frac{(1 + g_j)(A_{21} + g_i)}{(1 + g_j)(A_{21} + g_i) + (g_j - g_i)(1 - A_{21})c_j}$$

$$+ (1 + g_i)(g_j - g_i)c_j \cdot$$

$$\left(\frac{A_{12}}{(1 + g_j)(1 + A_{12}g_i) + (g_j - g_i)(A_{12} - 1)c_j} \right.$$

$$\left. - \frac{A_{21}}{(1 + g_j)(A_{21} + g_i) + (g_j - g_i)(1 - A_{21})c_j} \right) \qquad (9)$$

The result for component 1, $(\ln \gamma_1^G)/n_{11}$, is given by setting $i = 1$ and $j = 2$, while the result for component 2, $(\ln \gamma_2^G)/n_{12}$, is given by setting $i = 2$ and $j = 1$. In eq 9, the normalized residual activity coefficient $(\ln \gamma_i^G)/n_{1i}$ depends upon three distinct sets of variables. The first of these, group ratios g_1 and g_2, describe the functional group composition of the molecular components. These two ratios replace the four functional group variables n_{kj} in the original form of the ASOG model. The second set of variables, A_{12} and A_{21}, are the Wilson parameters for the functional groups. The third variables are size-weighted fractions c_1 or c_2, which describe molecular component composition in the solution.

None of these three sets of variables depends on the functional group size unit. The Wilson parameters are constants for given functional groups, while g_1 and g_2 are ratios of two n_{kj} values which depend on the size unit in the same linear way. The discussion following eq 5 showed

that c_1 and c_2 are independent of the functional group size unit for similar reasons. Hence, the right side of eq 9 will describe the same function of composition for a given set of Wilson parameters regardless of the size unit chosen for normalization. All of the normalization dependence of this equation is given explicitly by the denominator of the left side.

This result applies to any solution of functional groups methods which treat component activities as the sum of functional group activities given by the Wilson equation. The only distinction will be in the definition of size-weighted fraction in eq 5. For example, in UNIFAC, the size-weighted fraction will actually represent a molecular surface area fraction, whereas in ASOG-KT, it will essentially represent a molecular fraction of atoms other than hydrogen (as mentioned above, there are a few special cases in ASOG-KT which do not follow the general rule for determining group and molecule size).

The result given by eq 9 can also be extended to multicomponent solutions containing several distinct functional groups. This is done by defining additional group ratios so that the right side of the equation contains only group ratios, Wilson parameters, and component size-weighted composition variables. Such a generalized result will not be attempted in this paper. Instead, the dependence of eq 9 upon its existing parameters and variables will be interpreted.

In the remainder of this paper, the variables i and j in eq 9 will

arbitrarily be taken as 1 and 2. Hence, the results given will apply to the activity coefficient of component 1. Equivalent equations for component 2 can be obtained by interchanging g_1 with g_2, and c_1 with c_2 on the right side, giving $(\ln \gamma_2^G)/n_{12}$ on the left side.

TRANSFORMATION OF WILSON PARAMETERS

The expression for normalized residual activity coefficient $(\ln \gamma_1^G)/n_{11}$ given by eq 9 is rather complicated; however, by appropriate transformations of the Wilson parameters, simpler forms of the expression can be written. Begin by defining transformed parameters

$$B_{12} = \frac{(g_2 - g_1)(A_{12} - 1)}{(1 + g_2)(1 + A_{12}g_1)} \tag{10}$$

$$B_{21} = \frac{(g_2 - g_1)(1 - A_{21})}{(1 + g_2)(A_{21} + g_1)} \tag{11}$$

Each parameter B_{ij} is a function of the group ratios and only one of the Wilson parameters, so that B_{ij} can be regarded as the transformation of A_{ij}. When eq 9 is written in terms of these parameters, it simplifies to

$$\frac{\ln \gamma_1^G}{n_{11}} = -\ln (1 + B_{12}c_2) - g_1 \ln (1 + B_{21}c_2) + \frac{c_2}{1+g_2}\left(\frac{(g_2-g_1) + (1+g_2)B_{12}}{1 + B_{12}c_2} - \frac{(g_2-g_1) - (1+g_2)g_1B_{21}}{1 + B_{21}c_2}\right) \tag{12}$$

At infinite dilution of component 1 in component 2, c_2 approaches unity, and eq 12 can be further simplified to

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln (1 + B_{12}) - g_1 \ln (1 + B_{21}) + \frac{1}{1+g_2}\left(\frac{(g_2-g_1) + (1+g_2)B_{12}}{1 + B_{12}} - \frac{(g_2-g_1) - (1+g_2)g_1B_{21}}{1 + B_{21}}\right) \quad (13)$$

A further transformation of parameters B_{12} and B_{21} provides additional simplification.

$$C_{12} = 1 + B_{12} = \frac{(1 + g_1)(1 + A_{12}g_2)}{(1 + g_2)(1 + A_{12}g_1)} \quad (14)$$

$$C_{21} = 1 + B_{21} = \frac{(1 + g_1)(A_{21} + g_2)}{(1 + g_2)(A_{21} + g_1)} \quad (15)$$

Application of these parameters to eq 13 gives

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - g_1 \ln C_{21} - \frac{1+g_1}{1+g_2}\left(\frac{1}{C_{12}} + \frac{g_2}{C_{21}}\right) + (1+g_1) \quad (16)$$

Eq 16 is the simplest possible form of the infinite dilution normalized residual activity coefficient in a binary solution. The only parameters required for calculation of this quantity are the group ratios g_1 and g_2, which measure the functional group composition of the molecular components, and C_{12} and C_{21}, transformations of the Wilson parameters A_{12} and A_{21}. This equation is simple enough so that its properties can be thoroughly investigated.

BASIC PROPERTIES OF INFINITE DILUTION NORMALIZED RESIDUAL ACTIVITY COEFFICIENTS AND BOUNDS ON THEIR PARAMETERS

The quantity calculated by eq 16 classifies solution behavior into positive or negative deviation (from Raoult's Law) or athermality, depending upon its sign. By inspection of eq 16, the condition

$$C_{12} - C_{21} - 1 \tag{17}$$

is seen to be sufficient for prediction of athermal behavior, since it forces the expression to zero. Three distinct types of athermal behavior can be described, dependent upon the group ratios and Wilson parameters.

The first type is true athermality due to identical functional group composition of components, occuring when g_1 equals g_2. An example of this would be the binary system methanol-ethylene glycol, in which the ratio of hydroxyl to hydrocarbon groups is unity in both molecules. (ASOG-KT counts $-CH_2-$, $-CH_3$, and -OH all as a having a size of one; this would not be true in UNIFAC.) Eqs 14 and 15 are seen to reduce to eq 17 when g_1 and g_2 are equal.

A second type is true athermality due to non-interaction of functional groups, occuring when A_{12} and A_{21} both equal unity, the standard value of Wilson parameters in an ideal solution. Again, eqs 14 and 15 reduce to satisfy the condition given by eq 17 when this is the case.

The final type of athermality is accidental athermality, occuring when the value given by eq 16 is zero, but the sufficient condition given by eq 17 is not met. Examples of this behavior will be given later.

It is possible for the group ratios g_1 and g_2 to take on any nonnegative values, including zero and infinity. A group ratio will equal zero (or infinity) when the molecular component it describes contains only a single functional group, while the other molecular component contains both functional groups, e.g., water and ethanol. If each of the two molecular components in a binary solution contain a single different functional group, one group ratio will equal zero while the other becomes infinite, e.g., hexane and water. This case represents the most nonideal extreme of functional group composition, with increasing ideality occuring in order for the following cases: one group ratio zero (or infinite), the other finite and nonzero; both group ratios finite and nonzero (e.g., 1-hexanol and ethanol); group ratios equal.

For each case where at least one of the group ratios becomes zero or infinite, special forms of eq 16 are possible. When g_1 is zero, eq 16 reduces to

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - \frac{1}{1+g_2}\left(\frac{1}{C_{12}} + \frac{g_2}{C_{21}}\right) + 1 \qquad (18)$$

when g_2 is zero, it reduces to

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - g_1 \ln C_{21} + (1+g_1)\left(1 - \frac{1}{C_{12}}\right) \qquad (19)$$

and when g_1 is zero and g_2 is infinite, eq 16 becomes

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - \frac{1}{C_{21}} + 1 \qquad (20)$$

There is no need to consider the situation when only one group ratio is infinite and the other is nonzero. By relabeling the groups, this becomes a situation where one group ratio is zero.

Interaction parameters A_{12} and A_{21} are physically interpreted as resulting from energy differences between like-like and like-unlike pairs in solution. Quantitatively, this is given by [14] as

$$A_{ij} = \frac{v_j}{v_i} \exp\left[- \frac{(\lambda_{ij} - \lambda_{ii})}{RT} \right] \qquad (21)$$

where v_i is the molar volume of component i and λ_{ij} is the interaction energy of an i-j pair ($\lambda_{ij} = \lambda_{ji}$). When applied to functional groups rather than molecules, the preexponential factor v_j/v_i is of magnitude unity. The argument of the exponential factor varies from negative values when like-like interactions are favored to positive values when like-unlike interactions are favored. The magnitude of this argument depends on the exact strength of secondary bonds, and can probably be bounded by the maximum bond energy of a hydrogen bond, about 50 kJ/mole [15]. Division by R gives a bound of approximately 6000/T, where T is

in K. Interestingly, this is similar to the maximum values assigned to the argument in several versions of the UNIFAC parameter tables (3000/T in [6] and 10000/T in [7]).

At normal temperatures, then, the interaction parameters A_{kl} can probably be bounded by the values exp(-20) and exp(+20). This essentially allows them to take on any positive values. However, the transformed parameters, C_{kl}, are generally more restricted in their domain. If eqs 14 and 15 are differentiated with respect to A_{12} and A_{21}, respectively, several properties follow for unequal values of the group ratios. First, C_{12} and C_{21} are either monotone increasing or monotone decreasing functions of A_{12} and A_{21}. Second, if C_{12} is an increasing function of A_{12}, C_{21} will be a decreasing function of A_{21} and vice versa. Third, the direction of variation is given in all cases by either g_2-g_1 or g_1-g_2, as Table 1 indicates. Taking limits on eqs 14 and 15 for these cases results in a general set of bounds on C_{12} and C_{21}.

$$\frac{1+g_1}{1+g_2} < C_{12}\ ,\ C_{21} < \frac{1+g_1}{1+g_2}\frac{g_2}{g_1} \quad \text{when } g_2 > g_1 \tag{22}$$

$$\frac{1+g_1}{1+g_2}\frac{g_2}{g_1} < C_{12}\ ,\ C_{21} < \frac{1+g_1}{1+g_2} \quad \text{when } g_2 < g_1 \tag{23}$$

Equality of g_1 and g_2 results in athermal behavior as discussed above, with the condition of eq 17 holding.

Table 1. Sign of dC_{kl}/dA_{kl} as a Function of g_1 and g_2.

	$g_1 < g_2$	$g_1 = g_2$	$g_1 > g_2$
dC_{12}/dA_{12}	+	0	-
dC_{21}/dA_{21}	-	0	+

CONSTANT INFINITE DILUTION NORMALIZED RESIDUAL ACTIVITY RELATIONSHIPS

In the presence of a large amount of experimental data, optimal values of the parameters C_{12} and C_{21} can be derived. The interaction parameter databases of UNIFAC and ASOG are derived in such a way from many sets of multicomponent, multifunctional group experimental data. For the simplified binary component-binary group case presented here, two experimental data points (e.g., two infinite dilution activity coefficients) suffice to determine the interaction parameters C_{12} and C_{21}. There are cases, however, where only one data point can be determined at infinite dilution. An example would be the case of a concentrated polymer solution for which only an infinite dilution solvent activity coefficient was available. An analogous situation arises in the multifunctional group case even when several experimental values are available, because the number of interaction parameters required for a system containing n distinct functional groups is $n(n+1)/2$.

Given a constant value of the infinite dilution normalized residual activity coefficient, as might be derived from experimental data using suitable choices for the non-residual part of component activity and the unit size normalization, a relationship between the parameters C_{12} and

C_{21} can be defined. Such a relationship would be given by eq 16 (or eq 18, 19, or 20 for special cases of group ratios). In addition, eq 22 or 23 would place bounds on C_{12} and C_{21}. It is possible to solve eqs 18-20 for an explicit function of one parameter in terms of the other at constant $[(\ln \gamma_1^G)/n_{11}]^\infty$; such a solution is not possible for the general case of eq 16 where the relationship remains implicit. In that general case, a numerical solution for the (C_{12},C_{21}) relation can be made.

Bounds on the maximum and minimum possible values of $[(\ln \gamma_1^G)/n_{11}]^\infty$ for a given set of group ratios are also possible. Eq 16 can be differentiated with respect to each interaction parameter C_{12} or C_{21} with the other held constant. This allows necessary and sufficient conditions for $[(\ln \gamma_1^G)/n_{11}]^\infty$ to be an increasing function of each interaction parameter to be written.

$$\frac{1+g_1}{1+g_2} > C_{12} \tag{24}$$

$$\frac{1+g_1}{1+g_2}\frac{g_2}{g_1} > C_{21} \tag{25}$$

Combining these results with those given in Table 1, the maximum value of $[(\ln \gamma_1^G)/n_{11}]^\infty$ (as a function of C_{12} and C_{21}) will always occur when

$$C_{12} = \frac{1+g_1}{1+g_2} \tag{26}$$

$$C_{21} = \frac{1+g_1}{1+g_2}\frac{g_2}{g_1} \tag{27}$$

and the minimum value of $[(\ln \gamma_1^G)/n_{11}]^\infty$ will always occur when

$$C_{12} = \frac{1+g_1}{1+g_2}\frac{g_2}{g_1} \tag{28}$$

$$C_{21} = \frac{1+g_1}{1+g_2} \tag{29}$$

These maxima and minima are given by

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^\infty_{max} = (1+g_1)\ln\frac{1+g_2}{1+g_1} + g_1 \ln\frac{g_1}{g_2} \tag{30}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^\infty_{min} = (1+g_1)\ln\frac{1+g_2}{1+g_1} + \ln\frac{g_1}{g_2} + (g_2-g_1)\left(\frac{1}{g_2} - 1\right) \tag{31}$$

If eq 30 is differentiated with respect to either group ratio with the other held constant, it can be shown that the expression takes on a minimum value when g_1 and g_2 are equal. Since the normalized residual activity coefficient equals zero under that condition, eq 30 necessarily predicts that the maximum normalized residual activity coefficient for distinct values of g_1 and g_2 must be positive. Similar arguments using eq 31 show that the minimum normalized residual activity coefficient for distinct values of g_1 and g_2 must be negative.

Maximum and minimum values of $[(\ln \gamma_1^G)/n_{11}]^{\infty}$ are listed in Table 2 for various finite values of g_1 and g_2. Some trends are apparent. Wider ranges of normalized residual activity coefficients result when g_1 and g_2 differ considerably from each other. The physical interpretation of this result is that greater nonideality is expected when the functional group similarity between two components decreases. When g_2 or both of the group ratios are zero or infinite, the range of normalized residual activity coefficients is unbounded both positively and negatively. This represents an even more nonideal case of functional group dissimilarity.

In all cases of finite group ratios, the minimum value of $[(\ln \gamma_1^G)/n_{11}]^{\infty}$ is larger in magnitude than the maximum. This has no physical significance; in fact, most nonideal systems exhibit positive deviations from Raoult's Law. It appears to be an artifact of Wilson's equation, indicating a mathematical tendency to predict negative values of the residual activity. Large values of g_1 lead to wider ranges of $[(\ln \gamma_1^G)/n_{11}]^{\infty}$ since the component activity coefficient is resulting from a sum of a larger number of functional group activity coefficients. The values in Table 2 may not be indicative of the magnitude of actual residual activity coefficients $\ln \gamma_1^G$ because of the normalization effect of dividing by the measurement n_{11} of functional groups of type 1 in component 1.

Table 2. Extrema of Normalized Residual Activity Coefficient of Component 1 as a Function of Component Group Ratios.

Group Ratios g_1	Group Ratios g_2	$[(\ln \gamma_1^G)/n_{11}]^\infty$ minimum	$[(\ln \gamma_1^G)/n_{11}]^\infty$ maximum
1	2	-0.382	0.118
1	5	-2.612	0.588
1	10	-6.993	1.107
2	4	-0.661	0.146
5	10	-1.556	0.171
2	1	-0.523	0.170
5	1	-4.982	1.456
1	0.5	-0.382	0.118
1	0.2	-2.612	0.588
1	0.1	-6.993	1.107
0	1	$-\infty$	0.693
0	2	$-\infty$	1.099
0	5	$-\infty$	1.792
0	10	$-\infty$	2.398
0	0.5	$-\infty$	0.405
0	0.2	$-\infty$	0.182
0	0.1	$-\infty$	0.095

For a given set of group ratios, eq 16 can be solved numerically for the set of parameters (C_{12}, C_{21}) that result in a given $[(\ln \gamma_1^G)/n_{11}]^\infty$. Figures 1 and 2 show this representation as a set of constant $[(\ln \gamma_1^G)/n_{11}]^\infty$ curves in (C_{12}, C_{21}) space for two sets of group ratios.

Figure 1 illustrates constant $[(\ln \gamma_1^G)/n_{11}]^\infty$ curves for a case when both group ratios are finite and nonzero. The case $g_1 = 1$, $g_2 = 2$ (e.g., methanol-ethanol) is relatively close to ideality. Parameters C_{12} and C_{21} are restricted to the domain between 2/3 and 4/3, and normalized residual activity coefficients between -0.382 and 0.118 can be predicted. Because $g_2 > g_1$, a decrease in $[(\ln \gamma_1^G)/n_{11}]^\infty$ is seen as the curves are crossed in a clockwise direction from the C_{21} axis to the C_{12} axis. Clockwise rotation in this quadrant means an increase in C_{12}

at constant C_{21} or a decrease in C_{21} at constant C_{12}.

Figure 2 represents a case where g_2 equals zero, meaning that component 2 contains only a single functional group (e.g., water). Parameters C_{12} and C_{21} are restricted to the domain between zero and two by eqs 22 and 23, but the range of $[(\ln \gamma_1^G)/n_{11}]^\infty$ that can be predicted is unbounded. In this case, $g_2 < g_1$, resulting in an increase in activity coefficient with clockwise rotation about the axes. The set of curves collapses into the C_{12} axis as C_{12} approaches zero; no asymptotic relationship between C_{12} and C_{21} seems to exist for this case.

The presence of a curve for $[(\ln \gamma_1^G)/n_{11}]^\infty = 0$ in Figures 1 and 2 illustrates the situation termed accidental athermality. Although eq 16 predicts $[(\ln \gamma_1^G)/n_{11}]^\infty = 0$ for all points on this curve, only the point (1,1) represents true athermality due to either identical functional group composition of molecular components or non-interaction of functional groups. All other points on this curve result from cancelling effects of positive deviations from ideality by one functional group and negative deviations by the other.

Figures 1 and 2 illustrate the wide range of behavior which can be predicted by eq 16. This is true both in terms of the possible values of the normalized residual activity coefficient which can be predicted as well as the (C_{12}, C_{21}) relationship which can generate a single activity value. In the absence of additional experimental data beyond a single point, it is not possible to determine which (C_{12}, C_{21}) point on

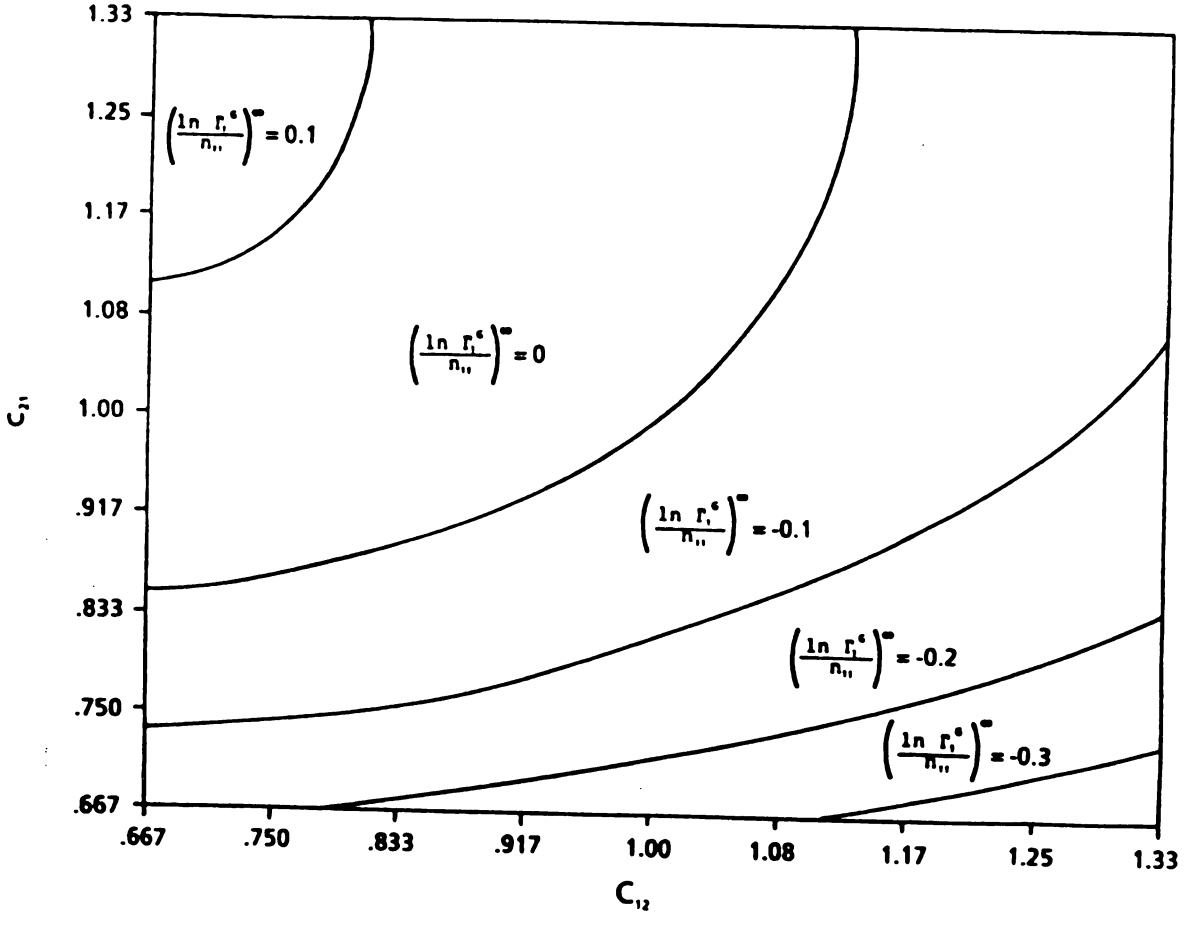

Figure 1. Constant Infinite Dilution Normalized Residual Activity Coefficient Relationships for $g_1 = 1$, $g_2 = 2$.

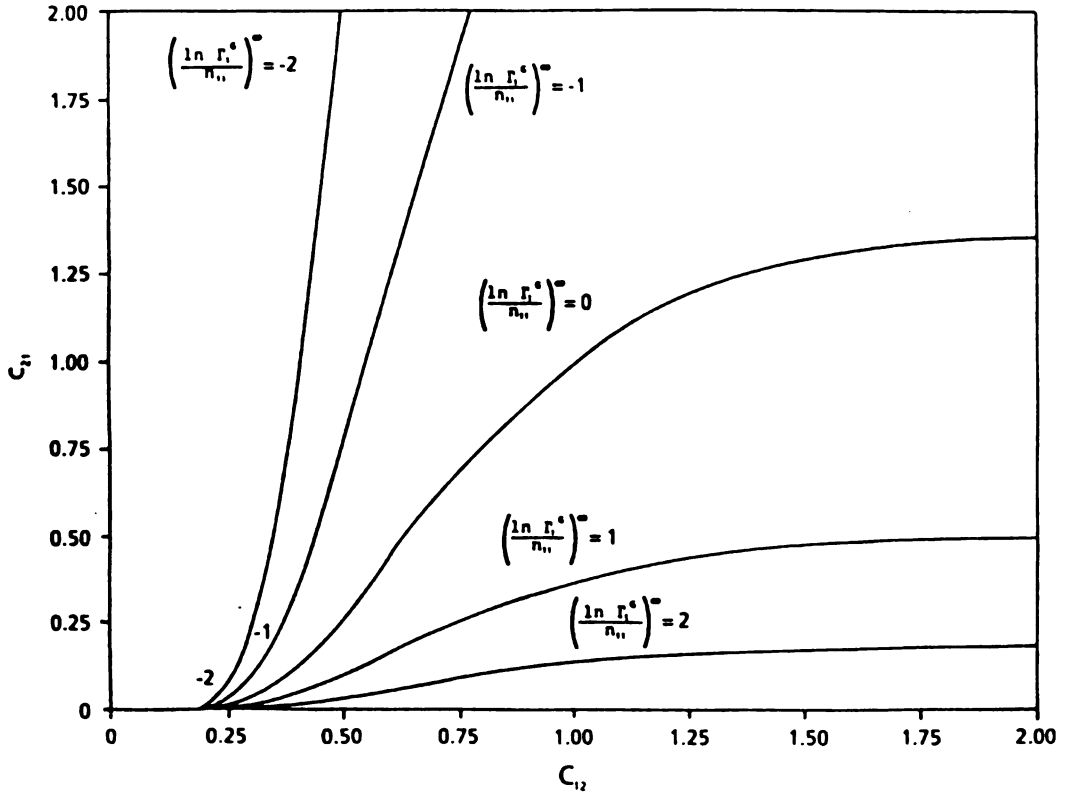

Figure 2. Constant Infinite Dilution Normalized Residual Activity Coefficient Relationships for $g_1 = 1$, $g_2 = 0$.

a constant $[(\ln \gamma_1^G)/n_{11}]^\infty$ curve to use in predicting the variation of activity coefficient with concentration. However, the restriction of interaction parameter values to a single curve can still provide useful information regarding bounds on the activity coefficient, as shall be seen.

BOUNDING THE CONCENTRATION DEPENDENCE OF NORMALIZED RESIDUAL ACTIVITY COEFFICIENTS

Since the results of the previous section indicated that a wide range of (C_{12}, C_{21}) points defined a given value of $[(\ln \gamma_1^G)/n_{11}]^\infty$, it is enlightening to consider the concentration dependence of normalized residual activity as a function of the interaction parameters for a fixed value of $[(\ln \gamma_1^G)/n_{11}]^\infty$. This can be investigated by taking the numerical results from eq 16 discussed above, applying eqs 14-15 to transform from interaction parameters (C_{12}, C_{21}) to interaction parameters (B_{12}, B_{21}). Eq 12 can then be used to give the concentration dependence of $[(\ln \gamma_1^G)/n_{11}]$.

Consideration of this point is useful in two regards. First, the concentration dependence of normalized residual activity for a given set of group ratios and infinite dilution value can be bounded over the entire concentration range. This helps in estimation of the concentration dependence when only a single infinite dilution property is known.

Second, this point leads directly into consideration of the normalization of n_{11}. For a given infinite dilution residual activity $[(\ln \gamma_1^G)]^\infty$, the value of the normalized infinite dilution residual activity $[(\ln \gamma_1^G)/n_{11}]^\infty$ will depend upon the normalization of n_{11}. If the concentration dependence of $[(\ln \gamma_1^G)/n_{11}]$ changes markedly with changes in $[(\ln \gamma_1^G)/n_{11}]^\infty$, then normalization of n_{11} will have a noticeable change on the concentration dependence of residual activity coefficients. This will be true even when a large body of experimental data is used to find the optimal values of interaction parameters, as in the databases of UNIFAC and ASOG. The interaction parameters databases must then be considered size-dependent or normalization-dependent as shown in [13].

The technique described above was applied to produce Figures 3 and 4. These plots illustrate bounds on the normalized residual activity coefficient as a function of concentration for various fixed values of the infinite dilution normalized residual activity coefficient. For positive fixed values of $[(\ln \gamma_1^G)/n_{11}]^\infty$, the bounds could always be derived assuming C_{12} and C_{21} values at the endpoints of a specific curve in Figures 1 and 2. Such endpoints can be found from numerical solution of eq 16, or by algebraic solution of eq 18, 19, or 20 in special cases. This is not necessarily the case for negative values of $[(\ln \gamma_1^G)/n_{11}]^\infty$, which are not shown in Figures 3 and 4.

Figure 3 is based upon the same group ratios as Figure 1, representing a solution not far from ideality. In this case, the bounding curves shown

are quite tight. Knowledge of the infinite dilution value allows estimation of the activity at any concentration with little uncertainty. Also, infinite dilution values near zero and near the maximum possible (0.118 for this case) result in the narrowest bounds on concentration dependence. The fact that there is some uncertainty for the case of zero infinite dilution value provides another example of accidental athermality, as discussed above.

Figure 4, corresponding to the same group ratios as in Figure 2, illustrates a case which is more nonideal than shown in Figure 3. As a consequence of g_2 equaling zero, a lower bounding curve could not be derived for this case, and only upper bounding curves are shown.

In general, molecular components which are more dissimilar in their functional group composition result in more uncertainty in the concentration dependence of residual activity. That is why Figure 3 illustrates narrow bounding curves while Figure 4 illustrates a situation which is unbounded in one direction. However, functional groups which are more dissimilar in terms of their secondary interactions result in less uncertainty in concentration dependence. The uppermost set of bounding curves in Figure 3 represent the greatest deviation from ideality by functional groups, yet show less uncertainty than the bounding curves for an infinite dilution value of 0.05. Combining these results, it seems that the tightest bounds occur for systems in which the functional groups themselves interact strongly, but the molecules are not too different in their functional group makeup,

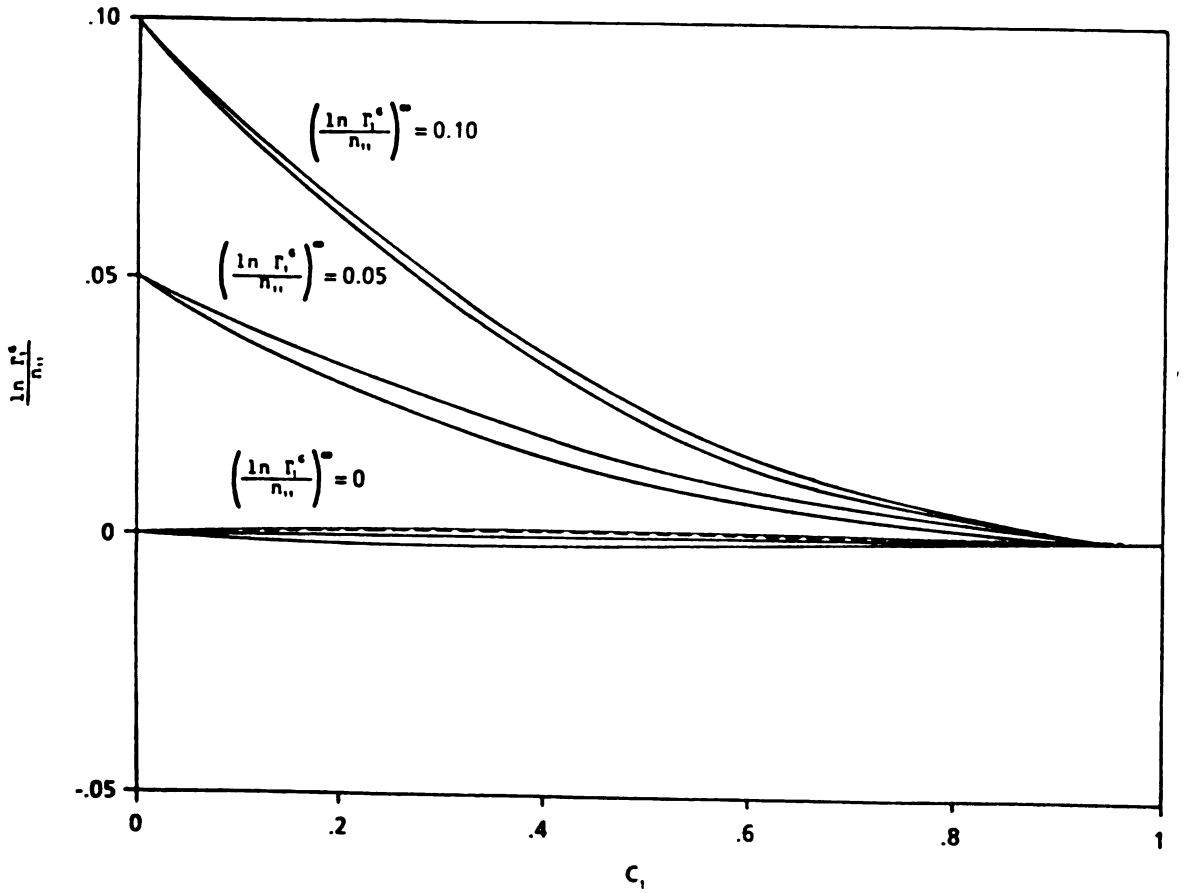

Figure 3. Bounding the Concentration Dependence of Normalized Residual Activity Coefficients for $g_1 = 1$, $g_2 = 2$. Labels are infinite dilution values; curves are upper and lower bounds.

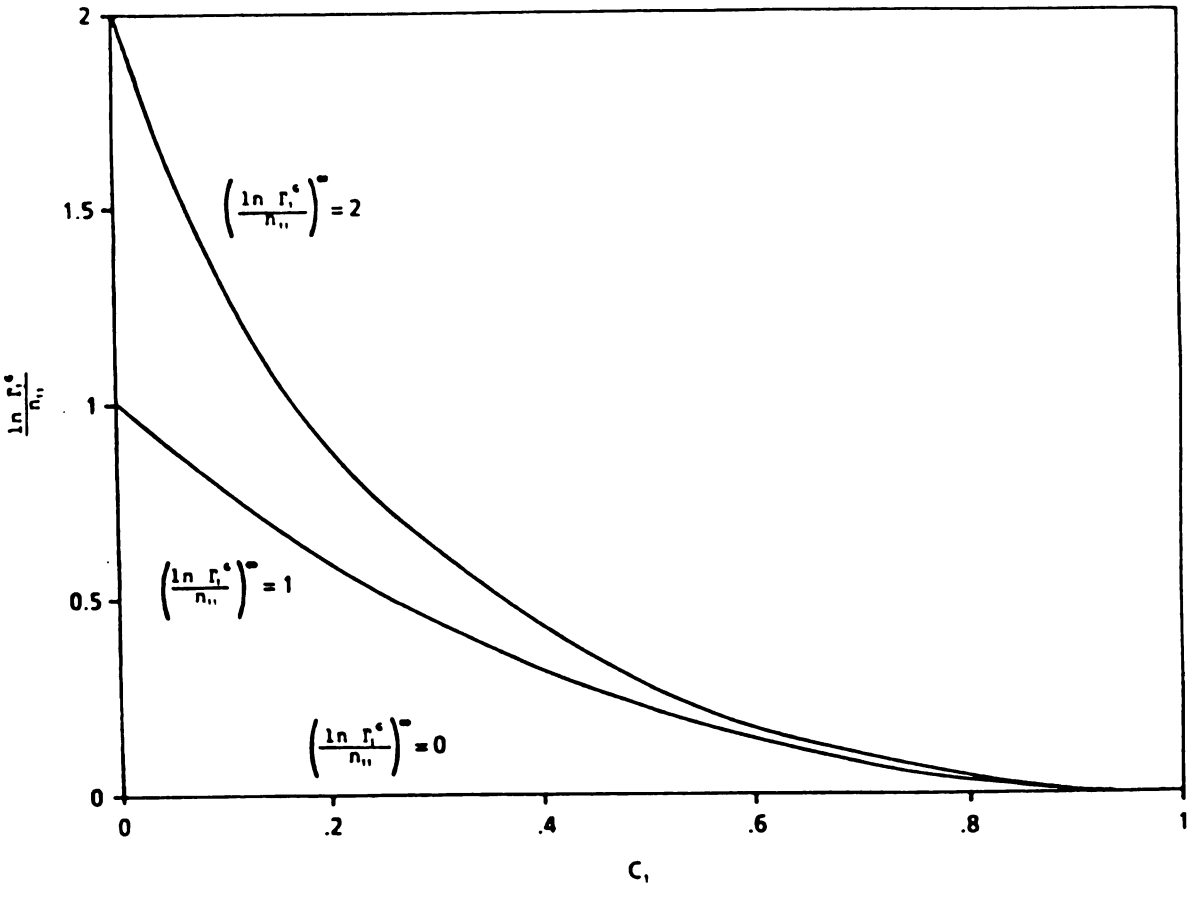

Figure 4. Bounding the Concentration Dependence of Normalized Residual Activity Coefficients for $g_1 = 1$, $g_2 = 0$. Labels are infinite dilution values; curves are upper bounds.

e.g., methanol-ethanol.

The relevance of this type of analysis is that it allows bounds on the concentration dependence of normalized residual activity to be accurately made by some analytical means. Such bounds are important in themselves, as they allow estimation of concentration dependence from a single data point without recourse to a group interaction database. They are also useful in providing bounds on the effect of normalization of n_{11} upon residual activity, as discussed later.

BOUNDING THE UNKNOWN ACTIVITY OF A SECOND COMPONENT

An approach similar to that of the previous section can be used to provide bounds for estimation of the activity of the second molecular component. Again, only a single value of the activity of the first component at infinite dilution is needed. The procedure for this calculation is similar to that for bounding the concentration dependence shown previously. An additional step is required because eqs 10-31 are specific to component 1 activity calculation.

The first step consists of finding the (C_{12}, C_{21}) endpoints of the constant infinite dilution residual activity curve for component 1 as described in the previous section. Since the transformed parameters C_{ij} are component-specific, it is necessary to invert eqs 14 and 15 to generate A_{ij} interaction parameters. The inverted equations are

$$A_{12} = \frac{(1 + g_2)C_{12} - (1 + g_1)}{g_2(1 + g_1) - g_1(1 + g_2)C_{12}} \tag{32}$$

$$A_{21} = \frac{g_1(1 + g_2)C_{21} - g_2(1 + g_1)}{(1 + g_1) - (1 + g_2)C_{21}} \tag{33}$$

At this point, C_{ij} values specific to component 2 can be generated by interchanging g_1 with g_2 in eq 14. Eq 12, with c_1 replacing c_2 in addition to interchanging g_1 with g_2, then gives the concentration dependence of component 2 activity, namely, $(\ln \gamma_2^G)/n_{12}$. Bounding curves like Figures 3 and 4 can be generated for component 2. The only qualitative difference between these curves and those for component 1 will be that the infinite dilution value for component 2 will not be a single point, i.e., the upper and lower bounding curves for component 2 will not merge at $c_2 = 0$.

Since a single infinite dilution value for component 1 can be used to generate bounds for the concentration dependence of component 2 activity, it can be used in particular to bound the infinite dilution activity coefficient of component 2. This provides another graphical relationship, shown in Figures 5 and 6. Values of $[(\ln \gamma_2^G)/n_{12}]^\infty$ are plotted versus values of $[(\ln \gamma_1^G)/n_{11}]^\infty$ ranging from zero to the maximum allowable. The bounding curves show the allowable range of component 2 activity at infinite dilution corresponding to a known component 1 activity at infinite dilution. Figure 5 corresponds to the fairly ideal case used for Figures 1 and 3; both upper and lower bounds are available. In Figure 6, corresponding to the less ideal case of

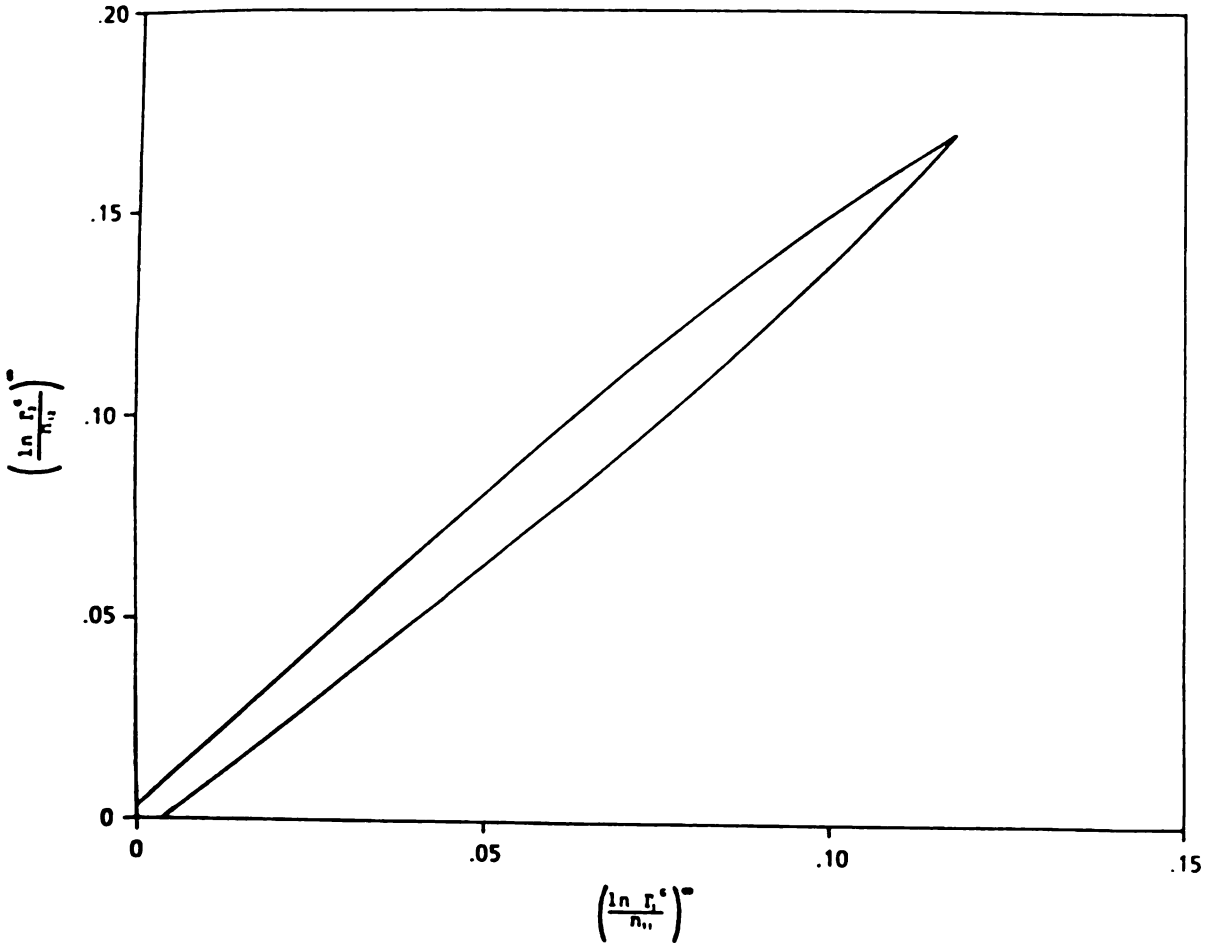

Figure 5. Bounding the Infinite Dilution Normalized Residual Activity Coefficient of the Second Component for $g_1 = 1$, $g_2 = 2$. Curves are upper and lower bounds.

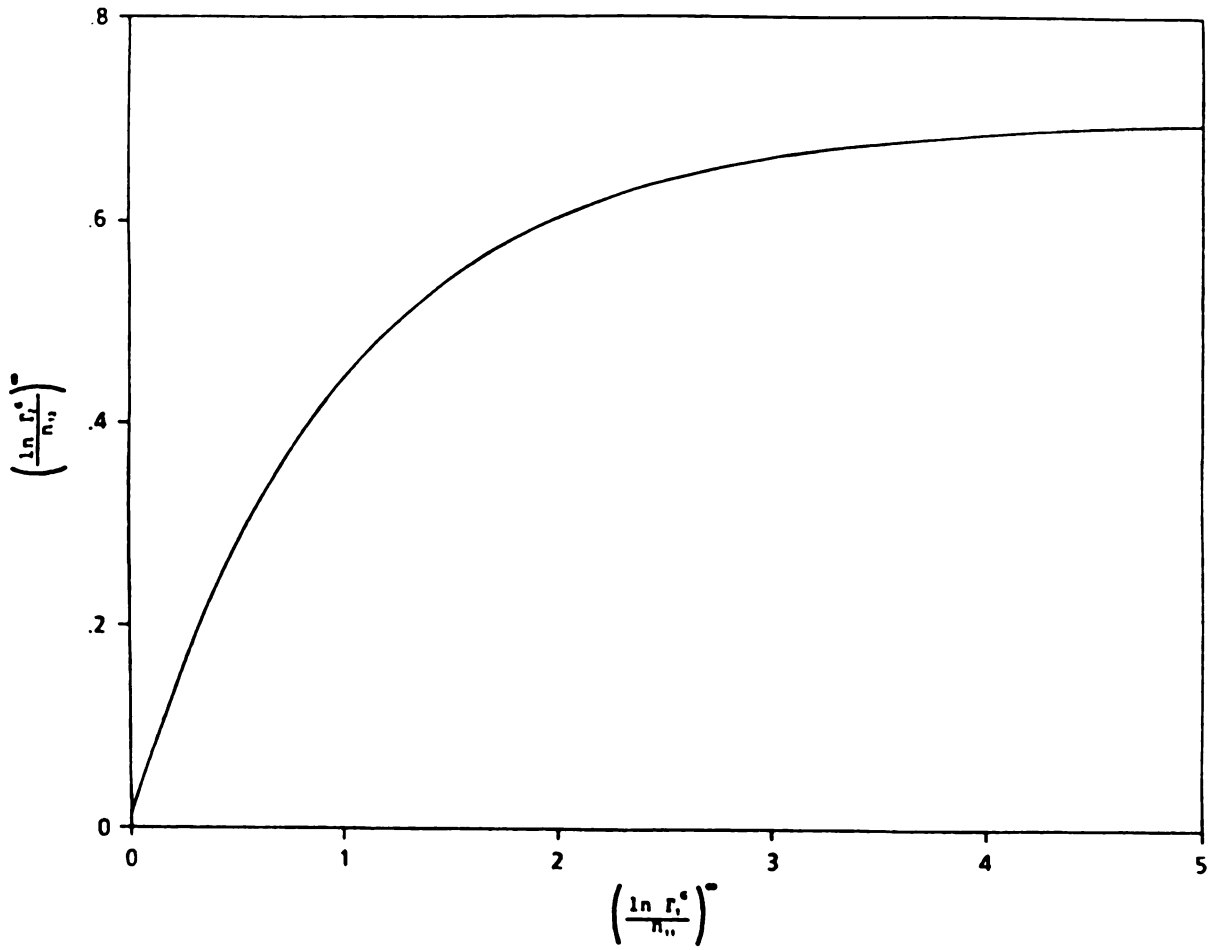

Figure 6. Bounding the Infinite Dilution Normalized Residual Activity Coefficient of the Second Component for $g_1 = 1$, $g_2 = 0$. Curve is upper bound.

Figures 2 and 4, only an upper bounding curve is possible.

This approach provides a more powerful tool than the Gibbs-Duhem relationship between activity coefficients of different components. Since the Gibbs-Duhem equation relates differential changes in the activity coefficients, it cannot be used to derive the activity of one component from that of a second component. The added power of this technique results from the assumption of a particular activity coefficient relationship given by the solution of groups model. However, the accuracy of the estimates depends on the validity of the solution of groups model, whereas the Gibbs-Duhem relationship is always thermodynamically correct.

Such a bounding approach is most useful for systems in which limited data are available, where interaction parameters themselves cannot be fit. In such cases, the bounding result can be used to help design an experiment to take additional data.

NORMALIZATION DEPENDENCE OF RESIDUAL ACTIVITY COEFFICIENTS

Previously, a technique for bounding the concentration dependence of $[(\ln \gamma_1^G)/n_{11}]$ was developed. In the reduction of experimental data to interaction parameter databases, a given normalization for n_{11} is assumed, and interaction parameters are chosen to best fit $[(\ln \gamma_1^G)/n_{11}]$ as a function of concentration. (In UNIFAC and ASOG, data points from various concentrations are used, not merely from

infinite dilution.) Using the bounding technique of the previous section, the effect of varying normalization of n_{11} can be quantitatively illustrated.

This will be done within the framework of fitting concentration dependence curves to an infinite dilution residual activity coefficient. Taking $(\ln \gamma_1^G)^\infty$ as a fixed value, but allowing n_{11} to vary, values of $[(\ln \gamma_1^G)/n_{11}]^\infty$ corresponding to different normalizations of n_{11} are produced. Each of these infinite dilution normalized residual activity coefficients has associated bounds as shown previously. If the bounds upon $[(\ln \gamma_1^G)/n_{11}]$ given by these curves are multiplied by n_{11}, a set of bounds for $(\ln \gamma_1^G)$ is produced for each normalization of n_{11} which is considered.

Figures 7 and 8 illustrate the results of this procedure for the same group ratios shown previously, with a sample value of $(\ln \gamma_1^G)^\infty$ chosen for each. Bounds derived from n_{11} values of 1 and 4 are compared. It is evident from this plot that increases in n_{11}, which are equivalent to decreases in the size of the unit of normalization, result in a wider possible variation in the concentration dependence of residual activity. This shows in Figure 7 as increases in the upper bound and decreases in the lower bound. In Figure 8, only an upper bound can be derived, and it increases with increasing n_{11}.

It is not necessarily true that wider bounds on the concentration dependence of residual activity result in a more inaccurate fit of

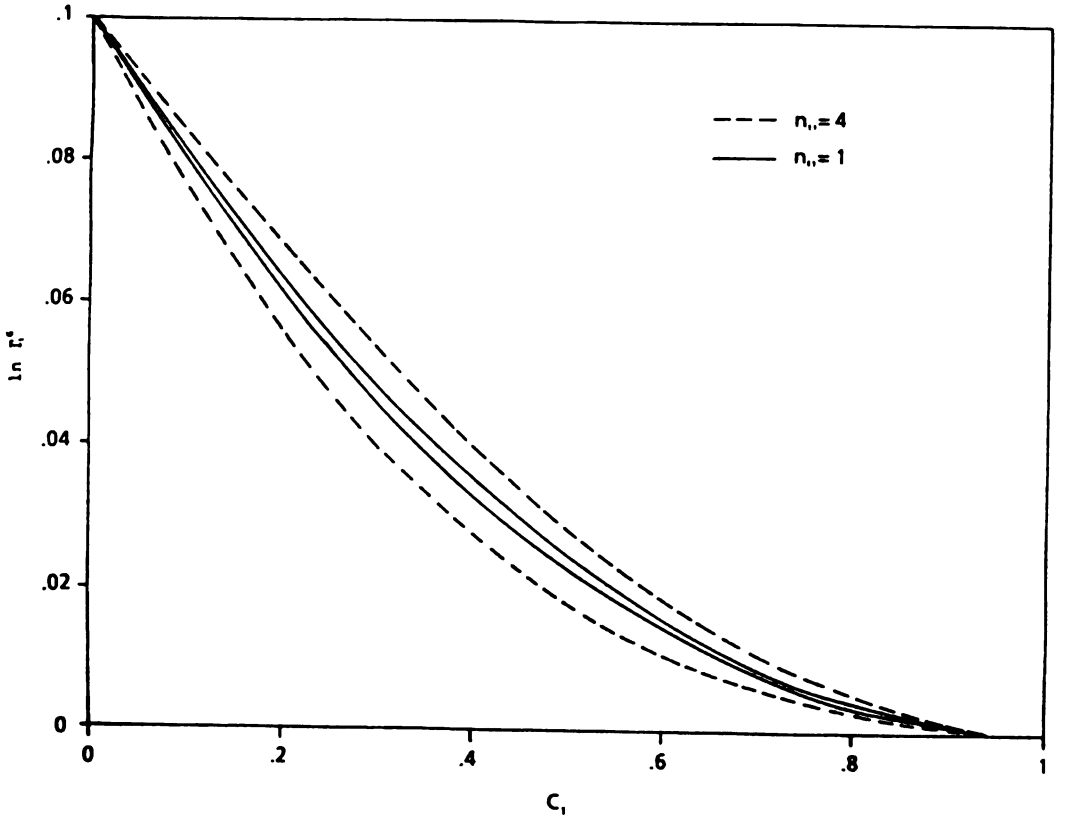

Figure 7. Bounding the Concentration Dependence of Residual Activity Coefficients for $g_1 = 1$, $g_2 = 2$. $(\ln \gamma_1^{G})^{\infty} = 0.1$. Solid curves are upper and lower bounds for $n_{11} = 1$; dashed curves are upper and lower bounds for $n_{11} = 4$.

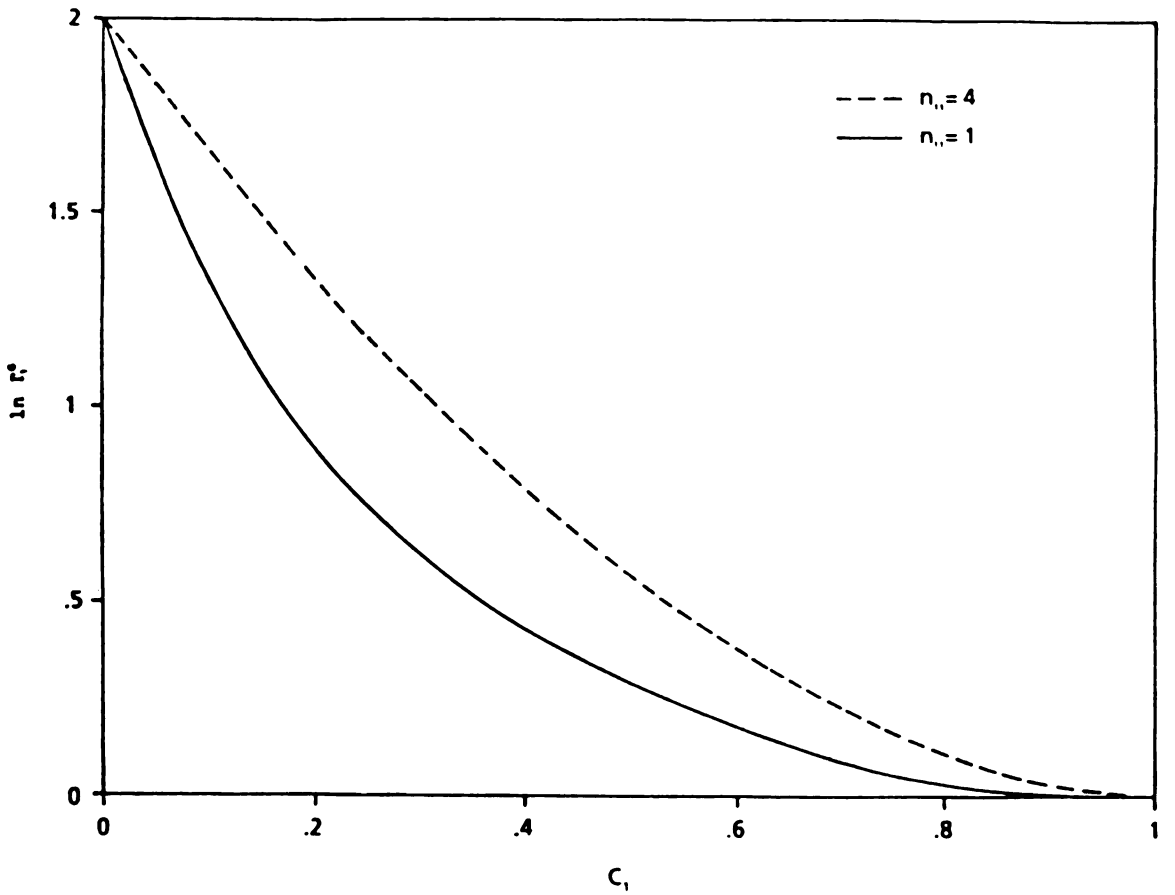

Figure 8. Bounding the Concentration Dependence of Residual Activity Coefficients for $g_1 = 1$, $g_2 = 0$. $(\ln \gamma_1^G)^\infty = 2$. Both curves are upper bounds, labels are n_{11} values.

experimental data. As shown in [13], the average accuracy of UNIFAC was increased when the unit of surface area was decreased in size. When attempting to use the results given here to make predictions for systems for which no interaction parameters are available, narrower bounds are preferable, which seems to imply that larger functional group size units would work best.

The results given here do not imply that normalization unit can be varied indiscriminately in applying the residual activity equations within solution of functional groups models. Such a procedure would produce chaotic and meaningless results. What is illustrated here is the effect of changes of normalization unit upon some aspects of residual activity coefficient prediction, specifically, the bounds upon concentration dependence given a fixed infinite dilution value. Such an approach may prove useful in determining a proper value for the normalization unit in solution of functional groups models.

CONCLUSIONS

The residual activity coefficient given by solution of groups models using forms analogous to Wilson's equation can be conveniently analyzed by the transformations presented here. Transformation of interaction parameters allows simple expressions for component activity coefficient to be written. The transformed parameters also are restricted to a narrow range of values in many cases. In the case of a binary solution with two functional groups, the concentration dependence of both

residual activity coefficients can be bounded using only a single infinite dilution activity value. Group contribution models measure functional groups present in a component molecule in various ways. Regardless of the measurement used, the size of the unit chosen for normalization has an effect on the predicted concentration dependence of activity coefficients given by such a model.

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CHAPTER 4

MODELING DIFFUSION COEFFICIENTS FOR CONCENTRATED POLYMER SOLUTIONS ABOVE T_G

Diffusion phenomena in polymer solutions have been difficult to study and interpret, due to the variety of effects observed. Differences in behavior occur dependent upon the state of the system, e.g., glassy, melt, dilute solution. In most cases, the behavior is non-Fickian, since the diffusion coefficient varies with composition and, under some conditions, relaxation occurs on the same time scale as diffusion.

At temperatures sufficiently above T_g, relaxation occurs more quickly than diffusion and may be ignored. In concentrated polymer solutions or melts, the mobility of polymer molecules can be neglected in comparison to solvent molecules. The remaining problems in determining binary mutual diffusivities are to model the self-diffusion coefficient (some authors refer to this as the tracer diffusion coefficient) of solvent in the system and to model the nonideal thermodynamic effects which cause the chemical potential gradient to differ from the concentration gradient. Both these effects must be considered as functions of temperature and of solvent concentration. Typically, an increase of solvent concentration results in an increase in solution free volume which tends to increase the diffusivity, while it simultaneously results

in a decrease in solvent activity coefficient which tends to decrease the diffusivity.

The major quantitative analysis of this phenomenon has been made by two sets of investigators over the last 25 years. Fujita (1961,1968) originally proposed a model for the dependence of diffusion coefficients upon free volume. Vrentas and Duda (1977) extended the model and relaxed many of its original assumptions. The complexity of their model and its use of different independent variables for the free volume term and for the chemical potential term somewhat obscured its interpretation. As an example of this, Fujita was unable to show that water, unlike organic solvents, seemed to show very little increase in diffusivity with increasing concentration in polymer. Vrentas and Duda were able to show the correct concentration dependence with their model. They apparently attributed this behavior to free volume effects. In this chapter, a reprint describing the prediction of diffusion coefficients in polymer solution is presented. The model given here shows clearly that it is thermodynamic (chemical potential) effects which cause the seemingly anomalous diffusion behavior of water.

A DIFFUSION COEFFICIENT MODEL FOR POLYMER DEVOLATILIZATION

The following reprint article develops a model for the prediction of binary mutual diffusivities in concentrated polymer solutions and melts. A general form of the model is based upon the work of Vrentas and Duda, but applies a version of the new thermodynamic results given in Chapter

2. A linearized version of this model is also described. In certain cases, e.g., polymer devolatilization, the linearized model or a constant diffusivity model is shown to be accurate for describing diffusion phenomena. Details of the derivation of new equations proposed in the article are given in Appendix I.

A Diffusion Coefficient Model for Polymer Devolatilization*

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Polymer devolatilizers are in widespread use in the polymer industry for removing solvents and monomers from polymer melts prior to product fabrication. Design equations for describing the solvent flux usually include both the diffusion coefficient of the solvent in the polymer melt and the equilibrium concentration of the solvent at the polymer-vapor interface. Several models make the assumption that the solvent diffusivity is constant over the ranges of solvent concentrations and temperatures in the devolatilizer. This is a critical assumption that may be difficult to check without obtaining diffusivity data at the operating temperatures and concentrations of the process equipment. There are three models that can be used for diffusion coefficients in devolatilizer design: the free volume model developed by Duda, Vrentas, and coworkers; a new linear model proposed in this study; and a constant diffusivity model. The linear model is obtained by combining a new correlation for solvent activity coefficients in molten polymers with free volume theory and linearizing the resulting equation. The error between using the complete free volume theory and using the linear model, or alternatively, using a constant diffusion coefficient, is calculated for several solvent-polymer systems. The linear model is convenient to use for determining the effects of the solvent activity coefficient on the diffusion coefficient. A method is presented for determining whether the complete model, the linear model, or the constant diffusivity model is appropriate for a given devolatilizer design.

INTRODUCTION

Diffusion processes play an important role in the manufacture and processing of commercial polymers. Processing steps such as polymerization, devolatilization, plasticization, and addition of additives require a knowledge of diffusion within polymer solutions and melts. Accurate modeling of diffusion coefficients of solutes in polymer systems above their glass transition temperatures is necessary for proper design of these processes.

Molten polymer devolatilization is often done in either rotating equipment, such as a vented extruder or a thin film evaporator, or in equipment which foams the polymer. Models for predicting the solvent flux in this equipment (1) often need diffusion coefficients of the solvent through the polymer at operating conditions. Some models, such as that of Newman and Simon (2) for foam devolatilization, are implemented with constant solvent diffusion coefficients even though the calculations are performed over a temperature range in which the temperature dependence of the diffusivity is significant. Devolatilization is frequently carried out with less than 5 weight percent solvent in the polymer. Over the temperature and concentration ranges in most commercial equip-

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ment, there can be a concentration-dependence of the diffusion coefficient.

While it is simple from a computational point of view to assume a constant value for the diffusion coefficient, there can be significant errors in doing so. Duda et al. (3) have predicted that the diffusion coefficient can vary significantly with temperature and concentration for the system, toluene-polystyrene. Their model shows good agreement with diffusivity data in some athermal polymer solutions above the glass transition temperature. Unfortunately, none of their comparisons are in the temperature and concentration ranges of actual devolatilization processes. There seem to be discrepancies between diffusivities determined from data taken in commerical devolatilizers (2) and diffusivities estimated by model extrapolation using parameters found at lower temperatures (3).

In this work, we use the free volume diffusion model and employ an improved correlation for the thermodynamic factor (4) to analyze the diffusion coefficient predictions at conditions typical of devolatilization for polystyrene. At temperatures well above T_g, solvent diffusion coefficients can be modeled by an equation linear in solvent weight fraction. For small solvent concentrations, the diffusion coefficient can be taken as a constant.

FREE VOLUME MODELS FOR DIFFUSIVITY

Free volume diffusion models for transport of solvent in polymers are based on previous descriptions of transport properties in liquid systems. Cohen and Turnbull (5, 6) derived an expression for self-diffusion coefficients as a function of free volume. Fujita (7, 8) used their work for describing solvent-polymer diffusion. Fujita's model is qualitatively correct but does not give quantitative agreement with available data.

Several assumptions of the Fujita model were relaxed by Vrentas and Duda (9, 10) to derive a free volume model showing good agreement with data. Modifications and improvements have been made to this model in a series of papers since 1977. The most recent version gives excellent agreement with data for the systems, toluene-polystyrene and ethylbenzene-polystyrene, over the temperature range of 110 to 178°C and concentration ranges up to 70 weight percent solvent (3).

The binary mutual diffusion coefficient is given by (3):

$$D = D_1 \frac{\rho_2 \hat{V}_{2\rho_1}}{RT} \left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,p} \tag{1}$$

D_1 on the right hand side of *Eq 1* computes the effect of free volume changes on the diffusion coefficient; and the second group, the chemical potential derivative, computes the effect of thermodynamic changes. The self diffusion coefficient of solvent, D_1, is given by:

$$D_1 = D_{01} \exp\left[\frac{-\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}}\right] \tag{2}$$

where the average hole free volume, $\hat{V}_{FH}$, is given by:

$$\frac{\hat{V}_{FH}}{\gamma} = \frac{K_{11}}{\gamma} \omega_1 (K_{21} + T - T_{g_1}) + \frac{K_{12}}{\gamma} \omega_2 (K_{22} + T - T_{g_2}) \tag{3}$$

The preexponential factor describing the energy needed to overcome neighboring attractive forces, D_{01}, is given by:

$$D_{01} = D_0 \exp(-E/RT) \tag{4}$$

Equations 1 through *4* define the binary mutual diffusion coefficient as a function of thermodynamic parameters, free-volume parameters, and an activation energy for diffusion, using solvent weight fraction as a basis. The free-volume parameters can be obtained from WLF equation data (3).

CHEMICAL POTENTIAL DERIVATIVE

In their solution for *Eq 1*, Duda and coworkers (3) used the Flory-Huggins theory and obtained the following equation for the thermodynamic factor:

$$\frac{\rho_2 \hat{V}_{2\rho_1}}{RT} \left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,p} = (1 - \phi_1)^2 (1 - 2\chi\phi_1) \tag{5}$$

For systems that are athermal (the enthalpy change on mixing is zero), the interaction parameter, χ, can be taken as a constant. The athermal assumption is good for a system such as toluene-polystyrene. However, for a number of solvent-polymer pairs, enthalpic interactions occur and χ is expected to vary with solvent concentration. In these cases, the variation of χ with concentration should be included in the model equations. This could be done by writing the chemical potential in terms of a concentration-dependent χ, taking the derivative with respect to mass concentration, and substituting the result for *Eq 5*. There is now no generally accepted model for describing the concentration dependence of χ.

Misovich and coworkers (4) have recently developed a correlation for solvent activity coefficients in concentrated polymer solutions which fits data for systems with enthalpic interactions at least as well as the Flory-Huggins equation. The correlation gives an improved result for the concentration dependence of the chemical potential and can be used to determine the value of the derivative in *Eq 1*. The result is:

$$\frac{\omega_2 \hat{V}_{FH}}{RT}\left(\frac{\partial \mu_1}{\partial \omega_1}\right) = x_2 \frac{d \ln a_1}{d \ln x_1} = \left[\frac{\frac{e}{\Omega_1^\infty}\omega_2}{\omega_1 + \frac{e}{\Omega_1^\infty}\omega_2}\right]^2 \quad (6)$$

Ω_1^∞ is the weight fraction activity coefficient of solvent in polymer at infinite dilution of solvent and can be determined by a variety of methods. For values of Ω_1^∞ between 2 and 20, the new correlation predicts the concentration dependence of activity coefficients in binary solvent-polymer systems. Since Ω_1^∞ in this correlation is a true constant at a given temperature, this equation can be used without revision for polymer solutions that are athermal and for some solutions with enthalpic interactions.

An additional advantage of *Eq 6* is that the weight fraction is used as the independent concentration variable, whereas the Flory-Huggins equation uses volume fraction. Applying *Eq 5* requires equilibrium and density data for the solvent and polymer at the temperature of interest, while *Eq 6* only requires equilibrium data. Blanks, *et al.* (11) show that the assumption of a constant density ratio between solvent and polymer is not a good one for devolatilization problems.

The chemical potential derivative could be obtained by differentiating expressions for the chemical potential. There are methods for obtaining the chemical potential based on equation-of-state approaches (12), lattice fluid theory (13), and UNIFAC-FV (14). UNIFAC-FV is based upon statistical mechanics and contains separate entropic (combinatorial) and enthalpic (residual) terms. One of its advantages is that many polymer-solvent systems can be described by the database built for UNIFAC (15, 16). Van den Berg (17) has recently proposed a method for generating UNIFAC-FV activity coefficients using a UNIFAC program. The disadvantage of using any of these methods to get the chemical potential derivative is that their differentials are complicated expressions which are difficult to analyze except by numerical means.

Eqs 1 to *4* and *6* can be combined to get an equation for the diffusion coefficient:

$$D = D_{01}\left[\frac{\frac{e}{\Omega_1^\infty}\omega_2}{\omega_1 + \frac{e}{\Omega_1^\infty}\omega_2}\right]^2 \cdot \exp\left[\frac{-(\hat{V}_1^\circ \omega_1 + \hat{V}_2^\circ \omega_2 \xi)}{\hat{V}_{FH}/\gamma}\right] \quad (7)$$

D_{01} and $\hat{V}_{FH}/\gamma$ are dependent on temperature. $\hat{V}_{FH}/\gamma$ is also dependent on concentration. Even though *Eq 7* includes concentration and temperature dependence, it is not a convenient form to use for modeling and design. In the next section, we will show how to modify *Eq 7* to get a form that is easy to apply to devolatilizer design.

LINEARIZED DIFFUSIVITY MODEL

Polymer devolatilization often takes place at solvent concentrations of less than 5 weight percent and temperatures well above T_g. Because the solvent diffusivity is required at low solvent weight fractions, we choose to linearize *Eq 7* with weight fraction at the point, $\omega_1 = 0$. The value of the diffusion coefficient at zero weight fraction of solvent is easy to determine and the differential of D with ω_1 is easy to evaluate. Linearized models have been proposed for describing the concentration dependence of the solute diffusivity both for polymer diffusion in dilute solutions (18) and for solvent diffusion in concentrated solutions (19).

The free volume terms in *Eq 3* vary with temperature. These terms are grouped as shown below and inserted in *Eq 7*:

$$A_1 = \frac{K_{11}}{\gamma}(K_{21} + T - T_{g_1}) \quad (8)$$

and

$$A_2 = \frac{K_{12}}{\gamma}(K_{22} + T - T_{g_2}) \quad (9)$$

giving

$$D = D_0\left[\frac{\frac{e}{\Omega_1^\infty}\omega_2}{\omega_1 + \frac{e}{\Omega_1^\infty}\omega_2}\right]^2 \cdot \exp\left[-\frac{\hat{V}_1^\circ \omega_1 + \hat{V}_2^\circ \omega_2 \xi}{A_1\omega_1 + A_2\omega_2} - \frac{E}{RT}\right] \quad (10)$$

for the diffusion coefficient. *Equation 10* assumes that the solvent and the polymer are in thermodynamic equilibrium at the vapor-polymer interface. This would seem to be met for most polymer-solvent systems. Even for those systems in which anomalous polymer behavior is claimed (such as the $T_{1,1}$ transition in polystyrene) (20), the equilibrium requirement should be met if the temperature is greater than 1.2 T_g. An implicit condition on the application of the thermodynamic model is that the solvent molecular weight should be much smaller than the polymer molecular weight (4).

Free volume parameters based on the WLF equation are usually assumed valid up to 100°C above T_g. Some commercial devolatilization conditions may exceed this temperature. There is no generally accepted method for estimating the polymer free-volume parameters for temperatures greater than T_g + 100°C. It is not clear that the WLF equation is a good model for extrapolating solvent-free volume parameters.

The linearized model is:

$$D(\omega_1) = D|_{\omega_1=0} + \left.\frac{\partial D}{\partial \omega_1}\right|_{\omega_1=0} (\omega_1 - 0) \quad (11)$$

which becomes:

$$D(\omega_1) = D(0)[1 + (K_1 - K_2)\omega_1] \quad (12)$$

where

$$K_1 = \frac{A_1\xi\hat{V}_2^* - A_2\hat{V}_1^*}{A_2^2} \quad (12a)$$

$$K_2 = 2\Big/\frac{c}{\Omega_1^*} \quad (12b)$$

$$D(0) = D_0 \exp\left[-\left(\frac{E}{RT} + \frac{\xi\hat{V}_2^*}{A_2}\right)\right] \quad (12c)$$

The term, K_1, is the free volume factor, and the term, K_2, is the thermodynamic factor. The exponential term in *Eq 12c* includes a term describing the attractive forces between neighboring molecules and a term describing the ratio of critical molar jumping units for the solvent and polymer.

COMPARISON OF LINEAR AND COMPLETE MODELS

The three levels of model complexity for describing the effects of solvent concentration on diffusivity in polymer devolatilizers: the complete model (*Eq 10*), the linear model proposed here (*Eq 12*), and the constant diffusivity model, provide a good range of choices for the design engineer. An advantage of the linearized model is that, at a given temperature, the difference between two constants describes the concentration dependence of D. The errors associated with using the simpler models depend on both the temperature and concentration ranges over which devolatilization is taking place. As shown in *Fig. 1*, there can be a significant effect of concentration, but its magnitude depends on the temperature.

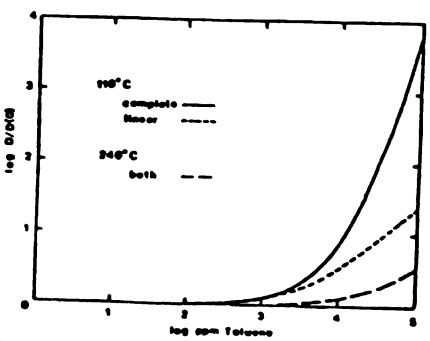


Fig. 1. Comparison of the concentration dependence of diffusion coefficients calculated by the complete and linear free volume models. Toluene and polystyrene.

Equation 12 should only be used for modeling after its accuracy has been evaluated. We have compared these models for the system, polystyrene-toluene, at a temperature just above T_g (110°C) and a temperature typical of commercial devolatilizers (240°C). The ratio between the diffusion coefficient at the specified weight fraction and that at zero solvent weight fraction is used to determine the difference between the two models.

Figure 1 shows the error associated with a linear model at the two temperatures. At 110°C, the calculations show that, below 100 ppm solvent, the diffusion coefficient can be considered constant. There is less than 2.4 percent error in the value of the diffusivity by this assumption. Up to 1000 ppm solvent, the linear model diffusivity is within 2 percent of the complete model diffusivity. The accuracy of the linear model decreases rapidly at greater solvent weight fractions and, in this case, underpredicts the diffusivity. It is not clear whether the condition of thermodynamic equilibrium at the interface is met for this system at 110°C. Anomalous transitions in the polymer melt might make the polymer relaxation time the same order of magnitude as the solvent diffusion time.

Figure 1 shows calculations for the same system at 240°C, a temperature in the range of typical devolatilization temperatures for polystyrene. At the higher temperature, diffusivity can be considered constant at solvent weight fractions less than 1000 ppm. In this case, the linear model value is within 1 percent of the value for the complete model up to 100,000 ppm or 10 weight percent solvent. The diffusivity of toluene in polystyrene at 5 weight percent (a typical concentration of solvent in polymer at the start of a devolatilization process) would be 2.21 times the value at zero weight fraction solvent, suggesting that a model using a constant diffusion coefficient could be in error.

Figure 1 does not show the temperature dependence of the diffusivity, which can be significant. We have calculated the infinite dilution solvent diffusion coefficients at two temperatures based on *Eq 12c* and using the constants suggested by Duda, *et al.* [3] for toluene/polystyrene. At 110°C, the diffusion coefficient is 6.1×10^{-11} cm²/s; and at 240°C, the diffusion coefficient is 5.5×10^{-6} cm²/s. In changing the temperature from near T_g to 1.4 T_g, the diffusion coefficient has increased by about 5 orders of magnitude. Since the free volume parameters of *Eqs 1* to *3* are temperature-dependent, the scaling of diffusivity with temperature does not follow a simple Arrhenius equation.

There are practical problems associated with determining the free volume parameters and thermodynamic parameters for *Eqs 10* and *12*. The concentration dependence of the solution free volume parameters is taken to be linear (*Eq*

3). The polymer and solvent free volume parameters are determined by fitting viscosity data with the WLF equation. For polymers, the viscosity can usually be determined over the temperature range of interest. For solvents, the WLF parameters are usually determined below the normal solvent boiling point (at atmospheric pressure). The thermodynamic terms in *Eqs 7* and *12* describe the concentration-dependence of the activity coefficients. However, Ω_1^* changes with temperature, as does the interaction parameter. Typical errors associated with these estimation techniques are discussed in the next section.

EFFECTS OF SOLVENT WLF PARAMETERS ON THE LINEAR MODEL

The WLF equation (3) may not describe the free volume changes of the solvent well, particularly if it is extrapolated to temperature well above T_{g1} + 100°C.

$$\ln \eta_1 = \ln A_1 + \frac{\gamma \hat{V}_1^*/K_{11}}{K_{21} + T - T_{g1}} \qquad (13)$$

Furthermore, the fits of some solvent viscosity data by the WLF equation seem to show systematic deviations rather than random error. Such deviations suggest that this model may not correctly predict the changes in solvent free volume with temperature. If the WLF model is used, it is preferable to determine its parameter values as close to the devolatilization temperature as possible. The comparisons below show typical differences in the linear diffusion model parameters caused by differences in the WLF parameters.

Table 1 lists solvent free volume constants and the values of K_1 for acetone and methyl acetate obtained from two different WLF fits of viscosity data. Liu (21) apparently combined two data sets (22) and (23), while only one set was used in this work (22). The two data sets covered similar temperature ranges. The WLF parameters appear to be sensitive to small changes in viscosity data. Poly(methyl methacrylate) is the polymer considered and has a T_{g2} of about 303 K. Both sets of WLF parameters generate viscosity models which average 1 percent relative error with the data.

The K_1 values, which describe the concentration-dependence of the diffusion coefficient, are compared in the lower portion of *Table 1*. We computed K_1 values at 378 K(1.25 T_{g2}) and 453 K(1.5 T_{g2}) since this might be the range of temperatures used in devolatilizing such polymer solutions. The K_1 values calculated for acetone in PMMA are similar for both sets of WLF parameters. However, the K_1 values for methylacetate differ by factors of 3 to 4. Since both sets of WLF parameters describe the viscosity data about the same, it is not clear which set of K_1 values is the better description of the free volume term. These calculations merely illustrate the sensitivity of K_1 to the values chosen for the solvent's WLF parameters.

Table 1. Comparison of K_1 Values Determined from Different Values of WLF Constants.

	Constants			
Solvent	ln A	$\gamma\hat{V}_1^*/K_{11}$	K_{21}-T_{g1}	Source
Acetone	−3 23	508	−53 3	(21)
	−3 11	466	−59 9	this study
Methyl-Acetate	−3 64	682	−38 5	(21)
	−2 26	165	−165	this study

System	T, °K	K_1 (21)	K_1 (this study)
Acetone-PMMA	378	56	61
	453	28	31
Methyl Acetate-PMMA	378	36	117
	453	18	68

Vrentas *et al.* (24) (*Eq. 5*) suggest that definition of K_{11}/γ permits a bound to be placed on this parameter, which results in a lower bound for the group, $\gamma\hat{V}_1^*/K_{11}$. For acetone, both values of $\gamma\hat{V}_1^*/K_{11}$ are above the lower bound of 450. For methylacetate, the value for $\gamma\hat{V}_1^*/K_{11}$ determined in this study is below the lower bound (380). Presumably, different WLF constants could be obtained by forcing this group to equal the lower bound and varying the other constants to fit the viscosity data with similar precision. The bounding of this group depends on the assumption that the WLF equation correctly describes free volume changes of the solvent.

We calculated the K_1 parameters for toluene, methanol, and water with polystyrene over the temperature range, 1.02 T_g to 1.42 T_g. The WLF parameters for the polymer were taken from Liu (21). *Figure 2* compares the results for toluene and methanol. For both solvents, the differences between the K_1 parameters are large near T_g and become smaller at high temperatures. *Figure 3* compares K_1 values based on WLF parameters from water viscosities below the normal boiling point (50 to 100°C) (20) with those based on WLF parameters for water viscosities taken between 110 and 160°C (23). The viscosity data between 50 and 100°C lead to negative values of K_1. Negative values of K_1 imply that the polymer expands with temperature more than the solvent, which is not expected.

These results suggest that it would be preferable to determine the solvent WLF parameters as close to the devolatilization temperature range as possible. For many cases, this would mean determining solvent viscosities at high pressures. An alternative approach might be to determine solvent free volume parameters from viscosity data of polymer melts containing solvent concentrations in the range of interest. A capillary rheometer might be used to take such data.

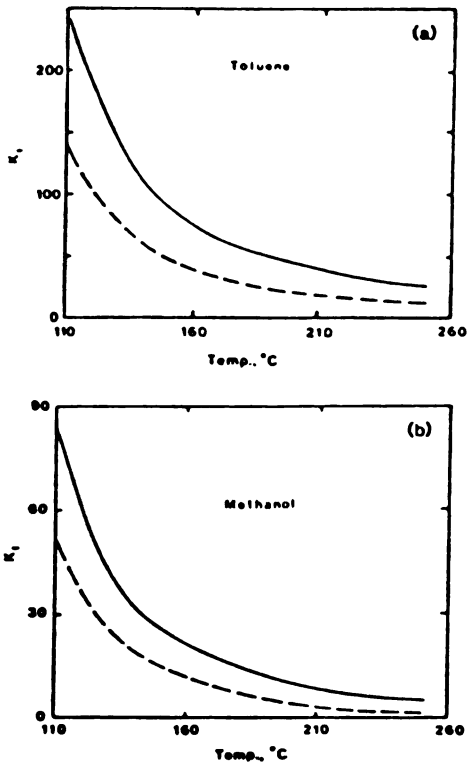


Fig. 2. Comparison of K_1 versus temperature for two sets of solvent WLF parameters. (a) toluene-polystyrene. (b) methanol-polystyrene. Solid line-Liu (21), dashed line-this work.

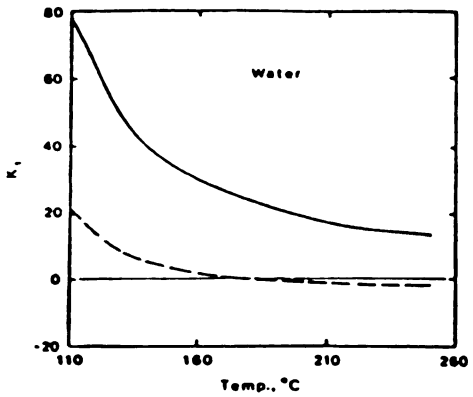


Fig. 3. Comparison for K_1 versus temperature for water-polystyrene. Solid line-WLF parameters from water viscosities between 50 and 100°C (22). Dashed line-WLF parameters from water viscosities between 110 and 160°C (27).

Table 2. Calculated Values of K_1 and K_2 for Several Solvent-Polystyrene Systems.

	System					
	Toluene/PS		MeOH/PS		Water/PS	
Temperature	K_1[a]	K_2[a]	K_1[b]	K_2[a]	K_1[c]	K_2[a]
162°C	36	5.8	33	30	33	180
172°C	30	5.4	28	25	27	130
220°C	15	4.8	17	12	14	57
230°C	13	3.6	12	7.6	13	56

[a] Liu (21).
[b] Liu (21).
[c] K_1 determined using viscosity data from 110 to 160°C (22).
[d] Determined from θ_1^∞ data taken at given temperature (26).

EFFECTS OF K_1 AND K_2 ON THE LINEAR MODEL

Equation 12 provides a convenient method for determining the effects of the thermodynamic and free volume terms on the concentration dependence of the diffusion coefficient. The difference between K_1 and K_2 gives the slope of diffusivity versus solvent weight fraction curve (as long as the linear model is valid). *Table 2* compares values of K_1 and K_2 for an athermal system (toluene/polystyrene), a system with moderate enthalpic interactions (methanol/polystyrene), and a system with strong enthalpic interactions (water/polystyrene). The WLF parameters for the solvents were determined by fitting viscosity data taken below the normal boiling point. The thermodynamic data were obtained by Gündüz and Dinçer (26), who measured weight fraction activity coefficients for 42 solvents in polystyrene as a function of temperature. Although their data seems internally consistent, the activity coefficients they report are factors of 1.5 to 2.0 higher than coefficients reported by other researchers (27, 28). We use their values because they seem to be the only values available for our solvents.

For toluene-polystyrene, the difference between K_1 and K_2 is always positive, and, while the linear model applies, the diffusivity will increase as the weight fraction of solvent increases. The difference between K_1 and K_2 for the methanol-polystyrene system is much less. The solvent diffusivity for this system should show very little concentration dependence. It should be noted that the ASOG-VSP model has successfully represented the dependence of the activity coefficient on solvent concentration for methanol in poly(methyl methacrylate) (4). It is not known whether this model adequately describes the solubility of methanol in polystyrene. We consider the calculations for the water-polystyrene system to be speculative, since the ASOG-VSP model has not been used on data with such large infinite dilution weight fraction activity coefficients. The negative difference between the free volume and thermodynamic terms suggests that there may be a range of water weight fractions for which the diffusion coefficient decreases with increasing water concentration. Performing measure-

ments on systems in which the concentration dependence of the solvent diffusivity was near zero, or negative, would constitute an interesting test of the free volume theory.

Figure 4 shows the slope of the diffusivity versus weight fraction curve for the three solvents from 110 to 260°C. Ω_1' values were extrapolated using a model linear in temperature. Over this temperature range, the diffusivity of toluene should always increase as its weight fraction increases (until the linear model is no longer valid). On the other hand, methanol shows very little concentration dependence of the diffusivity above 160°C. The model predicts that water should have the unusual property of a decreasing diffusivity through polystyrene as its weight fraction is increased. Again, this result should be considered speculative since the ASOG-VSP model has not been verified for systems with such large enthalpic interactions.

Using the linear model to analyze the effects of thermodynamic and free volume terms is valid as long as the linear model provides a good approximation to the complete model. The error associated with the linear model depends on the solvent-polymer system and the temperature. For the toluene-polystyrene system, the free volume term dominates the concentration-dependence of the diffusivity. Since diffusivity in the methanol-polystyrene system is much less dependent on solvent concentration, the linear model should approximate the complete model over larger concentration ranges than for the toluene-polystyrene system.

Figures 5 and *6* show this effect for two different sets of solvent free volume parameters. For most temperatures, the linear model will describe the complete model up to 10,000 ppm. The improved range of fit to the complete model is due to the lower concentration dependence of this system. The linear model will either predict a positive or negative (rarely zero) concentration dependence to the diffusivity and will not predict maxima or minima in D versus w_1 curves. Comparisons of *Figs. 5b* and *5d* with *Figs. 6b* and *6d* illustrate the sensitivity of the diffusion coefficient to the solvent-free volume parameters. For both *Figs. 6b* and *6d*, $K_1 - K_2$ is slightly above zero and the complete model should go through a maximum value.

Figures 4 to *6* show how the thermodynamic and free volume term affect the linear model and over what concentration ranges the linear model is valid. *Figure 7* illustrates the effect of the thermodynamic term on the diffusivity of the complete model for methanol-polystyrene at 155°C. For a 25 percent change in the value of Ω_1^∞, the diffusivity can change from monotonically decreasing to going through a small maximum.

While there is good agreement between measured solvent diffusivities and the free volume model in the papers of Duda and Vrentas, solvent diffusivities measured in actual devolatilizers do not agree well with predicted values. For example, in the foaming devolatilizer work of Newman and Simon (2), the estimated value for the diffusivity of styrene in polystyrene is 1×10^{-5} cm²/s. This value was assumed constant for fitting data between 200 and 250°C. At

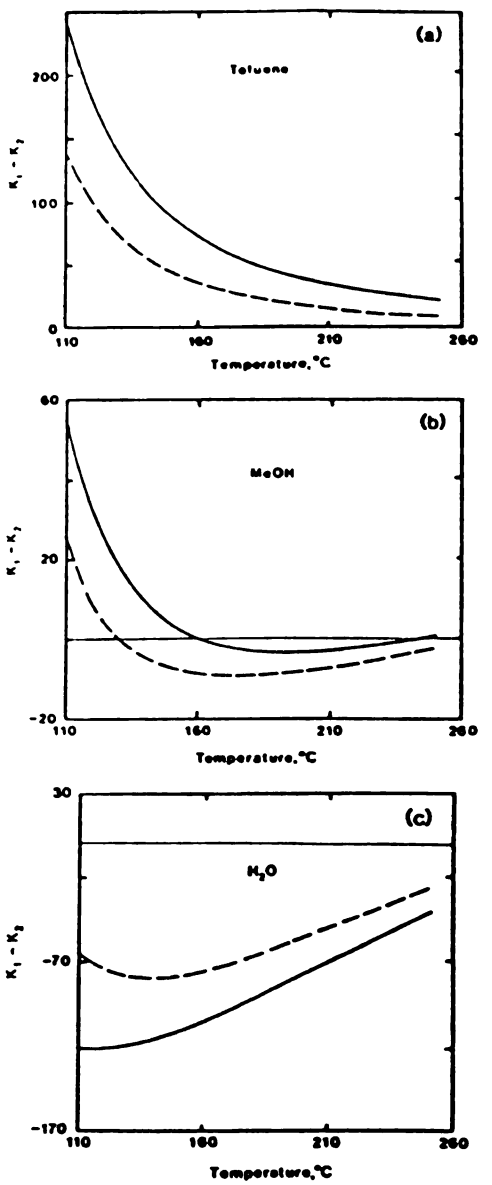
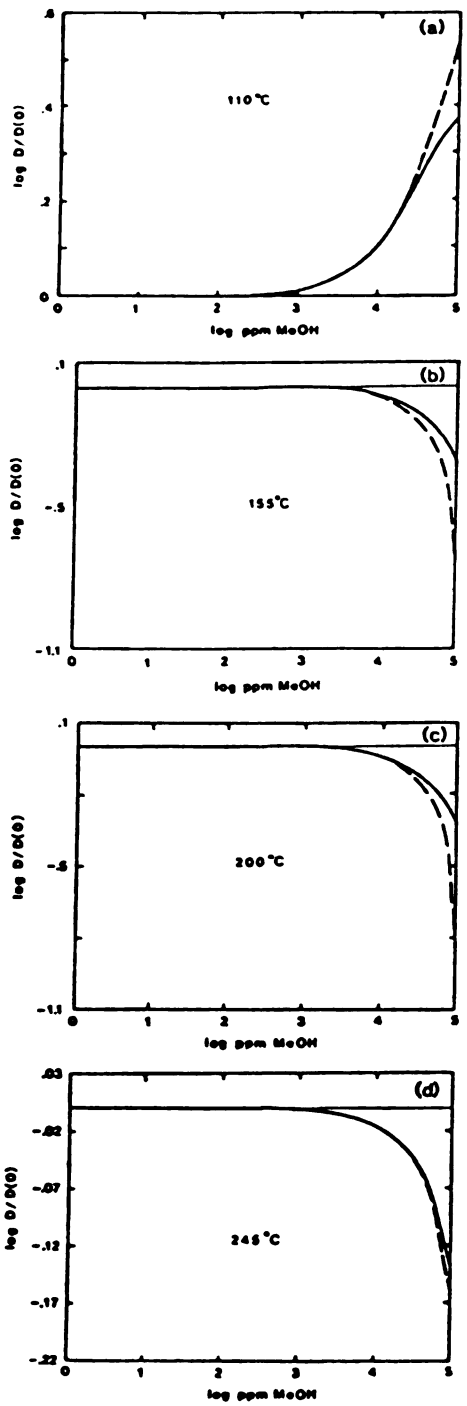


Fig. 4. K_1-K_2 versus temperature for three solvents in polystyrene. (a) toluene-polystyrene, (b) methanol polystyrene, (c) water-polystyrene. Lines identified per figures 2 and 3.



240°C, the free volume model predicts that the diffusivity should be 4.2×10^{-5} cm²/s. There is obviously a significant error associated with assuming a constant diffusivity over this temperature range.

There are also discrepancies between diffusivities measured in commercial equipment and those measured in research equipment. In an extruder devolatilizer, Biesenberger and Kessidis (29) report a diffusivity of styrene in polystyrene of 1.5×10^{-5} cm²/s at 177°C. Duda *et al.* (3) measure a value of 3×10^{-7} cm²/s at 178°C for ethylbenzene (which should be similar to styrene).

The linear diffusion coefficient model proposed in this work has the potential to be a convenient tool for designing and controlling the operation of commercial devolatilizers. The designer can determine by calculation whether to use the complete diffusion model, the linear diffusion model, or a constant diffusivity for his equipment conditions. The concentration-dependence of the solvent diffusivity is sensitive to extrapolations with the solvent-free volume parameters. Because of this sensitivity, it is preferable either to use solvent viscosities obtained at devolatilization temperatures or to devise another method for obtaining them. Finally, the effects of thermodynamics on the concentration-dependence of solvent diffusivity may be the same order of magnitude as the free-volume effects for some solvent-polymer systems.

NOMENCLATURE

- a_1 = activity of the solvent.
- A_1, A_2 = groups of parameters defined by *Eqs 8* and *9*.
- D = binary mutual diffusion coefficient.
- D_1 = self-diffusion coefficient of solvent.
- D_0 = defined by *Eq 4*.
- D_{01} = defined by *Eq 3*.
- e = base of the natural logarithm.
- E = critical energy per mole needed to overcome attractive forces.
- K_1 = free volume coefficient in the linearized model, *Eq 12a*.
- K_2 = thermodynamic coefficient in the linearized model, *Eq 12b*.
- K_{11}, K_{12} = free-volume parameters of solvent.
- K_{12}, K_{22} = free-volume parameters of the polymer.
- P = pressure.
- R = ideal gas constant.
- T = temperature.
- T_{gi} = glass transition temperature of component i.
- $\hat{V}_i$ = partial specific volume of component i.

Fig. 5. Log D/D(0) versus log (ppm solvent) for methanol-polystyrene. Solvent free volume parameters of this study. (a) 110°C, (b) 155°C, (c) 200°C, (d) 245°C. Solid line—Eq 12, dashed line—Eq 10.

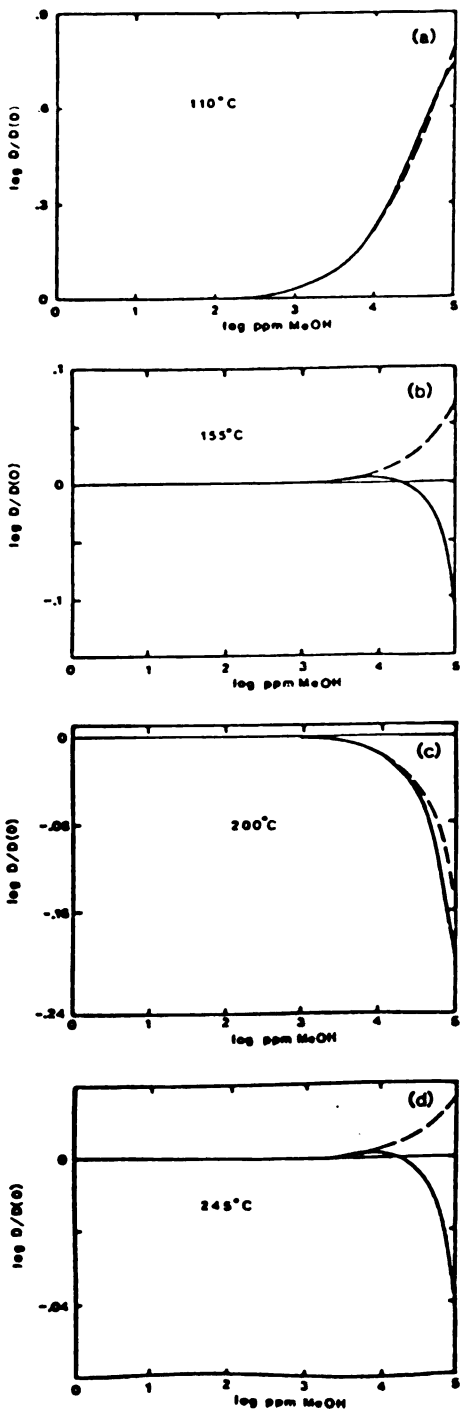


Fig. 6. Log D/D(0) versus log (ppm solvent) for methanol-polystyrene. Solvent free volume parameters of Liu (21). (a) 110°C. (b) 155°C. (c) 200°C. (d) 245°C. Solid line—Eq 12, dashed line—Eq 10.

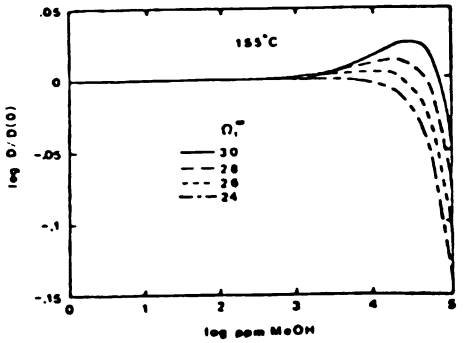


Fig 7. Effect of the thermodynamic term of D/D(0) for the complete Model. Methanol-polystyrene at 155°C.

$\hat{V}_1^*$ = specific critical hole free volume of component i required for a jump.
$\hat{V}_{FH}$ = average hole free volume per gram of mixture.
w_i = weight fraction of component i.
x_i = mole fraction of component i.

Greek Letters

γ = overlap factor for free volume.
μ_1 = chemical potential of solvent.
ξ = ratio of critical molar volume of solvent jumping unit to critical molar volume of jumping unit of polymer.
ρ_i = mass concentration of component i.
ϕ_i = volume fraction of component i.
χ = Flory-Huggins interaction parameter.
Ω_1 = solvent weight fraction activity coefficient.
Ω_1^∞ = solvent weight fraction activity coefficient at infinite dilution of solvent.

Subscripts

1 = solvent.
2 = polymer.

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CHAPTER 5

STATISTICAL DETERMINATION OF SYSTEMATIC ERROR IN NONLINEAR PARAMETER ESTIMATION

Statistical parameter estimation involves the determination of the value or values of some unknown quantity based upon data which may be inconsistent or contain error. Normally, the quantity or quantities to be estimated are in some ways characteristic of the sample from which the data were taken. The determination of an equation or model for some physical phenomenon normally involves the selection of an expression on theoretical (or empirical) grounds followed by a parameter estimation step to determine the unknown parameters of the model.

A set of estimated parameters is usually considered good if the predicted values of the dependent variable generated from the model do not deviate substantially from the observed values. A global criterion, such as the sum of the squared deviations of the predicted values from the observed values, is typically applied for this purpose. Use of a global criterion of this type may mask conditions which cause the model to be inadequate in other ways. One such problem is the existence of systematic error within the model, causing overprediction and underprediction of the dependent variable to be correlated to the independent variable rather than random.

Systematic error may indicate an underlying lack of agreement between the model and the physics of the problem. It is a particularly crucial type of error when results from a parameter estimation must be extrapolated outside the domain of the independent variable over which parameters were found. For this reason, testing for systematic error in a parameter estimation may be important in certain situations, even when the global fit of the model seems acceptable.

In order to do statistical testing, it is necessary to have a hypothesis, usually in the assumption of a particular random distribution of the variable or variables being studied. The standard approach is to evaluate the distribution of the test statistic under this random (or null) hypothesis. If the value of the test statistic calculated from the observed variables is unlikely to have occurred with random variables chosen under the null hypothesis, the null hypothesis can be rejected. A good test statistic will be able to discriminate between values taken under the null hypothesis and those taken under some alternative hypothesis; the ability to discriminate in this manner defines the power of the statistical test.

LINEAR AND NONLINEAR PARAMETER ESTIMATION

When the expression is linear in the unknown parameters, linear parameter estimation techniques based upon least squares can be applied

(Mendenhall, 1968; Graybill, 1961). Least squares means that values of the unknown parameters are chosen such that the sum of the squared deviation between each observed variable and predicted variable is minimized. It is possible for the expression to be linear in the unknown parameters even though it is nonlinear in the independent variables. For example, if y is the dependent variable, and x is the independent variable, the equation

$$y = ax^2 + bx + c \tag{1}$$

is linear in the parameters a, b, and c even though it is nonlinear in the independent variable x (since it contains a term in x^2). If x and y are variables which can be measured, linear least squares can be used to determine the best values of a, b, and c from measured data.

Least squares provides an optimal solution to the parameter estimation problem when the distribution of error is normal. If x_i and y_i are the observed or measured values, the error ϵ_i is defined by

$$\epsilon_i = y_i^{pred} - y_i \tag{2}$$

which becomes, in the case of eq 1.

$$\epsilon_i = ax_i^2 + bx_i + c - y_i \tag{3}$$

When the error distribution is not normal, the equations of least squares do not necessarily provide an optimal solution to the parameter estimation problem. Such a situation may occur when the data contains

outlier values due to measurement error or some other problem, or when the equation used to model the physical situation is systematically in error.

In cases where the expression is nonlinear in the unknown parameters, least squares analysis still provides a solution to the parameter estimation problem. However, the classical equations used for the linear case are not applicable, and often the sum of squared error must be minimized by a numerical method. Two examples of nonlinear parameter estimation are given by equations used in Chapters 2 and 4.

$$\Omega_1 = \frac{\exp\{ (e/\Omega_1^{\infty})w_2 \,/\, [w_1 + (e/\Omega_1^{\infty})w_2] \}}{w_1 + (e/\Omega_1^{\infty})w_2} \tag{4}$$

$$\ln \eta_1 = \ln A_1 + \frac{\xi \hat{V}_1^{*}/K_{11}}{K_{21} + T - T_{g1}} \tag{5}$$

In eq 4, the dependent variable is Ω_1, and w_1 is the independent variable, with $w_2 = 1 - w_1$. The parameter to be estimated is Ω_1^{∞}. In eq 5, the dependent variable is η_1, and T is the independent variable. Three parameters to be estimated are: A_1, the grouping $\xi V_1^{*}/K_{11}$, and the grouping $(K_{21} - T_{g1})$. In deriving the results in Chapters 2 and 4, eq 2 was applied numerically to data used with eqs 4 and 5, allowing "best fit" values to be determined for the necessary parameters.

DEFICIENCIES OF LINEAR LEAST SQUARES TEST IN DETERMINING ERROR DISTRIBUTION

One means of estimating the accuracy of a parameter fit is the calculation of a confidence interval for each parameter, or a confidence ellipsoid in parameter space. The Student's t statistic (Mendenhall, 1968) provides a means of generating a confidence interval for a linear least squares parameter, but is not applicable to the nonlinear case. One technique recommended for overcoming this problem is to linearize the equation using one term of a Taylor expansion. This technique is not useful if the domain and range of the measured variables fall partially outside the region in which the linearization is accurate. Confidence intervals estimated in this way may also be inaccurate if the parameters are not independent.

The amount of information available to determine the "goodness of fit" in parameter estimation may be limited in nonlinear cases. Taking this to be true, other, possibly simpler statistical procedures can be employed. As an example, consider the use of eq 5, with parameters estimated from data taken with the independent variable T in the range: $0 \leq T \leq 100$. Eq 5 is then to be used for prediction with values of T in the range: $140 \leq T \leq 240$. Extrapolation beyond the domain of the independent variable in the observed data is not always avoidable. A predominant consideration for the modeler is whether the distribution of error in the equation is a random function of the independent variable

T, or whether the equation has a tendency to systematically give inaccurate predictions.

Distribution of error can be analyzed statistically by using linear regression to examine the correlation between the variables ϵ, the error, and T, the independent variable. The correlation coefficient for these variables is defined by eq 6.

$$r = \frac{n \sum_{i=1}^{n} T_i \epsilon_i - \sum_{i=1}^{n} T_i \sum_{i=1}^{n} \epsilon_i}{\left[n \sum_{i=1}^{n} T_i^2 - \left(\sum_{i=1}^{n} T_i \right)^2 \right]^{1/2} \left[n \sum_{i=1}^{n} \epsilon_i^2 - \left(\sum_{i=1}^{n} \epsilon_i \right)^2 \right]^{1/2}} \qquad (6)$$

If the variables ϵ and T are not correlated, meaning that ϵ is not a function of T, the correlation coefficient, r, will be zero or near zero. When that is true, the null hypothesis that ϵ is not related to T can be accepted, and systematic error in the equation used for fitting data, eq 5, is assumed not to exist over the domain of T values observed.

Two problems arise in such an analysis. First, the test for correlation between two variables assumes <u>both</u> are normally distributed. If this is not true, eq 6 does not give an accurate test of correlation. Even if error is normally distributed, most physical data are taken at uniform intervals, resulting in a nonnormal distribution.

Second, nonlinear functions like eq 5, because of their curvature, have a tendency to exhibit an unusual pattern of systematic error in cases where systematic error is present. A typical example is overprediction of the dependent variable near either end of the domain of the independent variable, and underprediction in the middle of the domain of the independent variable. Since correlation examines the linear relationship between two variables, the effects will cancel and no correlation between ϵ and T will be observed. Yet, systematic error is present despite the lack of correlation, and extrapolation in this case would be greatly in error.

NONPARAMETRIC STATISTICAL TECHNIQUES

It is possible to devise statistical tests which do not assume a particular distribution (e.g., normal) for the random variables. Such techniques are termed nonparametric or distribution-free. Many nonparametric techniques are similar to standard parametric techniques, but with the actual data values replaced by their rank statistics, i.e., their position among the data values when the data is ordered. Since the distribution of ranks is known (from 1 to N, where N is the number of data items), it is possible to determine the distribution of various statistics which are functions of ranks (Kendall and Stuart, 1961).

Nonparametric tests are generally less powerful than parametric tests because less information is used. Information is lost when the actual

data values are replaced by their ranks. However, parametric tests are valid only when the distributions of the random variables being studied are the same as assumed by the test. Generally, this means normal distributions. If the distribution is not normal, parametric tests may be invalid, and even if valid, may become less powerful than nonparametric tests.

Another advantage of nonparametric statistics arises in the calculation of the distribution of a test statistic. Without knowledge of the distribution of a test statistic, inferences regarding statistical hypotheses cannot be made. The distribution provides a basis for deciding that a particular value of the test statistic observed in the data would be unlikely to occur by chance. The known discrete distribution of rank statistics can make it possible to derive the distribution of statistics in the nonparametric case which would be difficult to derive for a continuous normal distribution, or which might have to be estimated, or derived under impractical assumptions.

Two nonparametric statistical procedures relevant to this discussion are the runs test for randomness (Wald and Wolfowitz, 1940) and the rank correlation coefficient (Spearman, 1904). Both of these can be applied to the problem posed in the previous section: to determine whether the relationship between error, ϵ, and an independent variable, T, indicates systematic error within the equation being used.

The runs test for randomness consists of ordering the individual errors, ϵ_i, in order of the corresponding T_i values. Each error is then assigned a symbol, +, if it is positive and a symbol, -, if it is negative, producing a ordered sequence of the symbols, + and -. Each subsequence of successive symbols of the same type is termed a run. The underlying principle of the runs test is that a small number of runs indicates that similar ϵ values occur for values of T near one another, while a large number of runs indicates that ϵ values have little relationship to T values. Hence, the former situation describes a pattern of correlation between ϵ and T, or systematic deviation in the predictions of the model when compared to observation.

For the case where there are n occurences of the symbol + and m occurences of the symbol -, the probability of an even number of runs, 2k, or an odd number of runs, 2k+1, is given by eqs 7 and 8 for a random (null) distribution of ϵ. A table of the distribution of the number of runs, R, as a function of m and n can be compiled using these equations.

$$P(R = 2k) = \frac{2\binom{n-1}{k-1}\binom{m-1}{k-1}}{\binom{n+m}{n}} \tag{7}$$

$$P(R = 2k+1) = \frac{\binom{n-1}{k}\binom{m-1}{k-1} + \binom{n-1}{k-1}\binom{m-1}{k}}{\binom{n+m}{n}} \tag{8}$$

For large values of m and n, a normal approximation, z, to the distibution

of the random variable R can be used. This approximation is given by eqs 9, 10, and 11. The distribution of Z will be approximately N(0,1) (normal with zero mean and unit variance) so that a table of the normal distribution can be used to determine the probability that $Z \leq z$. Figure 1 illustrates the approximation for typical values of m and n.

The additional term 0.5 arises in the numerator of eq 11 because a continuous distribution of z is being used to approximate a discrete distribution of R. The best approximation to the probability of a given discrete value of R is given by the probability that the normal Z calculated by eq 11 lies between Z(R - 0.5) and Z(R + 0.5).

$$\mu_R = E(R) = \frac{2mn}{m + n} + 1 \tag{9}$$

$$Var(R) = \frac{2mn(2mn - m - n)}{(m + n)^2(m + n - 1)} \tag{10}$$

$$Z = \frac{R + 0.5 - \mu_R}{[Var(R)]^{1/2}} \tag{11}$$

To apply the runs test for randomness, the number of runs R is counted, and the probability of observing R runs or fewer is calculated from eqs 7 and 8, or eqs 9, 10, and 11. If this probability is less than some small number, α, the hypothesis that the error distribution is random with respect to T is rejected with probability $1-\alpha$.

The strength of the runs test lies in its flexibility, ease of

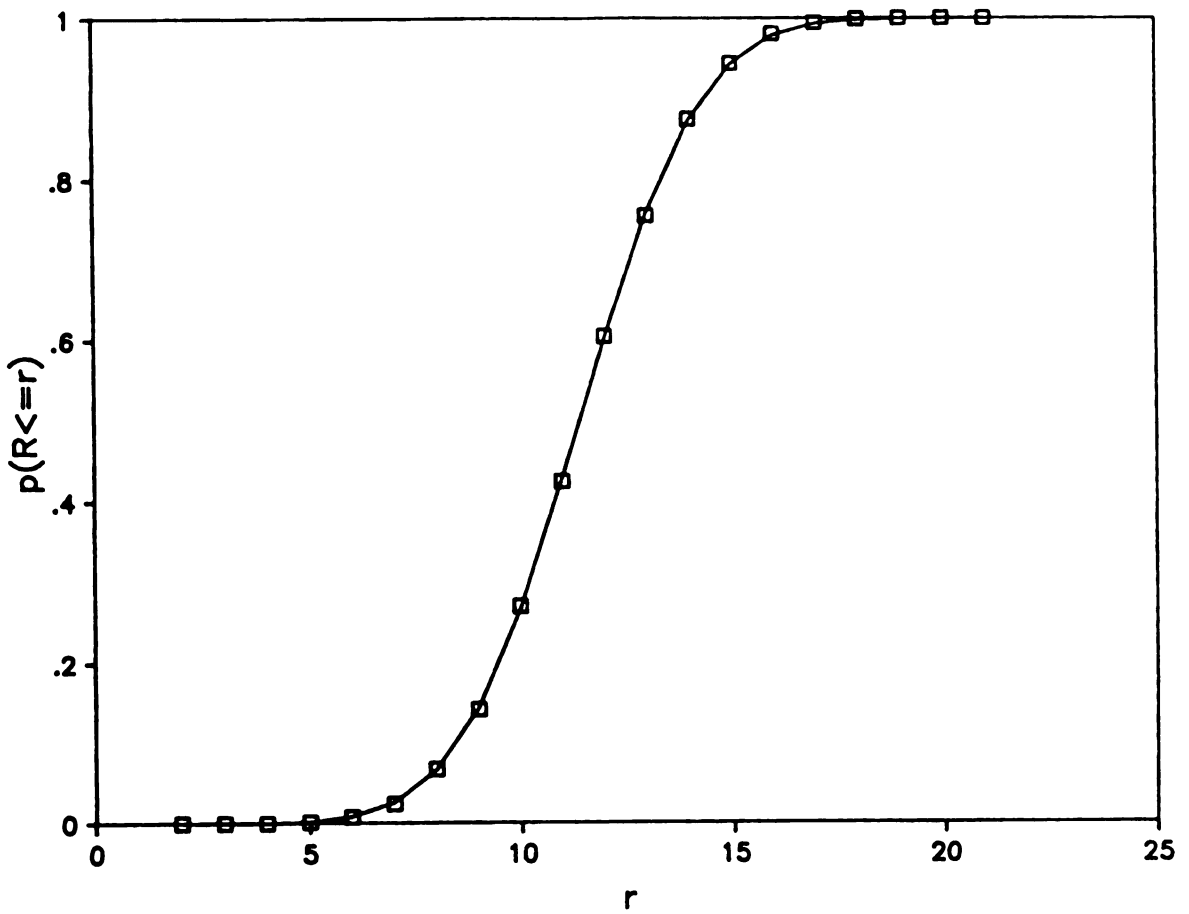

Figure 1. Normal Approximation to the Runs Statistic R. (Line denotes **normal distribution; points denote distribution of R.)**

application, and lack of assumptions about the underlying distributions of ϵ and T. However, the test is not very powerful, because it uses only a small amount of the available information: namely, whether each individual ϵ value is positive or negative. The magnitude of deviation from zero is ignored.

The rank correlation coefficient proposed by Spearman (1904), r_s, is analogous to the correlation coefficient used in linear regression. The difference is that the ranks of the data are correlated (as integers from 1 to n), rather than the actual data values. The Spearman rank correlation for the problem posed here would consist of replacing each error value, ϵ_i, by its rank when the ϵ_i values were ordered, and replacing each independent variable T_i by its rank when the T_i values were ordered. Once this is done, the rank correlation coefficient is computed by eqs 12 and 13, which are a simplified case of eq 6 when the variables being correlated each contain an arrangement of the integers from 1 to n.

$$d_i = \text{rank}(\epsilon_i) - \text{rank}(T_i) \tag{12}$$

$$r_s = 1 - \frac{6 \sum_{i=1}^{n} d_i^2}{n(n^2 - 1)} \tag{13}$$

To apply the rank correlation, the values of ϵ and T are ranked, rank differences for each data point are calculated by eq 12, and the rank correlation coefficient is calculated by eq 13. Critical values of r_s

are available in statistics references (Mendenhall and Scheaffer, 1973; Bradley, 1967) as a function of these parameters: n, the number of data points, and α, the probability that a value as large or larger than r_s would be observed in correlating two random distributions of ranks. If the absolute value of r_s exceeds the critical value for a particular α, the hypothesis that the error distribution is random with respect to t is rejected with probability $1-2\alpha$. (Since either positive or negative correlation indicates systematic error, the test described is two-sided, rejecting the randomness hypothesis if r_s is either too large or too small.)

Like the runs test, the rank correlation is flexible, easily applied, and makes no assumptions about the underlying distributions of ϵ and T. The rank correlation is generally more powerful than the runs test, although not quite as powerful as the ordinary correlation of linear regression, eq 6, when the underlying distributions are normal. This is because the information about the actual deviations of the ϵ values from one another is not used; only the relative ranks are.

The rank correlation satisfies one of the objections to the correlation coefficient from ordinary linear regression: the possibly erroneous assumption of normal distribution of the variables being correlated. However, the second problem discussed earlier still exists. If the equation used to model the data is nonlinear, predicted values may systematically overshoot and undershoot the actual observations over

ranges of the independent variable. Like the correlation coefficient from linear regression of the actual observations, the rank correlation coefficient will tend to cancel these effects, producing a "false negative" conclusion of no correlation. For this reason, it may also be a poor statistical test of the accuracy of extrapolation.

A PROPOSED NONPARAMETRIC STATISTIC FOR DETERMINATION OF SYSTEMATIC ERROR

The strengths of both the runs test and rank correlation test lie in their nonparametric, distribution-free nature. This allows application to any data, regardless of the form assumed for its underlying distribution or even the knowledge of its distribution. Furthermore, the distribution of the runs statistic, R, and the rank correlation statistic, r_s, and their critical values are relatively easy to calculate, because the distributions are discrete and involve only functions of positive integers.

Besides their general character as nonparametric procedures, the runs test and rank correlation have strengths and weaknesses that complement one another. The runs test lacks power because it reduces each data value to a simple binary value, indicated above by the symbols, + and -. Yet it is flexible in that it measures the deviation from randomness in gradations from complete monotonicity (e.g., all + symbols precede all - symbols; there are two runs), through randomness, to complete periodicity (the sequence of + and - symbols alternate; there are n

runs). The rank correlation retains a considerable amount of information contained in the original data within the ranks. However, it detects only a monotonic deviation from randomness.

A new statistical procedure, referred to as the Sum Square Rank Difference (SSRD), combines the strong points of runs test and rank correlation. The procedure begins by ordering the data values of the independent variable, T, in either increasing or decreasing order, just as the runs test did. The ranks of the ϵ_i values corresponding to each T_i value are used in calculating the statistic, R_d, by eq 14.

$$R_d = \sum_{i=1}^{n-1} [\text{Rank}(\epsilon_{i+1}) - \text{Rank}(\epsilon_i)]^2 \qquad (14)$$

If the error values are similar at neighboring values of the independent variable, the difference in ranks will be small and the statistic, R_d, will be relatively small. If the value of R_d calculated from data is so small as to be unlikely to have occurred by chance, this would indicate that systematic error is present within the equation when fit to this data. If the distribution of error is random, R_d will tend to take on larger values, and the null hypothesis of no association between error and the independent variable could be accepted.

In order to determine critical values of R_d, its distribution must be derived. For small values of n, this can be done by exhaustive listing of all possible orderings of the ranks (integers from 1 to n) and

calculation of R_d for each case. For larger values of n, numerical approximation of the distribution can be made by Monte Carlo techniques. If the distribution of R_d obeys the Central Limit Theorem (assumed here without proof), a normal approximation to the distribution of R_d (analogous to eq 11 for the runs test) can be used. This is given by eqs 15 to 17.

$$Z = \frac{R_d - E(R_d)}{[Var(R_d)]^{1/2}} \tag{15}$$

$$E(R_d) = \frac{n(n - 1)(n + 1)}{6} \tag{16}$$

$$Var(R_d) = \frac{n(n - 2)(n + 1)(5n^2 - 2n - 9)}{180} \tag{17}$$

The expected value (mean) and variance formulas were derived from exhaustive listing for the cases n = 2 up to n = 8. Since the largest value that a single term in the summation of eq 14 can have is $(n - 1)^2$, and since there are (n - 1) terms, R_d is bounded above by $(n - 1)^3$. Therefore, the distribution mean, $E(R_d)$, can be represented as a function of n which is no larger than a polynomial of degree three. The result of fitting a cubic polynomial with unknown coefficients to the mean derived from exhaustive enumeration of all cases from n = 2 to n = 5 was eq 16. Similar arguments apply to the variance: since it results from the difference of the square of the expected value of R_d and the expected value of R_d^2, it can be represented as a polynomial of degree six or less. Eq 17 resulted from fitting a sixth degree

polynomial to calculated distribution variances for n = 2 to n = 8.

Since the SSRD statistic, R_d, is nonparametric, it is valid even when the underlying distributions of the variables are nonnormal. The use of ranks retains more of the information contained in the actual observations than the binary value (+ or -) used by the runs test. At the same time, the comparison of neighboring values allows systematic patterns of similarity to be detected when the rank correlation would find no overall linear correlation. For these reasons, the SSRD statistic appears to be a useful procedure for determining whether a nonlinear parameter fit exhibits systematic error.

AN EXAMPLE CALCULATION FOR DETERMINATION OF SYSTEMATIC ERROR

The data in Table 1 represent a typical example of data fitting using eq 5. The dependent variable, η_i, is solvent viscosity as a function of the independent variable, T_i, which is temperature. The predicted value of the dependent variable is labeled η_i^{pred}, and the relative error in prediction is labeled ϵ_i. (Since eq 5 actually predicts the logarithm of η_i, the ϵ_i values shown are derived from subtracting logarithms, which makes them the logarithms of relative errors in the dependent variable.) Figure 2 shows the observed data and predictions, and a visual inspection seems to indicate the fit is good. The relative error is plotted versus temperature in Figure 3, and the plot does not show a regular linear pattern of systematic error; there appears to be

Table 1. Acetone Viscosity Data and Predictions of Equation 5.

The values of the parameters are:

A_1 = -3.603 $\quad \xi V_1^*/K_{11}$ = -642.7 $\quad (K_{21} - T_{g1})$ = 240.3

T_i, °C	η_i, cP	η_i^{pred}, cP	ϵ_i
-92.50	2.1480	2.1100	-0.0179
-80.00	1.4870	1.5030	0.0107
-59.60	0.9320	0.9557	0.0251
-42.50	0.6950	0.7026	0.0109
-30.00	0.5750	0.5792	0.0072
-20.90	0.5100	0.5102	0.0004
-13.00	0.4700	0.4608	-0.0198
-10.00	0.4500	0.4441	-0.0131
0.00	0.3990	0.3954	-0.0090
7.86	0.3638	0.3633	-0.0014
11.72	0.3495	0.3492	-0.0010
15.00	0.3370	0.3379	0.0027
15.24	0.3376	0.3371	-0.0015
19.02	0.3258	0.3250	-0.0025
23.01	0.3131	0.3130	-0.0004
25.00	0.3160	0.3073	-0.0279
27.22	0.3007	0.3012	0.0016
30.00	0.2950	0.2938	-0.0039
32.43	0.2863	0.2877	0.0048
36.00	0.2772	0.2790	0.0066
40.04	0.2675	0.2698	0.0087
41.00	0.2800	0.2677	-0.0448
44.12	0.2584	0.2611	0.0105
47.62	0.2503	0.2540	0.0148
52.20	0.2405	0.2453	0.0198
53.86	0.2377	0.2423	0.0191

References: Weast, 1979; Washburn, 1929.

Table 2. Calculation of Linear Correlation Coefficient, r.

$n = 26 \qquad \Sigma T_i = 172.84 \qquad \Sigma \epsilon_i = -0.0003$

$\Sigma T_i \epsilon_i = 0.3069 \qquad \Sigma T_i^2 = 41205.9 \qquad \Sigma \epsilon_i^2 = 0.0059309$

$$r = \frac{26 \cdot 0.3069 - 172.84 \cdot (-0.0003)}{(26 \cdot 41205.9 - (172.84)^2)^{1/2} \, (26 \cdot 0.0059309 - (-0.0003)^2)^{1/2}}$$

$r = 0.0005$

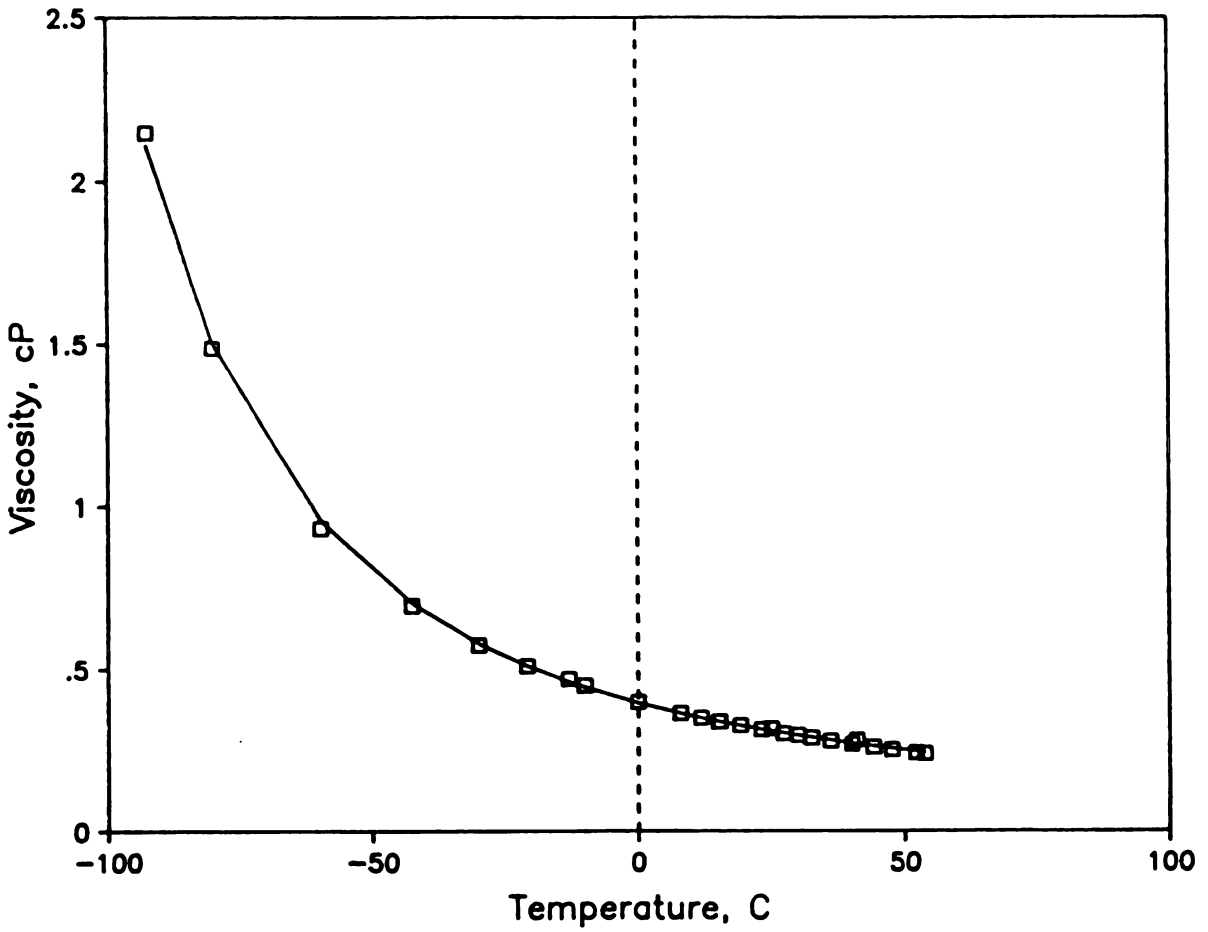

Figure 2. Viscosity of Pure Acetone as a Function of Temperature.

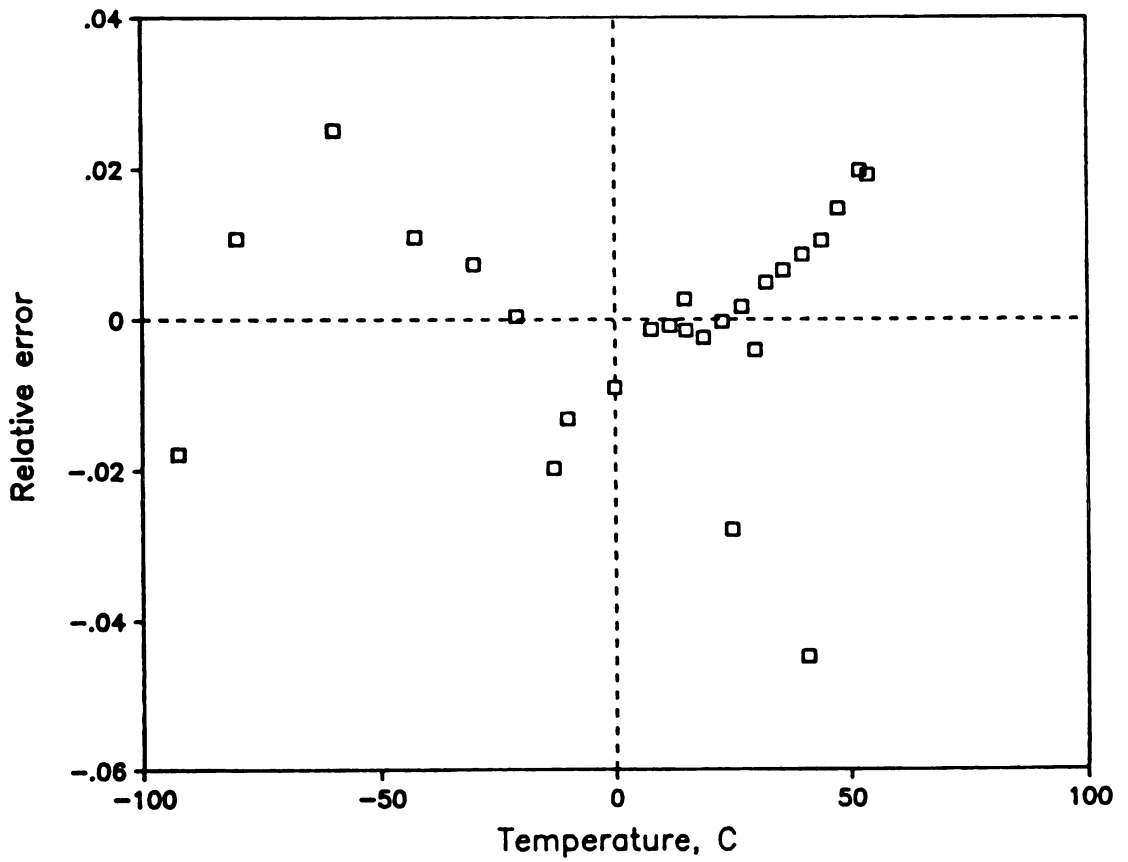

Figure 3. Error Distribution as a Function of Temperature.

considerable scatter.

The T_i values given in Table 1 would probably not have come from a normal distribution. Such a contention could be demonstrated by a statistical procedure, such as the Kolmogorov-Smirnov goodness of fit test (Kolmogorov, 1941; Smirnov, 1948), which allows an empirical distribution (like the T_i values) to be compared to a hypothesized distribution function (the normal distribution). That type of demonstration will not be pursued here; mere observation of the values will be used as evidence against an underlying normal distribution.

Applying the linear correlation coefficient, eq 6, using the summations of the data given in Table 2, results in a correlation coefficient of $r = 0.0005$, indicating nearly perfect lack of correlation between ϵ and T. The chance of observing a correlation coefficient with magnitude at least this large in a chance arrangement of 26 normally distributed pairs of values would be 99.8 percent! The correlation coefficient gives us no reason to suspect the error in eq 5 is systematic. This example shows that the linear regression correlation coefficient can be a poor statistical test for systematic error in a nonlinear parameter fit.

The details of the calculation of the runs test are given in Table 3. Replacement of the data with the + and - symbols gives 10 runs, with 14 positive data values and 12 negative data values. Since m and n are

both larger than 10, use of the limiting normal distribution is valid. The mean and variance of this distribution are calculated according to eqs 9 and 10, then eq 11 is applied. The resulting normal variable, $Z \leq -1.379$, would occur by chance in only 8.5 percent of randomly distributed pairs of values. The runs test allows the rejection of the null hypothesis (no correlation between ϵ and T) at the 90 percent confidence level, although not at the 95 percent level. This rejection would be evidence for the presence of systematic error.

Table 3. Calculation of Runs Test Statistic, R.

```
- + + + + + - - - - - + - - - - + - + + + - + + + +
1 2         3         4 5       6 7 8     9 10
```

R = 10 runs n = 14 (+) m = 12 (-)

$$\mu_R = E(R) = \frac{2 \cdot 12 \cdot 14}{12 + 14} + 1 = 13.923$$

$$Var(R) = \frac{2 \cdot 12 \cdot 14 \cdot (2 \cdot 12 \cdot 14 - 12 - 14)}{\cdot\ (12 + 14)^2 (12 + 14 - 1)} = 6.163$$

$$p(R \leq 10) = p(Z \leq z)$$

$$z = \frac{(10.5 - 13.923)}{(6.163)^{1/2}} = -1.379$$

$$p(Z \leq -1.379) = 0.085$$

The data in Table 4 are used for calculation of both the rank correlation coefficient and the SSRD statistic. These data were produced by replacing the observed values in Table 1 by their ranks within the 26 data points. The third and fourth columns contain quantities used in the statistic calculations.

Table 4. Ranked Temperature and Error Data.

Rank(T_i)	Rank(ϵ_i)	d_i^2, eq 12	$[\text{Rank}(\epsilon_{i+1})-\text{Rank}(\epsilon_i)]^2$, eq 14
1	4	9	289
2	21	361	25
3	26	529	16
4	22	324	16
5	18	169	25
6	13	49	100
7	3	16	4
8	5	9	1
9	6	9	16
10	10	0	1
11	11	0	16
12	15	9	36
13	9	16	1
14	8	36	16
15	12	9	100
16	2	196	144
17	14	9	49
18	7	121	81
19	16	9	1
20	17	9	4
21	19	4	324
22	1	441	361
23	20	9	9
24	23	1	4
25	25	0	1
26	24	4	
		$\sum_{i=1}^{26} d_i^2 = 2348$	$\sum_{i=1}^{25} [\text{Rank}(\epsilon_{i+1})-\text{Rank}(\epsilon_i)]^2 = 1640$

The data in Table 4 were used to determine the rank correlation coefficient in Table 5, by use of eq 13. The value, $r_s = 0.1973$, is not significant at the 80 percent level, i.e., a value of this magnitude would arise more than 20 percent of the time from a randomly chosen sample. The hypothesis that the variation of ϵ with T in the data is random could not be rejected.

The rank correlation seems to show considerably more relationship between ϵ and T than the linear correlation coefficient based on the original data. Even though the data in Table 4 contain less information than the data in Table 1 from which they were derived, the fact that the T_i observations are not normally distributed makes the linear correlation coefficient an inappropriate statistical test for this data. The rank correlation coefficient assumes no form for the distribution of the original data: hence, it is appropriate and in fact detects some correlation, although not at a statistically significant level.

Table 5. Calculation of Rank Correlation Coefficient, r_s.

$$r_s = 1 - \frac{6 \cdot 2348}{26(26^2 - 1)} = 0.1973$$

$p(|r_s| \geq 0.259) = 0.20$ $\qquad$ $p(|r_s| \geq 0.329) = 0.10$

Calculation of the SSRD statistic using eqs 15 to 17 is shown in Table 6. The required summation in eq 14 which defines R_d is already given in Table 4. When the mean and variance are calculated and substituted into the normal approximation formula, the resulting normal variable,

$Z \leq -2.305$, would occur only 1.06 percent of the time by chance if the pairs were random. The null hypothesis can be rejected at virtually the 99 percent confidence level when the SSRD statistic is used. The test gives strong evidence to what may not be apparent to a casual viewer of the data: that a systematic, nonlinear pattern of overprediction and underprediction is present.

Table 6. Calculation of Sum Square Rank Difference, R_d.

$$R_d = \sum_{i=1}^{25} [\text{Rank}(\epsilon_{i+1}) - \text{Rank}(\epsilon_i)]^2 = 1640$$

$$E(R_d) = \frac{26 \cdot (26 - 1) \cdot (26 + 1)}{6} = 2925$$

$$[\text{Var}(R_d)]^{1/2} = \left[\frac{26 \cdot (26 - 2)(26 + 1)(5 \cdot 26^2 - 2 \cdot 26 - 9)}{180} \right]^{1/2} = 557.37$$

$$z = \frac{1640 - 2925}{557.37} = -2.305$$

$$p(Z \leq -2.305) = 0.0106$$

In summary, the newly proposed SSRD procedure for testing whether a nonlinear parameter estimation is systematically in error (alternative hypothesis) or randomly in error (null hypothesis) was more successful then standard procedures on the sample data set. This is believed to be because it combines the flexibility in detecting patterns of similarity found in the runs test with the additional information present in rankings found in the rank correlation coefficient. Since the new procedure is nonparametric, it may be applied to any data without

concern about the form of the underlying distribution from which the observations were made. This makes the SSRD procedure more appropriate for use with physical data observed over uniform intervals than linear parametric tests such as the correlation coefficient.

Appendix C contains additional examples of the SSRD statistic used with thermodynamic data for solvent activity which were fit using the nonlinear eq 4. An additional, similarly defined statistic is also shown there: the Sum Absolute Rank Difference (SARD) defined by eq 18.

$$R_d' = \sum_{i=1}^{n-1} |\mathrm{Rank}(\epsilon_{i+1}) - \mathrm{Rank}(\epsilon_i)| \qquad (18)$$

Both the new statistics give similar results. From a mathematical standpoint, the SSRD is probably preferable to the SARD because general results are more difficult to derive mathematically for expressions involving absolute values.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

In view of the theoretical results given above and their comparison to available data, the following conclusions can be made.

1) Use of a variable size parameter concept to modify the athermal Flory-Huggins form of the entropy of mixing, incorporating an empirical free volume correction, was successful. The resulting VSP correlation technique provided predictions of polymer solution thermodynamics that were more accurate than the original Flory-Huggins method or the UNIFAC-FV method in most cases. When combined with appropriate terms to model residual (enthalpic) interactions, the accuracy of the VSP technique was increased further. Except for the case in which the residual term contained an adjustable constant, the VSP technique required only a single adjustable binary parameter, like the Flory-Huggins model. Although the UNIFAC-FV model requires no adjustable binary parameters, it does require more extensive pure component data which may not be available.

2) The VSP method with an expression for residual interaction given by the Analytical Solution of Groups (ASOG) provided a more accurate correlation of experimental data than the VSP method with no residual

interaction term. No additional adjustable binary parameters were needed to use ASOG, since a tabulated group interaction database is available.

3) In some cases when the overall fits of different correlations were similar in accuracy, predicted infinite dilution weight fraction activity coefficients showed considerable sensitivity to the particular correlation chosen. This seemed especially true in cases where these infinite dilution values were larger than approximately six.

4) A framework for analyzing residual interactions in group contribution thermodynamic models based upon their mathematical properties was proposed for the binary component case including at most two distinct functional groups. The analysis indicated that the unit of size chosen to normalize the measurement of functional groups in a molecule has an effect on the predictions of the model. Equations for removing this normalization dependence were given. These equations were also able to provide bounds on the magnitude of residual interactions based upon limited data. Such bounds were due to the additional constraint imposed upon the solution by the functional group composition of the molecular components.

5) Three models for predicting binary mutual diffusion coefficients in concentrated polymer solutions were studied: constant diffusivity, linear variation of diffusivity with concentration, and a complete free

volume model. Techniques for determining which model was appropriate for a given range of temperature and composition were shown. Under typical devolatilization conditions, it was shown that the simpler models often gave the same predictions as the complete free volume model.

6) The linear diffusivity model allowed free volume effects and chemical potential effects to be separated and described by single parameters. When applied to typical data for polystyrene and various solvents, this approach explained why diffusivity increases with solvent concentration (at low solvent concentrations) in some systems, while it decreases or remains roughly constant in others. Although the free volume term typically leads to a moderately strong increase in diffusivity, the thermodynamic term leads to a decrease in diffusivity, the effect of which is proportional to the nonideality of the solvent-polymer mixture.

7) When viscosity data were fit to equations to evaluate free volume parameters, these parameters were extremely sensitive to slight variations in the data. Alternative free volume parameters could be chosen which fit the viscosity data equally well as the original parameters, but which led to considerably different diffusivity predictions.

8) A general statistical procedure for determining whether a nonlinear

data fit exhibits systematic rather than random error was proposed and demonstrated on viscosity data as a function of temperature. The procedure was based on nonparametric statistics and combined the strong points of the runs test for randomness and the rank correlation coefficient. When applied to the viscosity data set, the new test statistic, Sum Square Rank Difference, was able to detect a complicated pattern of systematic error which was not detected in a statistically significant fashion by standard correlation, rank correlation, and runs test procedures. The new test appeared to be particularly powerful in cases where the underlying distribution of the data is not normal, and contains outlier values.

Several recommendations can be made for additional study into the topics discussed in this dissertation.

1) The VSP technique could be generalized to apply to ternary or higher multicomponent systems. Since the ASOG model is a multicomponent model, it can be applied for the residual term in these general cases. Only the VSP free volume/entropy term needs to be generalized.

2) Generation of the adjustable parameter in the VSP technique (the infinite dilution weight fraction solvent activity coefficient) by some a priori approach such as group contribution could be attempted. This would make VSP equivalent in nature to UNIFAC-FV. Predictions of some polymer properties, such as solubility parameter, already make use of

additive group contributions to the molar volume. These could be adapted for use in a simple equation of state approach for the free volume contribution to solution nonideality. The combination of experimental and tabulated volumes, as done in UNIFAC-FV, should be avoided.

3) A model for the temperature dependence of the adjustable parameter in the VSP technique could be proposed. Since the ASOG-KT constants contain a temperature dependence, this would give a complete temperature dependence to the VSP model, making it equivalent in nature to the equation of state techniques. This might be possible in conjunction with recommendation 2 above, if the temperature dependence of free volume were effectively modeled.

4) The analysis of residual terms in group contribution models should be extended to the general multicomponent, multifunctional group case. This would make the approach less of a novelty and more of a practical technique for estimating activity coefficients. The nomenclature chosen lends itself to such a generalization, with the exception of the group ratios g_1 and g_2: the use of g_{jk} to represent to ratio of functional groups of type j to those of an (arbitrary) type 1 in molecular component k would be more appropriate in the general case.

5) A more complete study of the sensitivity of predictions of the group contribution models to the normalization unit size could be attempted.

Perhaps the optimal normalization unit (in terms of predictive accuracy) would be different for different functional groups. This seems unphysical, but the present mathematical property of normalization unit size dependence in these models is already unphysical. Why should there be a different result when a functional group volume is taken as 5 A^3 rather than $5x10^{-3}$ nm^3?

6) A group contribution model which did not have this property of normalization dependence could be proposed. In the present models, the component activity coefficient is taken as the sum of functional group activity coefficients, each of which are given by a Wilson-type equation. If instead, the component interaction parameters as taken as the sum of functional group interaction parameters, and then the Wilson equation is applied to these parameters, the resulting model should no longer contain a normalization dependence. If the Wilson equation is used, however, it will also unfortunately lose the ability to model liquid phase immiscibility. Alternatively, NRTL might be used as the basis for the model to preserve this ability.

7) Only the simplest VSP model, with no residual interaction, was applied to the prediction of the chemical potential dependence of diffusivity. Since the various residual interaction terms can lead to large differences in infinite dilution behavior, it would be useful to try applying some of these other terms to the prediction of diffusivity.

8) When fitting experimental viscosity data to equations for the evaluation of free volume parameters, care must be taken to avoid extrapolation errors. Since the recommended procedure is to fit data from low temperatures where activation energy effects are negligible compared to free volume effects, the fit should be analyzed very carefully if diffusivity predictions are to be made at higher temperatures. The statistical test proposed in Chapter 5 would be useful in this regard.

9) The present procedure of fitting viscosity data at low temperature to derive free volume parameters, then assuming these free volume parameters and fitting diffusivity data to derive an activation energy and preexponential factor, seems unnecessarily complicated. Further, it leads to unphysical results, such as a large difference in activation energy and (consequently) several orders of magnitude difference in preexponential factor, for the similar systems poly(styrene)-toluene and poly(styrene)-ethylbenzene. Instead, viscosity data over a large temperature range should be fit to a combined free volume and activation energy model, and analogies between mass and momentum transport should be used to generate an activation energy for diffusion from the activation energy for viscosity. This will leave only the preexponential diffusivity factor to be evaluated from data fit.

10) Further analysis of the Sum Square Rank Difference statistical procedure should be attempted. Although the equations given for the

mean and variance were derived in a mathematically valid way, it might be possible to produce a more satisfying (elegant) derivation. The assumption that the Central Limit Theorem applies to the distribution should be proved in a rigorous manner. If possible, the power function of the statistic should be calculated (or estimated), and the asymptotic relative efficiency of the statistic compared to alternative statistical tests should be derived under various standard distributions of observed data.

APPENDIX A.

Data used in Thermodynamic Modeling.

The following data were used as input to computer programs which generated the results of thermodynamic models used in Chapter 2 of this dissertation. Each data set contains solvent activity as a function of concentration for a particular solvent-polymer pair at a particular temperature. In order to use the data as input to a computer program, a standard format was followed throughout.

A line by line description of the data set contents is given here. Lines 1 to 4 define the compounds and the temperature. Lines 5 to 7 define the infinite dilution activity to be used as a parameter in the model, or give a data point from which the parameter can be extrapolated. The units of measurement are also given here. Lines 8 and 9 define polymer and solvent density data and their units. Line 10 and all following lines define the solvent activity data for these compounds at this temperature as a function of concentration.

Line 1: A heading for the data set, giving the solvent, the polymer, and the temperature.

Line 2: The solvent name in upper case letters.

Line 3: The polymer name in upper case letters.

Line 4: The temperature (K) as a real number. This equals the Celsius temperature plus 273.16.

Line 5: The infinite dilution weight fraction solvent activity coefficient, Ω_1^{∞}, as a real number, or zero if unknown. In the data sets presented here, Ω_1^{∞} was assumed unknown, so zero was always entered.

Line 6: If Ω_1^{∞} was not given (line 5 was zero), an solvent activity or activity coefficient as a real number, followed by the lower case letter a (for activity), w (for weight fraction activity coefficient), or x (for mole fraction activity coefficient). If line 5 was nonzero, only the letter a, w, or x should be given.

Line 7: If Ω_1^{∞} was not given (line 5 was zero), a concentration as a real number, followed by the lower case letter w (for weight fraction solvent), m (for mass ratio of solvent to polymer), or x (for mole fraction solvent). If line 5 was nonzero, only the letter w, m, or x should be given.

Line 7a: If mole fraction solvent is the concentration variable (line 7 contained the lower case letter x), the polymer molecular

weight and solvent molecular weight are given as real numbers. Otherwise, this line is not present. It is not present in the data sets presented here because mole fraction solvent was never used for the concentration variable.

Line 8: The density or a related quantity for the polymer as a real number, followed by the lower case letter d (for density in g/cm^3), v (for specific volume in cm^3/g), or m (for molar volume in cm^3/g mol).

Line 9: The density or a related quantity for the solvent as a real number in the same units as were given for the polymer in line 8.

Lines 10 and following: Each line contains a solvent concentration as a real number in the same units as line 7 followed by a solvent activity or activity coefficient as a real number in the same units as line 6. The end of the data set is marked by a line containing a concentration value which is out of the legal range.

It is assumed that line 1 of a new data set follows a line containing an illegal concentration value, so that multiple data sets can be read from a single computer disk file. The data used in this work is listed below as Table A-1, in the exact format of the computer disk file, with two exceptions. The first exception is that blank lines have been

interspersed between data sets. The second exception is that the reference for each data set is listed to the right of the data.

Dr. Eric A. Grulke of Michigan State University has a disk copy of the data file. The file name is ASOGVSP.DAT.

Table A-1. Data Used in Thermodynamic Modeling.

```
Toluene-Polystyrene at 25 C
TOLUENE
PS
298.16
0
0.403a
0.111w
1.083 d
0.8610
0.191 0.611          (Bawn, Freeman, and Kamaliddin, 1950)
0.273 0.740
0.476 0.918
0.156 0.523
0.236 0.704
0.304 0.791
0.380 0.866
0.599 0.969
0.744 0.997
0.918 1.000
-1 0

Toluene-Polystyrene at 60 C
TOLUENE
PS
333.16
0
0.383a
0.102w
1.074 d
0.82355
0.179 0.576          (Bawn, Freeman, and Kamaliddin, 1950)
0.261 0.725
-1 0

Toluene-Polystyrene at 80 C
TOLUENE
PS
353.16
0
0.706a
0.246w
1.068 d
0.8075
0.458 0.914          (Bawn, Freeman, and Kamaliddin, 1950)
0.671 0.984
-1 0
```

Table A-1 (cont'd.).

```
Methyl ethyl ketone-Polystyrene at 25 C
MEK
PS
298.16
0
0.517a
0.091w
1.091 d
0.79970
0.215 0.808          (Bawn, Freeman, and Kamaliddin, 1950)
0.279 0.882
0.298 0.906
-1 0

Benzene-Polyisobutylene at 25 C
BENZENE
PIB
298.16
0
0.2990a
0.0457m
0.91693 d
0.87382
0.5948 0.9476        (Eichinger and Flory, 1968a)
0.4732 0.9227
0.4226 0.9120
0.340 0.8759
0.3251 0.8548
0.2258 0.7602
0.1787 0.7029
0.1767 0.6919
0.1044 0.5169
0.0676 0.4058
-2 0

Benzene-Polyisobutylene at 10 C
BENZENE
PIB
283.16
0
0.8388a
0.291m
0.92 d
0.8895
0.5543 0.9595        (Eichinger and Flory, 1968a)
0.8331 0.9811
-2 0
```

Table A-1 (cont'd.).

```
Cyclohexane-Polyisobutylene at 25 C
CYCLOHEXANE
PIB
298.16
0
0.4625a
0.147m
1.0906v
1.2921
1.318 0.9598          (Eichinger and Flory, 1968b)
0.668 0.8758
0.434 0.7836
0.390 0.708
0.307 0.6937
0.232 0.6105
0.198 0.5537
-2 0

N-pentane-Polyisobutylene at 25 C
N-PENTANE
PIB
298.16
0
0.2120a
0.0294m
1.0906v
1.6094
1.405 0.9897          (Eichinger and Flory, 1968c)
0.4760 0.9263
0.488 0.9208
0.3634 0.8804
0.2688 0.8093
0.227 0.7684
0.1530 0.6434
0.0786 0.4414
-2 0
```

Table A-1 (cont'd.).

```
Triisopropylbenzene-Polystyrene at 165 C
TRIISOPROPYLBENZENE
PS
438.16
0
0.296a
0.02979w
1.022 d
0.7
0.06557 0.500        (Liu, 1980)
0.08622 0.620
-2 0

Triisopropylbenzene-Polystyrene at 175 C
TRIISOPROPYLBENZENE
PS
448.16
0
0.203a
0.02036w
1.022 d
0.7
0.03793 0.267        (Liu, 1980)
0.06591 0.530
-2 0

Carbon disulfide-Polystyrene at 115 C
CS2
PS
388.16
0
0.0526a
0.01439w
1.054 d
1.1608
0.02448 0.0873       (Liu, 1980)
0.04078 0.1413
-2 0
```

Table A-1 (cont'd.).

```
Carbon disulfide-Polystyrene at 140 C
CS2
PS
413.16
0
0.03179a
0.008182w
1.039 d
1.1418
0.01112 0.04260      (Liu, 1980)
0.01833 0.05490
0.02900 0.0855
-2 0

Methanol-Polymethyl methacrylate at 120 C
METHANOL
PMMA
393.16
0
0.044a
0.002738w
1.141 d
0.6900
0.006183 0.0952      (Liu, 1980)
0.009214 0.1410
-2 0

Methanol-Polymethyl methacrylate at 130 C
METHANOL
PMMA
403.16
0
0.0316a
0.002724w
1.135 d
0.677
0.005787 0.0707      (Liu, 1980)
0.008197 0.1043
-2 0
```

Table A-1 (cont'd.).

```
Toluene-Polymethyl methacrylate at 130 C
TOLUENE
PMMA
403.16
0
0.1768a
0.01662w
1.135 d
0.775
0.05976 0.3480      (Liu, 1980)
0.1120 0.5550
-2 0

Toluene-Polymethyl methacrylate at 160 C
TOLUENE
PMMA
433.16
0
0.0743a
0.005851w
1.120 d
0.756
0.01402 0.1393      (Liu, 1980)
0.02516 0.2129
0.02259 0.2111
0.03676 0.2780
-2 0

Toluene-Polyvinyl acetate at 35 C
TOLUENE
PVA
308.16
0
0.5106a
0.08397w
1.182 d
0.847
0.11725 0.6304      (Ju, 1981)
0.16142 0.7530
0.19490 0.8200
-2 0
```

Table A-1 (cont'd.).

```
Toluene-Polyvinyl acetate at 40 C
TOLUENE
PVA
313.16
0
0.3505a
0.05131w
1.178 d
0.842
0.07616 0.4723      (Ju, 1981)
0.08900 0.5283
0.09366 0.5369
0.12762 0.6750
0.13879 0.7016
0.17080 0.7590
-2 0

Toluene-Polyvinyl acetate at 47.5 C
TOLUENE
PVA
320.66
0
0.3384a
0.05201w
1.172 d
0.835
0.07102 0.4524      (Ju, 1981)
0.10747 0.6032
-2 0

Chloroform-Polyvinyl acetate at 35 C
CHLOROFORM
PVA
308.16
0
0.2590a
0.16316w
1.182 d
1.463
0.23146 0.3289      (Ju, 1981)
0.27614 0.3885
0.32688 0.4498
0.38099 0.5197
0.41592 0.5691
0.46433 0.6373
-2 0
```

Table A-1 (cont'd.).

```
Chloroform-Polyvinyl acetate at 45 C
CHLOROFORM
PVA
318.16
0
0.1375a
0.09303w
1.174 d
1.444
0.12100 0.1704      (Ju, 1981)
0.13925 0.1956
0.16448 0.2329
0.19824 0.2708
0.20573 0.2988
0.22683 0.3175
0.24657 0.3402
0.27616 0.3817
0.29528 0.4074
0.32486 0.4435
0.35519 0.4797
0.42694 0.5929
0.46082 0.6350
0.47794 0.6665
0.49949 0.7073
-2 0

Benzene-Polyethylene oxide at 70 C
BENZENE
PEO
343.16
0
4.3118w
0.06163w
1.10 d
0.825
0.06711 4.2311      (Chang and Bonner, 1975)
0.0991 3.8095
0.1387 3.4739
0.1926 3.0925
0.261 2.6898
0.3881 2.1527
-2 0
```

Table A-1 (cont'd.).

```
Benzene-Polyethylene oxide at 70 C (second run)
BENZENE
PEO
343.16
0
4.1031w
0.05005w
1.10 d
0.825
0.08908 3.7426       (Chang and Bonner, 1975)
0.1422 3.3435
0.2006 2.9955
0.2649 2.7017
-2 0

Benzene-Polyethylene oxide at 75.1 C
BENZENE
PEO
348.26
0
3.9837w
0.05254w
1.095 d
0.82
0.08096 3.7549       (Chang and Bonner, 1975)
0.1083 3.5608
0.1454 3.3316
-2 0

Benzene-Polyethylene oxide at 88.1 C
BENZENE
PEO
361.26
0
4.2337w
0.02687w
1.082 d
0.81
0.05012 3.9859       (Chang and Bonner, 1975)
0.06671 3.8503
0.0906 3.6668
-2 0
```

Table A-1 (cont'd.).

```
Benzene-Polyethylene oxide at 102 C
BENZENE
PEO
375.16
0
4.3033w
0.02076w
1.065 d
0.80
0.02192 4.2801      (Chang and Bonner, 1975)
0.02502 4.2717
0.02919 4.2248
0.03687 4.1477
0.04418 4.0704
0.04777 4.0423
0.05834 3.9496
0.07706 3.7134
0.09184 3.5198
0.1180 3.1694
-2 0

Benzene-Polyethylene oxide at 125.4 C
BENZENE
PEO
398.56
0
4.249w
0.01094w
1.042 d
0.78
0.01769 4.1411      (Chang and Bonner, 1975)
0.02392 4.0804
0.03278 3.9928
-2 0

Benzene-Polyethylene oxide at 125.7 C
BENZENE
PEO
398.86
0
4.1547w
0.01115w
1.042 d
0.78
0.01734 4.0733      (Chang and Bonner, 1975)
0.02474 3.9452
0.03313 3.8742
-2 0
```

Table A-1 (cont'd.).

```
Benzene-Polyethylene oxide at 150.4 C
BENZENE
PEO
423.56
0
4.3113w
0.007975w
1.017 d
0.76
0.01130 4.2015      (Chang and Bonner, 1975)
0.01635 4.0606
0.02256 3.9560
-2 0
```

APPENDIX B.

Results of Thermodynamic Modeling Using Data Extrapolated from Low Solvent Concentrations.

The results given in this appendix were produced as output by a computer program using the data in Appendix A. This output was used as results in Chapter 2 of the dissertation. The program itself and instructions for its execution are given in Appendix D. Experimental data for a given polymer-solvent system and given temperature were fit to the VSP model (the column headed ASOGVSP in the table) and the Flory-Huggins model using a single data point at low solvent concentration to evaluate an adjustable parameter. The UNIFAC-FV model was also applied to the data for comparison.

Each data set in Table B-1 begins with a heading which gives the polymer and solvent used and the temperature. The next three lines give the concentration data point from which adjustable parameters were extrapolated, and the values of those parameters. The remainder of each data set contains a comparison of experimental and predicted weight fraction solvent activity coefficients for each concentration in the data set. At the bottom of each column, the root mean square error for

the data set is given.

Table B-1. Results Using Thermodynamic Data Extrapolated from Low Solvent Concentrations.

Toluene-Polystyrene at 25 C

By correlating activity at finite conc 0.111
Infinite dilution wt frac activity coefficient was 4.6807
Flory-Huggins chi parameter was 0.3140

Wt Frac	Activity Coefficients and Percent Error						
Solvent	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.156	3.353	3.305	-1.4	3.347	-0.2	3.220	-4.0
0.191	3.199	3.081	-3.7	3.124	-2.3	3.003	-6.1
0.236	2.983	2.826	-5.3	2.867	-3.9	2.758	-7.5
0.273	2.711	2.640	-2.6	2.679	-1.2	2.580	-4.8
0.304	2.602	2.499	-4.0	2.535	-2.6	2.444	-6.1
0.380	2.279	2.198	-3.6	2.227	-2.3	2.157	-5.3
0.476	1.929	1.893	-1.9	1.913	-0.8	1.866	-3.2
0.599	1.618	1.590	-1.7	1.602	-1.0	1.577	-2.5
0.744	1.340	1.323	-1.3	1.327	-0.9	1.318	-1.6
0.918	1.089	1.088	-0.1	1.088	-0.0	1.088	-0.2
Avg pct error		2.5		1.5		4.1	

Toluene-Polystyrene at 60 C

By correlating activity at finite conc 0.102
Infinite dilution wt frac activity coefficient was 4.7774
Flory-Huggins chi parameter was 0.2984

Wt Frac	Activity Coefficients and Percent Error						
Solvent	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.179	3.218	3.189	-0.9	3.229	0.3	3.187	-1.0
0.261	2.778	2.720	-2.1	2.756	-0.8	2.700	-2.8
Avg pct error		1.5		0.6		1.9	

Table B-1 (cont'd.).

Toluene-Polystyrene at 80 C

By correlating activity at finite conc 0.246
Infinite dilution wt frac activity coefficient was 5.0991
Flory-Huggins chi parameter was 0.3495

Wt Frac Solvent	Activity Coefficients and Percent Error						
	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.458	1.996	1.971	-1.2	1.998	0.1	1.934	-3.1
0.671	1.466	1.454	-0.9	1.462	-0.3	1.442	-1.7
Avg pct error		1.1		0.2		2.4	

Methyl ethyl ketone-Polystyrene at 25 C

By correlating activity at finite conc 0.091
Infinite dilution wt frac activity coefficient was 8.6856
Flory-Huggins chi parameter was 0.8510

Wt Frac Solvent	Activity Coefficients and Percent Error						
	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.215	3.758	3.700	-1.5	4.113	9.5	4.164	10.8
0.279	3.161	3.099	-2.0	3.431	8.5	3.456	9.3
0.298	3.040	2.953	-2.9	3.261	7.3	3.282	7.9
Avg pct error		2.1		8.4		9.4	

Table B-1 (cont'd.).

Benzene-Polyisobutylene at 25 C

By correlating activity at finite conc 0.043
Infinite dilution wt frac activity coefficient was 8.4655
Flory-Huggins chi parameter was 1.0878

Wt Frac Solvent	Activity Coefficients and Percent Error						
	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.063	6.409	6.274	-2.1	6.871	7.2	6.016	-6.1
0.094	5.468	5.520	1.0	6.224	13.8	5.452	-0.3
0.150	4.608	4.506	-2.2	5.251	14.0	4.620	0.3
0.152	4.636	4.484	-3.3	5.229	12.8	4.601	-0.8
0.184	4.127	4.032	-2.3	4.752	15.1	4.199	1.8
0.245	3.484	3.370	-3.3	4.001	14.8	3.572	2.5
0.254	3.452	3.294	-4.6	3.911	13.3	3.497	1.3
0.297	3.070	2.946	-4.0	3.485	13.5	3.144	2.4
0.321	2.873	2.779	-3.3	3.275	14.0	2.970	3.4
0.373	2.541	2.472	-2.7	2.881	13.4	2.642	4.0
Avg pct error			2.9		13.2		2.3

Benzene-Polyisobutylene at 10 C

By correlating activity at finite conc 0.225
Infinite dilution wt frac activity coefficient was 10.0386
Flory-Huggins chi parameter was 1.2727

Wt Frac Solvent	Activity Coefficients and Percent Error						
	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.357	2.691	2.616	-2.8	3.226	19.9	2.749	2.2
0.454	2.159	2.122	-1.7	2.516	16.5	2.236	3.6
Avg pct error			2.2		18.2		2.9

Table B-1 (cont'd.).

Cyclohexane-Polyisobutylene at 25 C

By correlating activity at finite conc 0.128
Infinite dilution wt frac activity coefficient was 4.9119
Flory-Huggins chi parameter was 0.4221

Wt Frac Solvent	Activity Coefficients and Percent Error						
	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.165	3.350	3.330	-0.6	3.409	1.8	3.220	-3.9
0.188	3.242	3.173	-2.1	3.253	0.3	3.070	-5.3
0.235	2.953	2.890	-2.1	2.966	0.4	2.799	-5.2
0.281	2.523	2.649	5.0	2.719	7.8	2.570	1.9
0.303	2.589	2.544	-1.8	2.611	0.8	2.471	-4.6
0.400	2.187	2.148	-1.8	2.199	0.5	2.098	-4.1
0.569	1.688	1.665	-1.4	1.689	0.0	1.642	-2.7
Avg pct error			2.1		1.7		3.9

N-pentane-Polyisobutylene at 25 C

By correlating activity at finite conc 0.028
Infinite dilution wt frac activity coefficient was 8.5781
Flory-Huggins chi parameter was 0.7601

Wt Frac Solvent	Activity Coefficients and Percent Error						
	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.072	6.057	6.077	0.3	6.433	6.2	5.654	-6.7
0.133	4.849	4.816	-0.7	5.205	7.3	4.487	-7.5
0.185	4.153	4.040	-2.7	4.394	5.8	3.777	-9.1
0.212	3.820	3.721	-2.6	4.050	6.0	3.488	-8.7
0.267	3.303	3.193	-3.3	3.465	4.9	3.011	-8.8
0.322	2.872	2.776	-3.3	2.992	4.2	2.635	-8.3
0.328	2.808	2.741	-2.4	2.952	5.1	2.603	-7.3
0.584	1.694	1.679	-0.9	1.733	2.3	1.644	-3.0
Avg pct error			2.0		5.2		7.4

Table B-1 (cont'd.).

Triisopropylbenzene-Polystyrene at 165 C

By correlating activity at finite conc 0.029
Infinite dilution wt frac activity coefficient was 12.4354
Flory-Huggins chi parameter was 1.1421

Wt Frac Solvent	Activity Coefficients and Percent Error					
	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.065	7.625	7.901	3.6	8.984	17.8	5.551	-27.2
0.086	7.191	7.031	-2.2	8.172	13.6	5.187	-27.9
Avg pct error		2.9		15.7		27.5	

Triisopropylbenzene-Polystyrene at 175 C

By correlating activity at finite conc 0.020
Infinite dilution wt frac activity coefficient was 11.5246
Flory-Huggins chi parameter was 1.0661

Wt Frac Solvent	Activity Coefficients and Percent Error					
	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.037	7.039	8.894	26.3	9.582	36.1	6.084	-13.6
0.065	8.041	7.544	-6.2	8.427	4.8	5.528	-31.3
Avg pct error		16.3		20.5		22.4	

Carbon disulfide-Polystyrene at 115 C

By correlating activity at finite conc 0.014
Infinite dilution wt frac activity coefficient was 3.7485
Flory-Huggins chi parameter was 0.4179

Wt Frac Solvent	Activity Coefficients and Percent Error					
	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.024	3.566	3.592	0.7	3.607	1.1	4.685	31.4
0.040	3.465	3.493	0.8	3.516	1.5	4.503	30.0
Avg pct error		0.8		1.3		30.7	

Table B-1 (cont'd.).

Carbon disulfide-Polystyrene at 140 C

By correlating activity at finite conc 0.008
Infinite dilution wt frac activity coefficient was 3.9461
Flory-Huggins chi parameter was 0.4671

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.011	3.831	3.864	0.9	3.874	1.1	4.488	17.1
0.018	2.995	3.812	27.3	3.827	27.8	4.414	47.4
0.029	2.948	3.737	26.7	3.760	27.5	4.309	46.1
Avg pct error			18.3		18.8		36.9

Methanol-Polymethyl methacrylate at 120 C

By correlating activity at finite conc 0.002
Infinite dilution wt frac activity coefficient was 16.5646
Flory-Huggins chi parameter was 1.3043

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.006	15.397	15.483	0.6	15.905	3.3	21.457	39.4
0.009	15.303	14.996	-2.0	15.594	1.9	20.775	35.8
Avg pct error			1.3		2.6		37.6

Methanol-Polymethyl methacrylate at 130 C

By correlating activity at finite conc 0.002
Infinite dilution wt frac activity coefficient was 11.8452
Flory-Huggins chi parameter was 0.9552

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.005	12.217	11.336	-7.2	11.473	-6.1	21.021	72.1
0.008	12.724	11.134	-12.5	11.323	-11.0	20.493	61.1
Avg pct error			9.9		8.6		66.6

Table B-1 (cont'd.).

Toluene-Polymethyl methacrylate at 130 C

By correlating activity at finite conc 0.016
Infinite dilution wt frac activity coefficient was 12.0574
Flory-Huggins chi parameter was 1.1082

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.059	5.823	8.029	37.9	8.993	54.4	5.382	-7.6
0.112	4.955	6.082	22.7	7.131	43.9	4.508	-9.0
Avg pct error			30.3		49.2		8.3

Toluene-Polymethyl methacrylate at 160 C

By correlating activity at finite conc 0.005
Infinite dilution wt frac activity coefficient was 13.3599
Flory-Huggins chi parameter was 1.1992

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.014	9.936	11.864	19.4	12.378	24.6	6.398	-35.6
0.022	9.345	11.084	18.6	11.825	26.5	6.189	-33.8
0.025	8.462	10.867	28.4	11.666	37.9	6.128	-27.6
0.036	7.563	9.973	31.9	10.982	45.2	5.866	-22.4
Avg pct error			24.6		33.6		29.8

Toluene-Polyvinyl acetate at 35 C

By correlating activity at finite conc 0.084
Infinite dilution wt frac activity coefficient was 9.2829
Flory-Huggins chi parameter was 0.8949

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.117	5.377	5.295	-1.5	5.862	9.0	3.970	-26.2
0.161	4.665	4.492	-3.7	5.031	7.9	3.512	-24.7
0.195	4.207	4.014	-4.6	4.511	7.2	3.221	-23.4
Avg pct error			3.3		8.0		24.8

Table B-1 (cont'd.).

Toluene-Polyvinyl acetate at 40 C

By correlating activity at finite conc 0.051
Infinite dilution wt frac activity coefficient was 8.8537
Flory-Huggins chi parameter was 0.8450

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.076	6.201	6.114	-1.4	6.565	5.9	4.515	-27.2
0.089	5.936	5.791	-2.4	6.263	5.5	4.341	-26.9
0.093	5.732	5.682	-0.9	6.158	7.4	4.280	-25.3
0.128	5.289	4.978	-5.9	5.466	3.3	3.877	-26.7
0.139	5.055	4.778	-5.5	5.262	4.1	3.757	-25.7
0.171	4.444	4.277	-3.8	4.737	6.6	3.447	-22.4
Avg pct error		3.3		5.5		25.7	

Toluene-Polyvinyl acetate at 47.5 C

By correlating activity at finite conc 0.052
Infinite dilution wt frac activity coefficient was 8.3169
Flory-Huggins chi parameter was 0.7793

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.071	6.370	6.003	-5.8	6.356	-0.2	4.621	-27.5
0.107	5.613	5.202	-7.3	5.597	-0.3	4.139	-26.3
Avg pct error		6.5		0.3		26.9	

Chloroform-Polyvinyl acetate at 35 C

By correlating activity at finite conc 0.163
Infinite dilution wt frac activity coefficient was 1.6518
Flory-Huggins chi parameter was -0.2848

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.231	1.421	1.556	9.5	1.572	10.6	1.168	-17.8
0.276	1.407	1.535	9.1	1.551	10.3	1.165	-17.2
0.327	1.376	1.509	9.6	1.526	10.9	1.162	-15.5
0.381	1.364	1.479	8.4	1.497	9.8	1.160	-14.9
0.416	1.368	1.459	6.7	1.477	7.9	1.159	-15.3
0.464	1.373	1.430	4.2	1.447	5.5	1.158	-15.6
Avg pct error		7.9		9.2		16.1	

Chloroform-Polyvinyl acetate at 45 C

By correlating activity at finite conc 0.093
Infinite dilution wt frac activity coefficient was 1.4937
Flory-Huggins chi parameter was -0.3918

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.121	1.408	1.473	4.6	1.489	5.8	1.207	-14.3
0.139	1.405	1.469	4.6	1.488	5.9	1.204	-14.3
0.164	1.416	1.463	3.3	1.485	4.8	1.200	-15.3
0.198	1.366	1.455	6.5	1.480	8.3	1.195	-12.5
0.206	1.452	1.453	0.0	1.478	1.8	1.195	-17.7
0.227	1.400	1.448	3.5	1.475	5.3	1.192	-14.8
0.247	1.380	1.443	4.6	1.471	6.6	1.190	-13.7
0.276	1.382	1.434	3.8	1.464	5.9	1.187	-14.1
0.295	1.380	1.429	3.6	1.459	5.7	1.186	-14.1
0.325	1.365	1.420	4.0	1.451	6.3	1.183	-13.3
0.355	1.351	1.410	4.4	1.441	6.7	1.181	-12.6
0.427	1.389	1.383	-0.4	1.415	1.9	1.177	-15.3
0.461	1.378	1.369	-0.6	1.400	1.6	1.175	-14.8
0.478	1.395	1.362	-2.3	1.393	-0.1	1.174	-15.8
0.499	1.416	1.353	-4.5	1.382	-2.4	1.172	-17.2
Avg pct error		3.4		4.6		14.7	

Benzene-Polyethylene oxide at 70 C

By correlating activity at finite conc 0.061
Infinite dilution wt frac activity coefficient was 5.0642
Flory-Huggins chi parameter was 0.3345

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.067	4.231	4.253	0.5	4.291	1.4	3.524	-16.7
0.099	3.810	3.936	3.3	3.982	4.5	3.317	-12.9
0.139	3.474	3.591	3.4	3.642	4.8	3.085	-11.2
0.193	3.093	3.192	3.2	3.244	4.9	2.809	-9.2
0.261	2.690	2.779	3.3	2.826	5.0	2.510	-6.7
0.388	2.153	2.207	2.5	2.239	4.0	2.070	-3.8
Avg pct error		2.7		4.1		10.1	

Table B-1 (cont'd.).

Benzene-Polyethylene oxide at 70 C (second run)

By correlating activity at finite conc 0.050
Infinite dilution wt frac activity coefficient was 4.6088
Flory-Huggins chi parameter was 0.2403

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.089	3.743	3.765	0.6	3.785	1.1	3.379	-9.7
0.142	3.344	3.368	0.7	3.392	1.5	3.066	-8.3
0.201	2.996	3.001	0.2	3.026	1.0	2.771	-7.5
0.265	2.702	2.663	-1.4	2.686	-0.6	2.494	-7.7
Avg pct error			0.7		1.0		8.3

Benzene-Polyethylene oxide at 75.1 C

By correlating activity at finite conc 0.052
Infinite dilution wt frac activity coefficient was 4.4790
Flory-Huggins chi parameter was 0.2102

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.081	3.755	3.749	-0.2	3.764	0.2	3.416	-9.0
0.108	3.561	3.543	-0.5	3.559	-0.0	3.247	-8.8
0.145	3.332	3.289	-1.3	3.307	-0.7	3.038	-8.8
Avg pct error			0.7		0.3		8.9

Benzene-Polyethylene oxide at 88.1 C

By correlating activity at finite conc 0.026
Infinite dilution wt frac activity coefficient was 4.5008
Flory-Huggins chi parameter was 0.2147

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.050	3.986	4.021	0.9	4.032	1.2	3.563	-10.6
0.066	3.850	3.879	0.7	3.893	1.1	3.454	-10.3
0.090	3.667	3.688	0.6	3.704	1.0	3.305	-9.9
Avg pct error			0.7		1.1		10.3

Table B-1 (cont'd.).

Benzene-Polyethylene oxide at 102 C

By correlating activity at finite conc 0.020
Infinite dilution wt frac activity coefficient was 4.5132
Flory-Huggins chi parameter was 0.2209

Wt Frac Solvent	Activity Coefficients and Percent Error						
	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.021	4.280	4.292	0.3	4.298	0.4	3.662	-14.4
0.025	4.272	4.262	-0.2	4.269	-0.0	3.641	-14.8
0.029	4.225	4.222	-0.0	4.230	0.1	3.613	-14.5
0.036	4.148	4.150	0.0	4.160	0.3	3.562	-14.1
0.044	4.070	4.084	0.3	4.094	0.6	3.515	-13.6
0.047	4.042	4.051	0.2	4.063	0.5	3.492	-13.6
0.058	3.950	3.959	0.2	3.972	0.6	3.426	-13.2
0.077	3.713	3.802	2.4	3.818	2.8	3.314	-10.7
0.091	3.520	3.685	4.7	3.703	5.2	3.230	-8.2
0.118	3.169	3.491	10.2	3.510	10.8	3.087	-2.6
Avg pct error			1.9		2.1		12.0

Benzene-Polyethylene oxide at 125.4 C

By correlating activity at finite conc 0.010
Infinite dilution wt frac activity coefficient was 4.3520
Flory-Huggins chi parameter was 0.1810

Wt Frac Solvent	Activity Coefficients and Percent Error						
	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.017	4.141	4.187	1.1	4.190	1.2	3.611	-12.8
0.023	4.080	4.131	1.2	4.136	1.4	3.571	-12.5
0.032	3.993	4.054	1.5	4.059	1.7	3.515	-12.0
Avg pct error			1.3		1.4		12.4

Table B-1 (cont'd.).

Benzene-Polyethylene oxide at 125.7 C

By correlating activity at finite conc 0.011
Infinite dilution wt frac activity coefficient was 4.2540
Flory-Huggins chi parameter was 0.1583

Wt Frac Solvent	Activity Coefficients and Percent Error						
	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.017	4.073	4.101	0.7	4.103	0.7	3.613	-11.3
0.024	3.945	4.038	2.4	4.041	2.4	3.566	-9.6
0.033	3.874	3.969	2.4	3.973	2.5	3.513	-9.3
Avg pct error			1.8		1.9		10.1

Benzene-Polyethylene oxide at 150.4 C

By correlating activity at finite conc 0.007
Infinite dilution wt frac activity coefficient was 4.3883
Flory-Huggins chi parameter was 0.1876

Wt Frac Solvent	Activity Coefficients and Percent Error						
	Exptl	ASOGVSP		Flory-Huggins		UNIFAC-FV	
0.011	4.202	4.280	1.9	4.282	1.9	3.569	-15.0
0.016	4.061	4.233	4.2	4.236	4.3	3.538	-12.9
0.022	3.956	4.176	5.6	4.180	5.7	3.501	-11.5
Avg pct error			3.9		4.0		13.1

APPENDIX C.

Results of Thermodynamic Modeling Using a Best Fit of All Data

The results given in this appendix were produced as output by a computer program using the data in Appendix A. This output was used as results in Chapter 2 of the dissertation. The program itself and instructions for its execution are given in Appendix E. Experimental data for a given polymer-solvent system and given temperature were fit to the VSP model assuming no residual interaction, the Flory-Huggins model, the VSP model assuming a Flory-Huggins type residual interaction term, and the VSP model assuming an interaction term given by Analytical Solution of Groups (ASOG).

For each data set, a heading is given, followed by the values of adjustable parameters determined by a least squares best fit criterion. (The ASOG-VSP enthalpic coefficient is determined a priori from the ASOG interaction parameter tables, not from fitting to the data, but is included in this section for comparison.) The next section contains a comparison of experimental and predicted weight fraction solvent activity coefficients for each concentration in the data set. At the bottom of each column, the root mean square error for the data set is given. The following section gives the results of nonparametric statistical tests of the randomness of the error in each model

prediction compared to experiment, as discussed in Chapter 5 of the dissertation. In cases where the Flory-Huggins or FH-VSP models predict phase separation, the concentration at which it is predicted to occur is given. (The VSP model using ASOG residual term is also capable of predicting phase separation, but such prediction was not included in this table.)

No ASOG interaction parameters are available for the ether oxygen (-O-) functional group with the aromatic hydrocarbon (ArCH) functional group. For this reason, calculations with the VSP model using ASOG residual term could not be made for benzene-polyethylene oxide. There are values given in the table for this system, but the ASOG-VSP results are invalid, as the computer program generating the table set the interaction parameters to zero for these functional groups. The results for the other three models are valid for benzene-polyethylene oxide, since those models do not use the ASOG parameter tables.

Table C-1. Results Using Thermodynamic Data Fit to the Entire Data Set.

Toluene-Polystyrene at 25 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 4.9495
Flory-Huggins chi parameter: 0.3394
FH-VSP inf diln parameters: wt frac act coeff 4.5644 enth coeff 1.7256
ASOG-VSP inf diln parameters: wt frac act coeff 4.9391 enth coeff 1.0064

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.111	3.631	3.769	3.7	3.739	3.0	3.673	1.2	3.767	3.7
0.156	3.353	3.411	1.7	3.403	1.5	3.375	0.7	3.410	1.7
0.191	3.199	3.168	-1.0	3.171	-0.9	3.164	-1.1	3.168	-1.0
0.236	2.983	2.893	-3.1	2.905	-2.6	2.917	-2.2	2.894	-3.0
0.273	2.711	2.694	-0.6	2.710	-0.0	2.732	0.8	2.695	-0.6
0.304	2.602	2.543	-2.3	2.562	-1.6	2.589	-0.5	2.545	-2.2
0.380	2.279	2.226	-2.3	2.245	-1.5	2.278	-0.0	2.228	-2.3
0.476	1.929	1.908	-1.1	1.924	-0.3	1.954	1.3	1.909	-1.0
0.599	1.618	1.597	-1.3	1.607	-0.7	1.628	0.6	1.598	-1.2
0.744	1.340	1.325	-1.1	1.329	-0.8	1.338	-0.1	1.325	-1.1
0.918	1.089	1.088	-0.1	1.088	-0.1	1.089	0.0	1.088	-0.1
Standard pct err			2.1		1.6		1.1		2.0

Analysis of model error randomness

Sum sqr rank difference test: mean = 220.00 sd = 61.55

Test statistic	158	187	210	158
Normal (Z)	-1.007	-0.536	-0.162	-1.007
Reject level	0.843114	0.704061	0.564541	0.843114

Sum abs rank difference test: mean = 40.00 sd = 6.66

Test statistic	34	35	40	34
Normal (Z)	-0.900	-0.750	0.000	-0.900
Reject level	0.816062	0.773481	0.500000	0.816062

Phase separation behavior prediction

FH-VSP model: wt frac = 0.919

Table C-1 (cont'd.).
Toluene-Polystyrene at 60 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 4.8456
Flory-Huggins chi parameter: 0.2938
FH-VSP inf diln parameters: wt frac act coeff 4.6321 enth coeff 1.5868
ASOG-VSP inf diln parameters: wt frac act coeff 4.8393 enth coeff 1.0052

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.102	3.755	3.792	1.0	3.777	0.6	3.750	-0.1	3.791	1.0
0.179	3.218	3.213	-0.2	3.220	0.1	3.227	0.3	3.213	-0.1
0.261	2.778	2.734	-1.6	2.750	-1.0	2.773	-0.2	2.735	-1.5
Standard pct err			1.3		0.8		0.4		1.3

Analysis of model error randomness

Sum sqr rank difference test: mean = 4.00 sd = 1.41

Test statistic	2	2	5	2
Normal (Z)	-1.414	-1.414	0.707	-1.414
Reject level	0.921358	0.921358	0.760243	0.921358

Sum abs rank difference test: mean = 2.67 sd = 0.47

Test statistic	2	2	3	2
Normal (Z)	-1.414	-1.414	0.707	-1.414
Reject level	0.921358	0.921358	0.760243	0.921358

Table C-1 (cont'd.).

Toluene-Polystyrene at 80 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 5.1655
Flory-Huggins chi parameter: 0.3195
FH-VSP inf diln parameters: wt frac act coeff 4.7192 enth coeff 1.5798
ASOG-VSP inf diln parameters: wt frac act coeff 5.1523 enth coeff 1.0045

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.246	2.870	2.884	0.5	2.880	0.3	2.870	-0.0	2.884	0.5
0.458	1.996	1.975	-1.0	1.984	-0.6	1.997	0.1	1.976	-1.0
0.671	1.466	1.454	-0.8	1.459	-0.5	1.465	-0.1	1.455	-0.8
Standard pct err			1.0		0.6		0.1		1.0

Analysis of model error randomness

Sum sqr rank difference test: mean = 4.00 sd = 1.41

Test statistic	5	5	5	5
Normal (Z)	0.707	0.707	0.707	0.707
Reject level	0.760243	0.760243	0.760243	0.760243

Sum abs rank difference test: mean = 2.67 sd = 0.47

Test statistic	3	3	3	3
Normal (Z)	0.707	0.707	0.707	0.707
Reject level	0.760243	0.760243	0.760243	0.760243

Table C-1 (cont'd.).

Methyl ethyl ketone-Polystyrene at 25 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 8.9345
Flory-Huggins chi parameter: 0.7101
FH-VSP inf diln parameters: wt frac act coeff 8.2319 enth coeff 1.6469
ASOG-VSP inf diln parameters: wt frac act coeff 7.7699 enth coeff 1.8783

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.091	5.681	5.774	1.6	5.515	-3.0	5.674	-0.1	5.575	-1.9
0.215	3.758	3.730	-0.8	3.817	1.6	3.777	0.5	3.805	1.2
0.279	3.161	3.116	-1.4	3.230	2.2	3.169	0.2	3.208	1.5
0.298	3.040	2.968	-2.4	3.082	1.4	3.019	-0.7	3.059	0.6
Standard pct err			1.9		2.4		0.6		1.6

Analysis of model error randomness

Sum sqr rank difference test: mean = 10.00 sd = 3.74

Test statistic	3	9	9	9
Normal (Z)	-1.871	-0.267	-0.267	-0.267
Reject level	0.969310	0.605367	0.605367	0.605367

Sum abs rank difference test: mean = 5.00 sd = 1.00

Test statistic	3	5	5	5
Normal (Z)	-2.000	0.000	0.000	0.000
Reject level	0.977241	0.500000	0.500000	0.500000

Phase separation behavior prediction

Flory-Huggins model: wt frac = 0.636

Table C-1 (cont'd.).

Benzene-Polyisobutylene at 25 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 8.7866
Flory-Huggins chi parameter: 0.9213
FH-VSP inf diln parameters: wt frac act coeff 8.1759 enth coeff 1.7336
ASOG-VSP inf diln parameters: wt frac act coeff 7.3466 enth coeff 1.7073

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.044	6.842	7.039	2.8	6.291	-8.4	6.809	-0.5	6.397	-6.7
0.063	6.409	6.435	0.4	5.942	-7.6	6.305	-1.6	6.023	-6.2
0.095	5.468	5.637	3.1	5.437	-0.6	5.612	2.6	5.486	0.3
0.150	4.608	4.575	-0.7	4.665	1.2	4.636	0.6	4.678	1.5
0.152	4.636	4.552	-1.8	4.647	0.2	4.615	-0.5	4.659	0.5
0.184	4.127	4.083	-1.1	4.262	3.2	4.164	0.9	4.262	3.2
0.245	3.484	3.401	-2.4	3.647	4.6	3.489	0.1	3.634	4.2
0.254	3.452	3.323	-3.8	3.572	3.4	3.410	-1.2	3.558	3.0
0.297	3.070	2.966	-3.5	3.217	4.7	3.045	-0.8	3.199	4.1
0.321	2.873	2.795	-2.7	3.040	5.7	2.869	-0.1	3.021	5.0
0.373	2.541	2.483	-2.3	2.704	6.2	2.545	0.2	2.685	5.5
Standard pct err			2.6		5.2		1.2		4.4

Analysis of model error randomness

Sum sqr rank difference test: mean = 220.00 sd = 61.55

Test statistic	43	22	202	38
Normal (Z)	-2.876	-3.217	-0.292	-2.957
Reject level	0.997978	0.999349	0.615025	0.998441

Sum abs rank difference test: mean = 40.00 sd = 6.66

Test statistic	19	14	38	18
Normal (Z)	-3.152	-3.902	-0.300	-3.302
Reject level	0.999184	0.999952	0.617967	0.999517

Phase separation behavior prediction

Flory-Huggins model: wt frac = 0.531
FH-VSP model: wt frac = 0.852

Table C-1 (cont'd.).

Benzene-Polyisobutylene at 10 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 10.6574
Flory-Huggins chi parameter: 0.8446
FH-VSP inf diln parameters: wt frac act coeff 7.9552 enth coeff 1.9196
ASOG-VSP inf diln parameters: wt frac act coeff 6.7035 enth coeff 1.8245

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.225	3.721	3.772	1.3	3.646	-2.0	3.727	0.1	3.661	-1.6
0.357	2.691	2.632	-2.2	2.714	0.9	2.674	-0.6	2.711	0.8
0.454	2.159	2.130	-1.4	2.224	3.0	2.170	0.5	2.218	2.7
Standard pct err			2.1		2.6		0.8		2.3

Analysis of model error randomness

Sum sqr rank difference test: mean = 4.00 sd = 1.41

Test statistic	5	2	5	2
Normal (Z)	0.707	-1.414	0.707	-1.414
Reject level	0.760243	0.921358	0.760243	0.921358

Sum abs rank difference test: mean = 2.67 sd = 0.47

Test statistic	3	2	3	2
Normal (Z)	0.707	-1.414	0.707	-1.414
Reject level	0.760243	0.921358	0.760243	0.921358

Phase separation behavior prediction

Flory-Huggins model: wt frac = 0.584
FH-VSP model: wt frac = 0.683

Table C-1 (cont'd.).

Cyclohexane-Polyisobutylene at 25 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 4.9719
Flory-Huggins chi parameter: 0.3891
FH-VSP inf diln parameters: wt frac act coeff 4.8958 enth coeff 1.2541
ASOG-VSP inf diln parameters: wt frac act coeff 4.9417 enth coeff 1.0595

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.128	3.609	3.636	0.8	3.597	-0.3	3.624	0.4	3.632	0.6
0.165	3.350	3.352	0.1	3.336	-0.4	3.347	-0.1	3.350	0.0
0.188	3.242	3.193	-1.5	3.187	-1.7	3.192	-1.6	3.192	-1.5
0.235	2.953	2.905	-1.7	2.914	-1.3	2.908	-1.5	2.906	-1.6
0.281	2.523	2.660	5.3	2.678	5.9	2.666	5.5	2.662	5.4
0.303	2.589	2.553	-1.4	2.573	-0.6	2.560	-1.1	2.556	-1.3
0.400	2.187	2.154	-1.5	2.176	-0.5	2.160	-1.2	2.156	-1.4
0.569	1.688	1.667	-1.3	1.681	-0.4	1.671	-1.0	1.668	-1.2
Standard pct err		2.4		2.4		2.6		2.4	

Analysis of model error randomness

Sum sqr rank difference test: mean = 84.00 sd = 26.61

Test statistic	88	87	84	88
Normal (Z)	0.150	0.113	0.000	0.150
Reject level	0.559757	0.544895	0.500000	0.559757

Sum abs rank difference test: mean = 21.00 sd = 3.87

Test statistic	20	21	20	20
Normal (Z)	-0.258	0.000	-0.258	-0.258
Reject level	0.601875	0.500000	0.601875	0.601875

Table C-1 (cont'd.).

N-pentane-Polyisobutylene at 25 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 8.7630
Flory-Huggins chi parameter: 0.6795
FH-VSP inf diln parameters: wt frac act coeff 8.3268 enth coeff 1.6386
ASOG-VSP inf diln parameters: wt frac act coeff 8.7630 enth coeff 1.0000

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.029	7.423	7.556	1.8	7.087	-4.6	7.336	-1.2	7.556	1.8
0.073	6.057	6.161	1.7	6.030	-0.5	6.120	1.0	6.161	1.7
0.133	4.849	4.863	0.3	4.933	1.7	4.917	1.4	4.863	0.3
0.185	4.153	4.069	-2.1	4.200	1.1	4.145	-0.2	4.069	-2.1
0.212	3.820	3.744	-2.0	3.886	1.7	3.822	0.1	3.744	-2.0
0.267	3.303	3.208	-2.9	3.349	1.4	3.280	-0.7	3.208	-2.9
0.322	2.872	2.786	-3.1	2.910	1.3	2.846	-0.9	2.786	-3.1
0.328	2.808	2.750	-2.1	2.872	2.3	2.809	0.0	2.750	-2.1
0.584	1.694	1.680	-0.8	1.718	1.4	1.696	0.1	1.680	-0.8
Standard pct err			2.2		2.2		0.9		2.2

Analysis of model error randomness

Sum sqr rank difference test: mean = 120.00 sd = 36.37

Test statistic	35	117	102	35
Normal (Z)	-2.337	-0.082	-0.495	-2.337
Reject level	0.990267	0.532877	0.689643	0.990267

Sum abs rank difference test: mean = 26.67 sd = 4.75

Test statistic	15	27	24	15
Normal (Z)	-2.457	0.070	-0.561	-2.457
Reject level	0.992975	0.527987	0.712757	0.992975

Phase separation behavior prediction

Flory-Huggins model: wt frac = 0.654

Table C-1 (cont'd.).

Triisopropylbenzene-Polystyrene at 165 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 12.3352
Flory-Huggins chi parameter: 1.0003
FH-VSP inf diln parameters: wt frac act coeff 12.2476 enth coeff 1.2180
ASOG-VSP inf diln parameters: wt frac act coeff 12.0454 enth coeff 1.0724

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.030	9.936	9.875	-0.6	9.377	-5.8	9.853	-0.8	9.793	-1.4
0.066	7.625	7.864	3.1	7.995	4.7	7.873	3.2	7.893	3.5
0.086	7.191	7.004	-2.6	7.324	1.8	7.018	-2.4	7.062	-1.8
Standard pct err			2.9		5.4		4.1		2.9

Analysis of model error randomness

Sum sqr rank difference test: mean = 4.00 sd = 1.41

Test statistic	5	5	5	5
Normal (Z)	0.707	0.707	0.707	0.707
Reject level	0.760243	0.760243	0.760243	0.760243

Sum abs rank difference test: mean = 2.67 sd = 0.47

Test statistic	3	3	3	3
Normal (Z)	0.707	0.707	0.707	0.707
Reject level	0.760243	0.760243	0.760243	0.760243

Phase separation behavior prediction

Flory-Huggins model: wt frac = 0.406

Table C-1 (cont'd.).

Triisopropylbenzene-Polystyrene at 175 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 10.6137
Flory-Huggins chi parameter: 0.9154
FH-VSP inf diln parameters: wt frac act coeff 9.8435 enth coeff 2.6559
ASOG-VSP inf diln parameters: wt frac act coeff 10.5095 enth coeff 1.0559

Wt Frac Solvent	Activity Coefficients and Percent Error							
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.020	9.971	9.296	-7.0	9.043	-9.8	9.014	-10.1	9.261	-7.4
0.038	7.039	8.366	17.3	8.375	17.4	8.373	17.3	8.369	17.3
0.066	8.041	7.178	-11.4	7.445	-7.7	7.474	-7.3	7.215	-10.8
Standard pct err		15.4		15.1		21.4		15.4	

Analysis of model error randomness

Sum sqr rank difference test: mean = 4.00 sd = 1.41

Test statistic	5	5	5	5
Normal (Z)	0.707	0.707	0.707	0.707
Reject level	0.760243	0.760243	0.760243	0.760243

Sum abs rank difference test: mean = 2.67 sd = 0.47

Test statistic	3	3	3	3
Normal (Z)	0.707	0.707	0.707	0.707
Reject level	0.760243	0.760243	0.760243	0.760243

Phase separation behavior prediction

Flory-Huggins model: wt frac = 0.452
FH-VSP model: wt frac = 0.435

Table C-1 (cont'd.).

Carbon disulfide-Polystyrene at 115 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 3.7286
Flory-Huggins chi parameter: 0.4079
FH-VSP inf diln parameters: wt frac act coeff 3.7286 enth coeff 1.0000
ASOG-VSP inf diln parameters: wt frac act coeff 3.7048 enth coeff 3.6140

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.014	3.655	3.637	-0.5	3.629	-0.7	3.637	-0.5	3.626	-0.8
0.024	3.566	3.574	0.2	3.573	0.2	3.574	0.2	3.572	0.2
0.041	3.465	3.476	0.3	3.484	0.6	3.476	0.3	3.487	0.6
Standard pct err			0.5		0.7		0.6		0.7

Analysis of model error randomness

Sum sqr rank difference test: mean = 4.00 sd = 1.41

Test statistic	2	2	2	2
Normal (Z)	-1.414	-1.414	-1.414	-1.414
Reject level	0.921358	0.921358	0.921358	0.921358

Sum abs rank difference test: mean = 2.67 sd = 0.47

Test statistic	2	2	2	2
Normal (Z)	-1.414	-1.414	-1.414	-1.414
Reject level	0.921358	0.921358	0.921358	0.921358

Table C-1 (cont'd.).

Carbon disulfide-Polystyrene at 140 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 3.4823
Flory-Huggins chi parameter: 0.3394
FH-VSP inf diln parameters: wt frac act coeff 3.4823 enth coeff 1.0000
ASOG-VSP inf diln parameters: wt frac act coeff 3.4761 enth coeff 4.1537

Wt Frac Solvent	Activity Coefficients and Percent Error							
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.008	3.885	3.438	-12.2	3.433	-12.4	3.438	-12.2	3.432	-12.4
0.011	3.831	3.423	-11.3	3.418	-11.4	3.423	-11.3	3.417	-11.4
0.018	2.995	3.384	12.2	3.383	12.2	3.384	12.2	3.379	12.1
0.029	2.948	3.329	12.2	3.332	12.2	3.329	12.2	3.324	12.0
Standard pct err			13.8		13.9		16.9		13.8

Analysis of model error randomness

Sum sqr rank difference test: mean = 10.00 sd = 3.74

Test statistic	6	3	6	6
Normal (Z)	-1.069	-1.871	-1.069	-1.069
Reject level	0.857484	0.969310	0.857484	0.857484

Sum abs rank difference test: mean = 5.00 sd = 1.00

Test statistic	4	3	4	4
Normal (Z)	-1.000	-2.000	-1.000	-1.000
Reject level	0.841351	0.977241	0.841351	0.841351

Table C-1 (cont'd.).

Methanol-Polymethyl methacrylate at 120 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 16.6476
Flory-Huggins chi parameter: 1.2827
FH-VSP inf diln parameters: wt frac act coeff 16.3347 enth coeff 2.7097
ASOG-VSP inf diln parameters: wt frac act coeff 16.2298 enth coeff 2.9717

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.003	16.070	16.148	0.5	15.924	-0.9	15.989	-0.5	15.934	-0.9
0.006	15.397	15.555	1.0	15.572	1.1	15.568	1.1	15.571	1.1
0.009	15.303	15.063	-1.6	15.271	-0.2	15.211	-0.6	15.262	-0.3
Standard pct err			1.4		1.0		1.4		1.0

Analysis of model error randomness

Sum sqr rank difference test: mean = 4.00 sd = 1.41

Test statistic	5	5	5	5
Normal (Z)	0.707	0.707	0.707	0.707
Reject level	0.760243	0.760243	0.760243	0.760243

Sum abs rank difference test: mean = 2.67 sd = 0.47

Test statistic	3	3	3	3
Normal (Z)	0.707	0.707	0.707	0.707
Reject level	0.760243	0.760243	0.760243	0.760243

Phase separation behavior prediction

Flory-Huggins model: wt frac = 0.279
FH-VSP model: wt frac = 0.312

Table C-1 (cont'd.).

Methanol-Polymethyl methacrylate at 130 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 12.7268
Flory-Huggins chi parameter: 1.0138
FH-VSP inf diln parameters: wt frac act coeff 10.7857 enth coeff 0.1860
ASOG-VSP inf diln parameters: wt frac act coeff 12.5597 enth coeff 2.8431

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.003	11.601	12.442	7.0	12.366	6.4	11.581	-0.2	12.365	6.4
0.006	12.217	12.135	-0.7	12.152	-0.5	12.274	0.5	12.152	-0.5
0.008	12.724	11.902	-6.7	11.987	-6.0	12.686	-0.3	11.988	-6.0
Standard pct err			6.9		6.2		0.6		6.2

Analysis of model error randomness

Sum sqr rank difference test: mean = 4.00 sd = 1.41

Test statistic	2	2	5	2
Normal (Z)	-1.414	-1.414	0.707	-1.414
Reject level	0.921358	0.921358	0.760243	0.921358

Sum abs rank difference test: mean = 2.67 sd = 0.47

Test statistic	2	2	3	2
Normal (Z)	-1.414	-1.414	0.707	-1.414
Reject level	0.921358	0.921358	0.760243	0.921358

Phase separation behavior prediction

Flory-Huggins model: wt frac = 0.367

Table C-1 (cont'd.).

Toluene-Polymethyl methacrylate at 130 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 9.6790
Flory-Huggins chi parameter: 0.7953
FH-VSP inf diln parameters: wt frac act coeff 9.6790 **enth coeff** 1.0000
ASOG-VSP inf diln parameters: wt frac act coeff 9.6920 **enth coeff** 0.9658

Wt Frac Solvent	Activity Coefficients and Percent Error							
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.017	10.638	8.772	-19.3	8.224	-25.7	8.772	-19.3	8.779	-19.2
0.060	5.823	6.980	18.1	6.921	17.3	6.980	18.1	6.985	18.2
0.112	4.955	5.517	10.7	5.706	14.1	5.517	10.7	5.526	10.9
Standard pct err		20.2		24.1		28.6		20.2	

Analysis of model error randomness

Sum sqr rank difference test: mean = 4.00 **sd =** 1.41

Test statistic	5	5	5	5
Normal (Z)	0.707	0.707	0.707	0.707
Reject level	0.760243	0.760243	0.760243	0.760243

Sum abs rank difference test: mean = 2.67 **sd =** 0.47

Test statistic	3	3	3	3
Normal (Z)	0.707	0.707	0.707	0.707
Reject level	0.760243	0.760243	0.760243	0.760243

Phase separation behavior prediction

Flory-Huggins model: wt frac = 0.536

Table C-1 (cont'd.).

Toluene-Polymethyl methacrylate at 160 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 10.9509
Flory-Huggins chi parameter: 0.9547
FH-VSP inf diln parameters: wt frac act coeff 10.9509 enth coeff 1.0000
ASOG-VSP inf diln parameters: wt frac act coeff 11.0656 enth coeff 0.9014

Wt Frac Solvent	Activity Coefficients and Percent Error							
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.006	12.699	10.514	-18.9	10.174	-22.2	10.514	-18.9	10.590	-18.2
0.014	9.936	9.951	0.2	9.791	-1.5	9.951	0.2	9.982	0.5
0.023	9.345	9.413	0.7	9.409	0.7	9.413	0.7	9.408	0.7
0.025	8.462	9.261	9.0	9.299	9.4	9.261	9.0	9.247	8.9
0.037	7.563	8.624	13.1	8.822	15.4	8.624	13.1	8.576	12.6
Standard pct err			12.4		14.3		14.3		11.9

Analysis of model error randomness

Sum sqr rank difference test: mean = 20.00 sd = 7.28

Test statistic	4	4	4	4
Normal (Z)	-2.198	-2.198	-2.198	-2.198
Reject level	0.986006	0.986006	0.986006	0.986006

Sum abs rank difference test: mean = 8.00 sd = 1.61

Test statistic	4	4	4	4
Normal (Z)	-2.481	-2.481	-2.481	-2.481
Reject level	0.993433	0.993433	0.993433	0.993433

Phase separation behavior prediction

Flory-Huggins model: wt frac = 0.426

Table C-1 (cont'd.).

Toluene-Polyvinyl acetate at 35 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 9.7100
Flory-Huggins chi parameter: 0.7772
FH-VSP inf diln parameters: wt frac act coeff 8.4101 enth coeff 2.0621
ASOG-VSP inf diln parameters: wt frac act coeff 8.2575 enth coeff 1.4046

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.084	6.081	6.240	2.6	6.038	-0.7	6.067	-0.2	6.039	-0.7
0.117	5.377	5.408	0.6	5.391	0.3	5.396	0.4	5.391	0.3
0.161	4.665	4.565	-2.2	4.676	0.2	4.663	-0.0	4.677	0.3
0.195	4.207	4.068	-3.4	4.224	0.4	4.202	-0.1	4.225	0.4
Standard pct err			2.8		0.5		0.3		0.5

Analysis of model error randomness

Sum sqr rank difference test: mean = 10.00 sd = 3.74

Test statistic	3	9	11	9
Normal (Z)	-1.871	-0.267	0.267	-0.267
Reject level	0.969310	0.605367	0.605367	0.605367

Sum abs rank difference test: mean = 5.00 sd = 1.00

Test statistic	3	5	5	5
Normal (Z)	-2.000	0.000	0.000	0.000
Reject level	0.977241	0.500000	0.500000	0.500000

Phase separation behavior prediction

Flory-Huggins model: wt frac = 0.564
FH-VSP model: wt frac = 0.598

Table C-1 (cont'd.).

Toluene-Polyvinyl acetate at 40 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 9.2644
Flory-Huggins chi parameter: 0.7733
FH-VSP inf diln parameters: wt frac act coeff 8.3495 enth coeff 2.0578
ASOG-VSP inf diln parameters: wt frac act coeff 8.2587 enth coeff 1.3804

Wt Frac Solvent	Activity Coefficients and Percent Error Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.051	6.831	7.057	3.3	6.777	-0.8	6.812	-0.3	6.782	-0.7
0.076	6.201	6.287	1.4	6.197	-0.1	6.211	0.2	6.199	-0.0
0.089	5.936	5.943	0.1	5.925	-0.2	5.930	-0.1	5.926	-0.2
0.094	5.732	5.826	1.6	5.830	1.7	5.833	1.7	5.831	1.7
0.128	5.289	5.081	-4.0	5.202	-1.7	5.189	-1.9	5.202	-1.7
0.139	5.055	4.871	-3.7	5.017	-0.8	5.000	-1.1	5.016	-0.8
0.171	4.444	4.346	-2.2	4.536	2.1	4.512	1.5	4.535	2.0
Standard pct err			2.9		1.4		1.4		1.4

Analysis of model error randomness

Sum sqr rank difference test: mean = 56.00 sd = 18.58

Test statistic	36	59	67	60
Normal (Z)	-1.076	0.161	0.592	0.215
Reject level	0.859100	0.564134	0.723042	0.585218

Sum abs rank difference test: mean = 16.00 sd = 3.06

Test statistic	12	17	17	16
Normal (Z)	-1.309	0.327	0.327	0.000
Reject level	0.904794	0.628285	0.628285	0.500000

Phase separation behavior prediction

Flory-Huggins model: wt frac = 0.567
FH-VSP model: wt frac = 0.602

Table C-1 (cont'd.).

Toluene-Polyvinyl acetate at 47.5 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 8.8654
Flory-Huggins chi parameter: 0.7609
FH-VSP inf diln parameters: wt frac act coeff 7.6321 enth coeff 3.0918
ASOG-VSP inf diln parameters: wt frac act coeff 8.1821 enth coeff 1.3458

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.052	6.506	6.815	4.6	6.704	3.0	6.587	1.2	6.704	3.0
0.071	6.370	6.257	-1.8	6.262	-1.7	6.248	-1.9	6.258	-1.8
0.107	5.613	5.380	-4.2	5.522	-1.6	5.653	0.7	5.516	-1.7
Standard pct err			4.6		2.7		2.4		2.7

Analysis of model error randomness

Sum sqr rank difference test: mean = 4.00 sd = 1.41

Test statistic	2	5	5	5
Normal (Z)	-1.414	0.707	0.707	0.707
Reject level	0.921358	0.760243	0.760243	0.760243

Sum abs rank difference test: mean = 2.67 sd = 0.47

Test statistic	2	3	3	3
Normal (Z)	-1.414	0.707	0.707	0.707
Reject level	0.921358	0.760243	0.760243	0.760243

Phase separation behavior prediction

Flory-Huggins model: wt frac = 0.577
FH-VSP model: wt frac = 0.467

Table C-1 (cont'd.).

Chloroform-Polyvinyl acetate at 35 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 1.4938
Flory-Huggins chi parameter: -0.4168
FH-VSP inf diln parameters: wt frac act coeff 1.4938 enth coeff 1.0000
ASOG-VSP inf diln parameters: wt frac act coeff 1.6218 enth coeff 0.4051

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.163	1.587	1.464	-8.1	1.450	-9.1	1.464	-8.1	1.501	-5.6
0.231	1.421	1.447	1.8	1.443	1.6	1.447	1.8	1.462	2.8
0.276	1.407	1.435	1.9	1.436	2.1	1.435	1.9	1.438	2.2
0.327	1.376	1.419	3.1	1.426	3.6	1.419	3.1	1.413	2.7
0.381	1.364	1.401	2.6	1.412	3.4	1.401	2.6	1.388	1.7
0.416	1.368	1.388	1.4	1.400	2.3	1.388	1.4	1.372	0.2
0.464	1.373	1.368	-0.3	1.383	0.7	1.368	-0.3	1.349	-1.7
Standard pct err			3.9		4.5		4.3		3.1

Analysis of model error randomness

Sum sqr rank difference test: mean = 56.00 sd = 18.58

Test statistic	25	25	25	47
Normal (Z)	-1.668	-1.668	-1.668	-0.484
Reject level	0.952360	0.952360	0.952360	0.685906

Sum abs rank difference test: mean = 16.00 sd = 3.06

Test statistic	11	11	11	13
Normal (Z)	-1.637	-1.637	-1.637	-0.982
Reject level	0.949147	0.949147	0.949147	0.836951

Table C-1 (cont'd.).

Chloroform-Polyvinyl acetate at 45 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 1.4417
Flory-Huggins chi parameter: -0.4604
FH-VSP inf diln parameters: wt frac act coeff 1.4048 enth coeff 0.6656
ASOG-VSP inf diln parameters: wt frac act coeff 1.4801 enth coeff 0.4490

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.093	1.478	1.432	-3.2	1.407	-4.9	1.412	-4.6	1.448	-2.1
0.121	1.408	1.428	1.4	1.409	0.0	1.413	0.3	1.439	2.1
0.139	1.405	1.425	1.5	1.410	0.4	1.413	0.6	1.433	2.0
0.164	1.416	1.421	0.4	1.411	-0.4	1.413	-0.2	1.425	0.6
0.198	1.366	1.416	3.6	1.411	3.2	1.412	3.3	1.415	3.5
0.206	1.452	1.414	-2.7	1.411	-2.9	1.411	-2.9	1.412	-2.8
0.227	1.400	1.410	0.8	1.410	0.7	1.410	0.7	1.406	0.4
0.247	1.380	1.406	1.9	1.409	2.1	1.408	2.0	1.400	1.4
0.276	1.382	1.400	1.3	1.406	1.7	1.405	1.6	1.391	0.6
0.295	1.380	1.396	1.1	1.404	1.8	1.402	1.6	1.385	0.4
0.325	1.365	1.388	1.7	1.400	2.5	1.397	2.3	1.376	0.8
0.355	1.351	1.380	2.2	1.395	3.2	1.392	3.0	1.367	1.2
0.427	1.389	1.358	-2.2	1.378	-0.8	1.374	-1.1	1.343	-3.3
0.461	1.378	1.347	-2.3	1.367	-0.8	1.363	-1.1	1.332	-3.4
0.478	1.395	1.341	-3.9	1.362	-2.4	1.357	-2.7	1.325	-5.1
0.499	1.416	1.332	-6.1	1.354	-4.5	1.349	-4.8	1.318	-7.2
Standard pct err		2.7		2.6		2.6		3.0	

Analysis of model error randomness

Sum sqr rank difference test: mean = 680.00 sd = 161.90

Test statistic	496	481	475	393
Normal (Z)	-1.137	-1.229	-1.266	-1.773
Reject level	0.872136	0.890503	0.897291	0.961857

Sum abs rank difference test: mean = 85.00 sd = 12.28

Test statistic	70	63	63	61
Normal (Z)	-1.222	-1.792	-1.792	-1.955
Reject level	0.889111	0.963423	0.963423	0.974690

Table C-1 (cont'd.).

Benzene-Polyethylene oxide at 70 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 4.9056
Flory-Huggins chi parameter: 0.2870
FH-VSP inf diln parameters: wt frac act coeff 4.9056 enth coeff 1.0000
ASOG-VSP inf diln parameters: wt frac act coeff 4.6698 enth coeff 1.1931

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.062	4.312	4.204	-2.5	4.177	-3.2	4.204	-2.5	4.118	-4.6
0.067	4.231	4.149	-2.0	4.125	-2.5	4.149	-2.0	4.073	-3.8
0.099	3.810	3.850	1.1	3.840	0.8	3.850	1.1	3.823	0.4
0.139	3.474	3.523	1.4	3.526	1.5	3.523	1.4	3.541	1.9
0.193	3.093	3.144	1.6	3.156	2.0	3.144	1.6	3.198	3.4
0.261	2.690	2.747	2.1	2.764	2.7	2.747	2.1	2.824	4.9
0.388	2.153	2.192	1.8	2.208	2.5	2.192	1.8	2.269	5.3
Standard pct err			2.0		2.5		2.2		4.1

Analysis of model error randomness

Sum sqr rank difference test: mean = 56.00 sd = 18.58

Test statistic	9	9	9	6
Normal (Z)	-2.529	-2.529	-2.529	-2.691
Reject level	0.994274	0.994274	0.994274	0.996426

Sum abs rank difference test: mean = 16.00 sd = 3.06

Test statistic	7	7	7	6
Normal (Z)	-2.946	-2.946	-2.946	-3.273
Reject level	0.998385	0.998385	0.998385	0.999466

Table C-1 (cont'd.).

Benzene-Polyethylene oxide at 70 C (second run)

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 4.5994
Flory-Huggins chi parameter: 0.2298
FH-VSP inf diln parameters: wt frac act coeff 4.5553 **enth coeff** 1.2775
ASOG-VSP inf diln parameters: wt frac act coeff 4.4055 **enth coeff** 1.1931

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.050	4.103	4.096	-0.2	4.080	-0.6	4.078	-0.6	4.007	-2.4
0.089	3.743	3.759	0.4	3.754	0.3	3.753	0.3	3.727	-0.4
0.142	3.344	3.364	0.6	3.368	0.7	3.369	0.8	3.385	1.2
0.201	2.996	2.998	0.1	3.008	0.4	3.009	0.5	3.052	1.9
0.265	2.702	2.661	-1.5	2.673	-1.1	2.675	-1.0	2.733	1.1
Standard pct err		0.8		0.8		0.9		1.7	

Analysis of model error randomness

Sum sqr rank difference test: mean = 20.00 sd = 7.28

Test statistic	13	15	15	10
Normal (Z)	-0.962	-0.687	-0.687	-1.374
Reject level	0.831861	0.753889	0.753889	0.915226

Sum abs rank difference test: mean = 8.00 sd = 1.61

Test statistic	7	7	7	6
Normal (Z)	-0.620	-0.620	-0.620	-1.240
Reject level	0.732418	0.732418	0.732418	0.892587

Table C-1 (cont'd.).

Benzene-Polyethylene oxide at 75.1 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 4.5056
Flory-Huggins chi parameter: 0.2106
FH-VSP inf diln parameters: wt frac act coeff 4.4221 enth coeff 1.4920
ASOG-VSP inf diln parameters: wt frac act coeff 4.3698 enth coeff 1.1635

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.053	3.984	4.004	0.5	3.996	0.3	3.977	-0.2	3.959	-0.6
0.081	3.755	3.766	0.3	3.765	0.3	3.761	0.2	3.756	0.0
0.108	3.561	3.557	-0.1	3.560	-0.0	3.567	0.2	3.574	0.4
0.145	3.332	3.300	-0.9	3.308	-0.7	3.326	-0.2	3.344	0.4
Standard pct err			0.6		0.5		0.2		0.5

Analysis of model error randomness

Sum sqr rank difference test: mean = 10.00 sd = 3.74

Test statistic	3	3	11	6
Normal (Z)	-1.871	-1.871	0.267	-1.069
Reject level	0.969310	0.969310	0.605367	0.857484

Sum abs rank difference test: mean = 5.00 sd = 1.00

Test statistic	3	3	5	4
Normal (Z)	-2.000	-2.000	0.000	-1.000
Reject level	0.977241	0.977241	0.500000	0.841351

Table C-1 (cont'd.).

Benzene-Polyethylene oxide at 88.1 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 4.4720
Flory-Huggins chi parameter: 0.2049
FH-VSP inf diln parameters: wt frac act coeff 4.4720 enth coeff 1.0000
ASOG-VSP inf diln parameters: wt frac act coeff 4.3992 enth coeff 1.0940

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.027	4.234	4.209	-0.6	4.202	-0.7	4.209	-0.6	4.175	-1.4
0.050	3.986	3.999	0.3	3.998	0.3	3.999	0.3	3.994	0.2
0.067	3.850	3.859	0.2	3.861	0.3	3.859	0.2	3.870	0.5
0.091	3.667	3.670	0.1	3.676	0.2	3.670	0.1	3.701	0.9
Standard pct err			0.4		0.5		0.5		1.0

Analysis of model error randomness

Sum sqr rank difference test: mean = 10.00 **sd =** 3.74

Test statistic	11	11	11	3
Normal (Z)	0.267	0.267	0.267	-1.871
Reject level	0.605367	0.605367	0.605367	0.969310

Sum abs rank difference test: mean = 5.00 **sd =** 1.00

Test statistic	5	5	5	3
Normal (Z)	0.000	0.000	0.000	-2.000
Reject level	0.500000	0.500000	0.500000	0.977241

Table C-1 (cont'd.).

Benzene-Polyethylene oxide at 102 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 4.4430
Flory-Huggins chi parameter: 0.2020
FH-VSP inf diln parameters: wt frac act coeff 4.4430 enth coeff 1.0000
ASOG-VSP inf diln parameters: wt frac act coeff 4.3920 enth coeff 1.0280

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.021	4.303	4.241	-1.5	4.233	-1.6	4.241	-1.5	4.214	-2.1
0.022	4.280	4.230	-1.2	4.222	-1.4	4.230	-1.2	4.205	-1.8
0.025	4.272	4.201	-1.7	4.194	-1.8	4.201	-1.7	4.179	-2.2
0.029	4.225	4.163	-1.5	4.157	-1.6	4.163	-1.5	4.145	-1.9
0.037	4.148	4.093	-1.3	4.089	-1.4	4.093	-1.3	4.083	-1.6
0.044	4.070	4.029	-1.0	4.026	-1.1	4.029	-1.0	4.026	-1.1
0.048	4.042	3.998	-1.1	3.996	-1.1	3.998	-1.1	3.998	-1.1
0.058	3.950	3.908	-1.1	3.909	-1.0	3.908	-1.1	3.917	-0.8
0.077	3.713	3.757	1.2	3.760	1.3	3.757	1.2	3.779	1.8
0.092	3.520	3.643	3.4	3.649	3.6	3.643	3.4	3.675	4.3
0.118	3.169	3.455	8.6	3.463	8.9	3.455	8.6	3.500	9.9
Standard pct err			3.2		3.3		3.4		3.8

Analysis of model error randomness

Sum sqr rank difference test: mean = 220.00 sd = 61.55

Test statistic	52	47	52	33
Normal (Z)	-2.729	-2.811	-2.729	-3.038
Reject level	0.996821	0.997522	0.996821	0.998805

Sum abs rank difference test: mean = 40.00 sd = 6.66

Test statistic	20	19	20	17
Normal (Z)	-3.002	-3.152	-3.002	-3.452
Reject level	0.998652	0.999184	0.998652	0.999720

Table C-1 (cont'd.).

Benzene-Polyethylene oxide at 125.4 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 4.3079
Flory-Huggins chi parameter: 0.1700
FH-VSP inf diln parameters: wt frac act coeff 4.3079 enth coeff 1.0000
ASOG-VSP inf diln parameters: wt frac act coeff 4.2956 enth coeff 0.9330

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.011	4.249	4.207	-1.0	4.206	-1.0	4.207	-1.0	4.202	-1.1
0.018	4.141	4.147	0.1	4.146	0.1	4.147	0.1	4.145	0.1
0.024	4.080	4.093	0.3	4.093	0.3	4.093	0.3	4.094	0.3
0.033	3.993	4.017	0.6	4.018	0.6	4.017	0.6	4.023	0.8
Standard pct err			0.7		0.7		0.8		0.8

Analysis of model error randomness

Sum sqr rank difference test: mean = 10.00 sd = 3.74

Test statistic	3	3	3	3
Normal (Z)	-1.871	-1.871	-1.871	-1.871
Reject level	0.969310	0.969310	0.969310	0.969310

Sum abs rank difference test: mean = 5.00 sd = 1.00

Test statistic	3	3	3	3
Normal (Z)	-2.000	-2.000	-2.000	-2.000
Reject level	0.977241	0.977241	0.977241	0.977241

Table C-1 (cont'd.).

Benzene-Polyethylene oxide at 125.7 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 4.1940
Flory-Huggins chi parameter: 0.1434
FH-VSP inf diln parameters: wt frac act coeff 4.1940 enth coeff 1.0000
ASOG-VSP inf diln parameters: wt frac act coeff 4.1816 enth coeff 0.9319

Wt Frac Solvent	Activity Coefficients and Percent Error								
	Exptl	VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.011	4.155	4.098	-1.4	4.097	-1.4	4.098	-1.4	4.092	-1.5
0.017	4.073	4.046	-0.7	4.046	-0.7	4.046	-0.7	4.044	-0.7
0.025	3.945	3.985	1.0	3.986	1.0	3.985	1.0	3.987	1.1
0.033	3.874	3.918	1.1	3.919	1.2	3.918	1.1	3.924	1.3
Standard pct err			1.2		1.3		1.5		1.4

Analysis of model error randomness

Sum sqr rank difference test: mean = 10.00 **sd =** 3.74

Test statistic	3	3	3	3
Normal (Z)	-1.871	-1.871	-1.871	-1.871
Reject level	0.969310	0.969310	0.969310	0.969310

Sum abs rank difference test: mean = 5.00 **sd =** 1.00

Test statistic	3	3	3	3
Normal (Z)	-2.000	-2.000	-2.000	-2.000
Reject level	0.977241	0.977241	0.977241	0.977241

Table C-1 (cont'd.).

Benzene-Polyethylene oxide at 150.4 C

Results of least squares fit:

VSP inf diln wt frac activity coefficient: 4.2609
Flory-Huggins chi parameter: 0.1576
FH-VSP inf diln parameters: wt frac act coeff 4.2609 enth coeff 1.0000
ASOG-VSP inf diln parameters: wt frac act coeff 4.2603 enth coeff 0.8493

Wt Frac Solvent	Exptl	Activity Coefficients and Percent Error VSP		Flory-Huggins		FH-VSP		ASOG-VSP	
0.008	4.311	4.189	-2.9	4.188	-2.9	4.189	-2.9	4.189	-2.9
0.011	4.202	4.160	-1.0	4.159	-1.0	4.160	-1.0	4.160	-1.0
0.016	4.061	4.116	1.4	4.116	1.4	4.116	1.4	4.116	1.4
0.023	3.956	4.063	2.7	4.064	2.7	4.063	2.7	4.063	2.7
Standard pct err			2.5		2.5		3.0		2.5

Analysis of model error randomness

Sum sqr rank difference test: mean = 10.00 sd = 3.74

Test statistic	3	3	3	3
Normal (Z)	-1.871	-1.871	-1.871	-1.871
Reject level	0.969310	0.969310	0.969310	0.969310

Sum abs rank difference test: mean = 5.00 sd = 1.00

Test statistic	3	3	3	3
Normal (Z)	-2.000	-2.000	-2.000	-2.000
Reject level	0.977241	0.977241	0.977241	0.977241

APPENDIX D.

Program Used to Apply Thermodynamic Models Using Data Extrapolated from Low Solvent Concentrations.

The program listed below was used to generate the results in Appendix B from the original data in Appendix A. These results were presented in Chapter 2 of the dissertation. Input in the form of polymer-solvent activity data at a given temperature is processed to fit adjustable parameters if necessary and then the predictions of the VSP, Flory-Huggins, and UNIFAC-FV models are compared to experimental results. Refer to Appendices A and B for a more detailed description of the input data format and the output produced by the program.

The source code given below was written in IBM Pascal Version 2 for the IBM Personal Computer XT. Since Pascal, unlike many version of Fortran and Basic, has a fairly standardized language description, this code should run with few revisions under any Pascal compiler. One possible source of incompatibility is the use of string types, which are an IBM Pascal extension not part of standard Pascal. Most Pascal compilers support this or a similar extension (a type equivalent to array of char). The use of file names in the program statement may not work in other versions of Pascal, or may not work in the same way. In IBM Pascal, the user is prompted for file names at the time execution

begins.

To run this program, it should be compiled and linked. When execution begins, the user is prompted to name the four files: infile, outfile, display, and auxfile. Infile is the input to the program as described in Appendix A. Outfile is the program output as shown is Appendix B. Display is a file which receives prompt lines when input is expected from infile. Auxfile receives auxiliary output containing intermediate values of calculation, useful mostly for debugging purposes, but not well labeled or documented.

Allowing file specification gives the program flexibility to accept data either from an already created file or directly from user keyboard input, and to produce output either to the monitor screen, or to the printer, or to an external disk file for later review and use. To accept input data from a file, give the file name (including the drive designator and extension, e.g., A:MYFILE.DAT). To accept input data from the keyboard, type USER. (USER is the IBM DOS filename for keyboard input.) To produce output to a file, give the file name; to produce it at the monitor, type USER; to produce it at the line printer, type PRN: (the IBM DOS device designation for the printer).

If you have chosen to enter input from the keyboard, it is helpful to specify USER for the Display file. This will result in messages appearing on the monitor every time the program requires input. It is probably not a good idea to specify USER for the Outfile file in this

case, as the program output will intermix with the prompt messages at certain points of program execution.

If you have chosen to enter input from an external file, specify NUL for the Display file so that prompt messages are not displayed at the monitor.

Since the Auxfile output is not generally useful, specify NUL for this file also.

File specification is summarized here as Table D-1.

Table D-1. File Specification for Program Execution.

To use an external data file:	To enter data from keyboard:
INFILE: <your file name>	INFILE: user
OUTFILE: <see below>	OUTFILE: <see below>
DISPLAY: nul	DISPLAY: user
AUXFILE: nul	AUXFILE: nul

To send output to the monitor:

OUTFILE: user

To send output to the printer:

OUTFILE: prn:

To save output on an external file (can be printed or sent to monitor at a later time using the PRINT, TYPE, or COPY commands in DOS.)

OUTFILE: <your output file name>

There are some points in program execution where terminal input may be necessary even if Infile is taking input from an external file. This will occur if a new compound name (not previously used during any

execution of this program) is specified on line 2 or 3 of a data set. In this case, prompt messages will appear on the monitor for input to be entered from the keyboard (regardless of your choices for Infile and Display). The input will consist of the functional group description of the compound, its molecular weight, and, if any new functional groups are specified, UNIFAC interaction parameters must also be supplied as input.

The functional group and compound information is stored on a file named ASOGVSP.TAB. The format of this file is given as Table D-2.

Table D-2. Format of Functional Group and Compound Information File.

Line 1: N, the number of functional groups (limit of 20).

Lines 2 to N+1: Each line contains this information for one functional group. The UNIFAC surface area parameter, q_i, as a real value, followed by the UNIFAC segment volume parameter, r_i, as a real value, followed by a group name (maximum 6 characters).

Lines N+2 to 2N+1: Each line contains the UNIFAC interaction parameters, a_{ij}, for group i with each of the N groups j, in order, as real values.

Line 2N+2: M, the number of compounds (limit of 50).

Lines 2N+3 to 4N+2: Each two lines contain this information for one compound. The first contains K, the number of different groups in the compound as an integer, followed by the compound molecular weight as a real value, followed by the compound name (maximum 20 characters). The second contains 2K integers, which represent K pairs of group information. Each pair is the number of that particular group found in that compound followed by the position of the group in rows 2 to N+1 of this file. Position is given as an integer between 1 and N (not between 2 and N+1).

Dr. Eric A. Grulke of Michigan State University has a disk copy of this program and necessary files. Source code for the program is found on

file ASOGVSP.PAS, and the executable version of the program is found on file ASOGVSP.EXE. This file can be executed by typing its name at the DOS prompt, i.e., A:ASOGVSP (assuming the floppy drive is device A:).

Table D-3. Source Code for Program to Extrapolate Low Solvent Concentration Thermodynamic Data.

```
program asogvsp(infile,outfile,display,auxfile,input,output);
type
   setptr = ^dataset;
   dataset = record
      concen:real;
      activity:real;
      next:setptr
      end;
   modeltype = (asogvsp,flory,unifacfv,asog);
   nametype = string(20);
const
   e = 2.7182818;
const
   compoundtablesize = 50;
   grouptablesize = 20;
   solutiontablesize = 10;
var
   w1,omegalexp,omegalinf,conc,act,m1,m2,m2r,chi,densityratio:real;
   tempomega1,rho1,rho2,lastw1,moment0error:real;
   omega1,pctdiff,lastpctdiff,momentlerror:array[modeltype] of real;
   rpoly,qpoly,rsolv,qsolv:real;
   rk,qk:array[1..grouptablesize] of real;
   a:array[1..grouptablesize,1..grouptablesize] of real;
   tk:real;
   count,i,j,solvindex,polyindex:integer;
   numgroups:0..grouptablesize;
   numcompounds:0..compoundtablesize;
   endofdata,found:boolean;
   concunit,actunit,rhounit,ch:char;
   heading:string(80);
   compoundname:array[1..compoundtablesize] of nametype;
   compoundmw:array[1..compoundtablesize] of real;
   compoundgroups:array[1..compoundtablesize] of integer;
   groupsinit:array[1..compoundtablesize] of integer;
   mw:array[1..compoundtablesize] of real;
   numgroup,group:array[1..compoundtablesize,1..solutiontablesize]
                  of integer;
   groupname:array[1..grouptablesize] of string(7);
   ptr,firstset,lastset,nextset:setptr;
   model:modeltype;
   infile,outfile,display,auxfile,data:text;
```

Table D-3 (cont'd.).

```
procedure getactunits;
begin
   writeln(display,'      a for activity');
   writeln(display,'      w for wt frac activity coef');
   writeln(display,'      x for mol frac activity coef');
end;
procedure getconcunits;
begin
   writeln(display,'      w for weight fraction solvent');
   writeln(display,'      m for mass ratio solvent/polymer');
   writeln(display,'      x for mole fraction solvent');
end;
procedure getmolecwts;
begin
   write(display,'Enter MW of polymer, MW of solvent ');
   readln(infile,m2,m1)
end;
function convertconc(conc:real;concunit:char):real;
begin
   case concunit of
      'w': convertconc:=conc;
      'x': convertconc:=conc/(conc+(m2/m1)*(1.0-conc));
      'm': convertconc:=1.0-1.0/(1.0+conc)
   end
end;
function convertact(act:real;actunit:char):real;
begin
   case actunit of
      'w': convertact:=act;
      'a': convertact:=act/w1;
      'x': convertact:=act*conc/w1;
   end
end;
function convertrho(rho:real;rhounit:char;mw:real):real;
begin
   case rhounit of
      'd': convertrho:=rho;
      'v': convertrho:=1.0/rho;
      'm': convertrho:=mw/rho;
   end
end;
procedure getcompound(solvorpoly:nametype;var r,q:real;
                      var index:integer);
var
   name:nametype;
   i:integer;
   getnew:boolean;
```

Table D-3 (cont'd.).

```
procedure getsizeparams;
var
   name:string(7);
   k:integer;
procedure getgroupparams;
var
   i,same:integer;
begin
   same:=0;
   if k > 1
   then
      begin
      writeln(output,'Enter group interaction parameter a for ',
               groupname[k],' with the following groups');
      for i:=1 to k-1 do
         if same = 0
         then
            begin
            write(output,groupname[i],' ');
            readln(input,a[k,i]);
            if a[k,i] = 0
            then same:=i
            end;
      readln(input);
      if same = 0
      then
         begin
         writeln('Now enter group interaction parameter a for each of ',
                  'the following groups with ',groupname[k]);
         for i:=1 to k-1 do write(output,groupname[i]);
            begin
            write(output,groupname[i]);
            readln(input,a[i,k])
            end
         end
      else for i:=1 to k-1 do a[i,k]:=a[i,same];
      end;
   a[k,k]:=0;
end;
begin
   writeln('For ',compoundname[index]);
   endofdata:=false;
   r:=0;
   q:=0;
   repeat
      writeln(output,'Enter number of groups followed by group name');
      write(output,'or: 0 - end of groups for component ');
      read(input,numgroup[index,i+1]);
```

Table D-3 (cont'd.).

```
      if numgroup[index,i+1] > 0
      then
         begin
         i:=i+1;
         readln(input,name);
         k:=0;
         if numgroups > 0
         then
            repeat
               k:=k+1;
            until (name = groupname[k]) or (k = numgroups);
         if (numgroups = 0) or (name <> groupname[k])
         then
            begin
            numgroups:=numgroups+1;
            groupname[numgroups]:=name;
            write(output,'Enter Rk, Qk, for group ',name);
            readln(input,rk[numgroups],qk[numgroups]);
            k:=numgroups;
            getgroupparams;
            end;
         group[index,i]:=k;
         r:=r+numgroup[index,i]*rk[k];
         q:=q+numgroup[index,i]*qk[k];
         writeln('Groups entered so far:');
         for k:=1 to i do write(numgroup[index,k],group[index,k]);
         writeln;
         end
      else
         begin
         readln(input);
         endofdata:=true;
         end;
   until endofdata;
end;
begin
   readln(infile,name);
   index:=0;
   getnew:=false;
   if numcompounds > 0
   then
      repeat
         index:=index+1;
      until (compoundname[index] = name) or (index = numcompounds)
   else getnew:=true;
   if (numcompounds > 0) and (compoundname[index] <> name)
   then getnew:=true;
```

Table D-3 (cont'd.).

```
   if getnew
   then
      begin
      numcompounds:=numcompounds+1;
      compoundname[numcompounds]:=name;
      index:=numcompounds;
      i:=0;
      getsizeparams;
      groupsinit[index]:=i;
      write('Enter molecular weight of the ',solvorpoly);
      readln(mw[index]);
      end
   else
      begin
      r:=0;
      q:=0;
      for i:=1 to groupsinit[index] do
         begin
         r:=r+numgroup[index,i]*rk[group[index,i]];
         q:=q+numgroup[index,i]*qk[group[index,i]];
         end;
      end;
   r:=r/mw[index];
   q:=q/mw[index];
end;
function findact(model:modeltype):real;
const
   z = 10.0;
   b = 1.28;
   c1 = 1.1;
var
   y,phi1,phi2,theta1,tempomegalinf:real;
   vlred,vmred,fv:real;
   arfrac:array[1..2,1..10] of real;
   grpindex:array[1..10] of integer;
   factor:array[1..2] of real;
   term,term2,residual,solvtotal,solntotal:real;
   i,j,k,l,solvgroups,solngroups:integer;
begin
   case model of
      asogvsp:
         begin
         y:=w1+(e/omegalinf)*(1.0-w1);
         findact:=exp((y-w1)/y)/y
         end;
```

Table D-3 (cont'd.).

```
      flory:
         begin
         phi1:=densityratio*w1/(densityratio*w1+(1.0-w1));
         phi2:=1.0-phi1;
         findact:=exp(ln(phi1)+chi*phi2*phi2+phi2)/w1
         end;
      unifacfv:
         begin
         theta1:=qsolv*w1/(qsolv*w1+qpoly*(1.0-w1));
         phi1:=rsolv*w1/(rsolv*w1+rpoly*(1.0-w1));
         phi2:=1.0-phi1;
         findact:=ln(phi1)+phi2;
         findact:=result(findact)+(z/2.0)*m1*qsolv*ln(theta1/phi1);
         findact:=result(findact)-(z/2.0)*m1*qsolv*(1.0-phi1/theta1);
         findact:=exp(result(findact))/w1;
         write(auxfile,w1:8:3);
         write(auxfile,result(findact):8:3);
         solvtotal:=0;
         solvgroups:=groupsinit[solvindex];
         for i:=1 to solvgroups do
            begin
            grpindex[i]:=group[solvindex,i];
            arfrac[1,i]:=qk[grpindex[i]]/m1*numgroup[solvindex,i]*w1;
            arfrac[2,i]:=arfrac[1,i];
            solvtotal:=solvtotal+arfrac[1,i];
            end;
         solngroups:=solvgroups;
         solntotal:=solvtotal;
         for i:=1 to groupsinit[polyindex] do
            begin
            j:=0;
            repeat
               j:=j+1
            until (group[polyindex,i] = grpindex[j]) or
                  (j = solngroups);
            if group[polyindex,i] = grpindex[j]
            then
               begin
               arfrac[2,j]:=arfrac[2,j]+qk[grpindex[j]]/m2r*numgroup
                            [polyindex,i]*(1.0-w1);
               end
```

Table D-3 (cont'd.).

```
            else
               begin
               solngroups:=solngroups+1;
               grpindex[solngroups]:=group[polyindex,i];
               arfrac[2,solngroups]:=qk[grpindex[solngroups]]/m2r*
                                    numgroup[polyindex,i]*(1.0-w1);
               arfrac[1,solngroups]:=0.0;
               j:=solngroups;
               end;
            solntotal:=solntotal+qk[grpindex[j]]*numgroup[polyindex,i]/
                       m2r*(1.0-w1);
            end;
         for i:=1 to solngroups do
            begin
            arfrac[1,i]:=arfrac[1,i]/solvtotal;
            arfrac[2,i]:=arfrac[2,i]/solntotal;
            end;
         residual:=0;
         for j:=1 to solvgroups do
            begin
            for i:=1 to 2 do
               begin
               term:=0;
               for k:=1 to solngroups do
                  begin
                  term:=term+arfrac[i,k]
                            *exp(-a[grpindex[k],grpindex[j]]/tk);
                  end;
               factor[i]:=1.0-ln(term);
               term2:=0;
               for k:=1 to solngroups do
                  begin
                  term:=0;
                  for l:=1 to solngroups do
                     term:=term+arfrac[i,l]
                               *exp(-a[grpindex[l],grpindex[k]]/tk);
                  term2:=term2+arfrac[i,k]
                               *exp(-a[grpindex[j],grpindex[k]]/tk)
                              /term;
                  end;
               factor[i]:=factor[i]-term2;
               end;
            residual:=residual+qk[grpindex[j]]*(factor[2]-factor[1])
                              *numgroup[solvindex,j];
            end;
```

Table D-3 (cont'd.).

```
         residual:=exp(residual);
         write(auxfile,residual:8:3);
         findact:=result(findact)*residual;
         vlred:=1.0/(rho1*15.17*b*rsolv);
         vmred:=(w1/rho1+(1.0-w1)/rho2)/(15.17*b*(rsolv*w1+rpoly*
                                                  (1.0-w1)));
         fv:=3.0*c1*ln((exp(ln(vlred)/3.0)-1)/(exp(ln(vmred)/3.0)-1));
         fv:=fv-c1*((vlred/vmred-1.0)/(1.0-exp(-ln(vlred)/3.0)));
         fv:=exp(fv);
         write(auxfile,fv:8:3);
         findact:=result(findact)*fv;
         writeln(auxfile);
         end;
      asog:
         begin
         tempomegalinf:=omegalinf;
         omegalinf:=e;
         findact:=findact(asogvsp);
         omegalinf:=tempomegalinf
         end
      end
end;
function findinfact(w1,omegal:real):real;
var
   y,newy,lnomegal:real;
   convergent:boolean;
begin
   convergent:=false;
   lnomegal:=ln(omegal);
   y:=exp(1.0-lnomegal);
   while not convergent do
      begin
      newy:=exp(1.0-w1/y-lnomegal);
      convergent:=abs(newy-y) < (1.0e-5*newy);
      y:=newy;
      end;
   findinfact:=e*(1.0-w1)/(y-w1);
   writeln(outfile,'By correlating activity at finite conc ',w1:8:3);
end;
begin
   reset(infile);
   assign(data,'asogvsp.tab');
   reset(data);
   rewrite(outfile);
   rewrite(display);
   rewrite(auxfile);
   readln(data,numgroups);
   for i:=1 to numgroups do readln(data,rk[i],qk[i],groupname[i]);
```

Table D-3 (cont'd.).

```
   for i:=1 to numgroups do
      begin
      for j:=1 to numgroups do read(data,a[i,j]);
      readln(data)
      end;
   readln(data,numcompounds);
   for i:=1 to numcompounds do
      begin
      readln(data,groupsinit[i],mw[i],compoundname[i]);
      for j:=1 to groupsinit[i] do read(data,numgroup[i,j],group[i,j]);
      readln(data);
      end;
   repeat
      writeln(display,'Enter a heading for this data set');
      readln(infile,heading);
      writeln(outfile,heading);
      writeln(outfile);
         writeln(auxfile,heading);
      write(display,'What is the solvent? ');
      getcompound('solvent molecule    ',rsolv,qsolv,solvindex);
      m1:=mw[solvindex];
      write(display,'What is the polymer? ');
      getcompound('polymer repeat unit ',rpoly,qpoly,polyindex);
      m2r:=mw[polyindex];
      write(display,'Enter the temperature in K ');
      readln(infile,tk);
      writeln(display,
               'Enter inf diln wt frac act coef, or 0 if unknown');
      readln(infile,omegalinf);
      if omegalinf = 0.0
      then
         begin
         writeln(display,
                  'Enter known activity or act coef, followed by:');
         getactunits;
         read(infile,act,actunit);
         while actunit = ' ' do read(infile,actunit);
         readln(infile);
         writeln(display,'Enter concentration, followed by units:');
         getconcunits;
         read(infile,conc,concunit);
         while concunit = ' ' do read(infile,concunit);
         readln(infile);
         if concunit = 'x' then getmolecwts;
         w1:=convertconc(conc,concunit);
         tempomegal:=convertact(act,actunit);
         omegalinf:=findinfact(w1,tempomegal);
         end
```

Table D-3 (cont'd.).

```
      else
         begin
         writeln(display,'Enter units of activity or act coef data');
         getactunits;
         repeat read(infile,actunit); until actunit <> ' ';
         readln(infile);
         writeln(display,'Enter units of concentration data');
         getconcunits;
         repeat read(infile,concunit); until concunit <> ' ';
         readln(infile);
         end;
      writeln(display,'Enter polymer density or sp vol followed by');
      writeln(display,'   d for density');
      writeln(display,'   v for specific volume');
      writeln(display,'   m for molar volume');
      read(infile,rho2,rhounit);
      while rhounit = ' ' do read(infile,rhounit);
      readln(infile);
      if (concunit <> 'x') and (rhounit = 'm') then getmolecwts;
      rho2:=convertrho(rho2,rhounit,m2);
      write(display,'Enter solvent ');
      case rhounit of
         'd': write(display,'density ');
         'v': write(display,'specific volume ');
         'm': write(display,'molar volume ')
         end;
      readln(infile,rho1);
      rho1:=convertrho(rho1,rhounit,m1);
      densityratio:=rho2/rho1;
      chi:=-ln(e/omegalinf*densityratio);
      firstset:=nil;
      repeat
         writeln(display,'Enter conc followed by activity or act coef');
         writeln(display,'or an out of range concentration to stop');
         readln(infile,conc,act);
         w1:=convertconc(conc,concunit);
         omegalexp:=convertact(act,actunit);
         endofdata:=(w1>1.0) or (w1<0.0);
         if not endofdata
         then
            begin
            nextset:=firstset;
            lastset:=firstset;
            found:=false;
            while not found do
               begin
               if nextset = nil
               then found:=true
```

Table D-3 (cont'd.).

```
            else
               begin
               found:=nextset^.concen > wl;
               if not found
               then
                  begin
                  lastset:=nextset;
                  nextset:=nextset^.next
                  end
               end;
            end;
         new(ptr);
         ptr^.concen:=wl;
         ptr^.activity:=omegalexp;
         ptr^.next:=nextset;
         if lastset = nextset
         then firstset:=ptr
         else lastset^.next:=ptr;
         end
      until endofdata;
      write(outfile,
            'Infinite dilution wt frac activity coefficient was ');
      writeln(outfile,omegalinf:10:4);
      writeln(outfile,'Flory-Huggins chi parameter was ',chi:8:4);
      writeln(outfile);
      writeln(outfile,
            ' Wt Frac          Activity Coefficients and Percent Error');
      writeln(outfile,
    ' Solvent   Exptl   ASOGVSP       Flory-Huggins UNIFAC-FV     ASOG');
      writeln(outfile);
      ptr:=firstset;
      moment0error:=0.0;
      for model := asogvsp to asog do momentlerror[model]:=0.0;
      while ptr <> nil do
         begin
         wl:=ptr^.concen;
         omegalexp:=ptr^.activity;
         ptr:=ptr^.next;
         moment0error:=moment0error+1.0;
         write(outfile,wl:8:3,omegalexp:8:3);
         for model := asogvsp to asog do
            begin
            omegal[model]:=findact(model);
            pctdiff[model]:=(omegal[model]/omegalexp-1.0)*100.0;
            momentlerror[model]:=momentlerror[model]
                                 +abs(pctdiff[model]);
            write(outfile,omegal[model]:8:3,pctdiff[model]:6:1)
            end;
```

Table D-3 (cont'd.).

```
         writeln(outfile);
      end;
      writeln(outfile);
      write(outfile,'Avg pct error ');
      for model := asogvsp to asog do write(outfile,momentlerror[model]/
                                              moment0error:14:1);
   writeln(outfile);
   page(outfile);
   until eof(infile);
   rewrite(data);
   writeln(data,numgroups);
   for i:=1 to numgroups do writeln(data,rk[i]:7:4,qk[i]:6:3
                                    ,groupname[i]);
   for i:=1 to numgroups do
      begin
      for j:=1 to numgroups do write(data,a[i,j]:10:2);
      writeln(data)
      end;
   writeln(data,numcompounds);
   for i:=1 to numcompounds do
      begin
      writeln(data,groupsinit[i],mw[i]:10:2,compoundname[i]);
      for j:=1 to groupsinit[i] do write(data,numgroup[i,j],group[i,j]);
      writeln(data);
      end
end.
```

APPENDIX E.

Program Used to Apply Thermodynamic Models Using Best Fit of All Experimental Data.

The program listed below was used to generate the results in Appendix C from the original data in Appendix A. These results were presented in Chapter 2 of the dissertation. Input in the form of polymer-solvent activity data at a given temperature is processed to fit adjustable parameters and then the predictions of the VSP method using no residual interaction, a Flory-Huggins type residual interaction, and an ASOG-KT residual interaction are compared to experimental results. Refer to Appendices A and C for a more detailed description of the input data format and the output produced by the program. Directions for program compilation, linking, and execution are identical to those given in Appendix D. Much of the program presented in this appendix is identical to that presented in Appendix D. Only the data analysis itself is substantially different.

There are some points in program execution where terminal input may be necessary even if Infile is taking input from an external file. This will occur if a new compound name (not previously used during any execution of this program) is specified on line 2 or 3 of a data set. In this case, prompt messages will appear on the monitor for input to be

entered from the keyboard (regardless of your choices for Infile and Display). The input will consist of the functional group description of the compound, its molecular weight, and, if any new functional groups are specified, ASOG-KT interaction parameters must also be supplied as input.

The functional group and compound information is stored on a file named VSP.TAB. The format of this file is given as Table E-1.

Table E-1. Format of Functional Group and Compound Information File.

Line 1: N, the number of compounds (limit of 50), followed by M, the number of functional groups (limit of 20).

N sets of lines follow, each set containing for a compound:

Line 1: J, the number of functional groups in the compound as an integer, followed by the molecular weight of the compound or repeat unit as a real value, followed by the compound name (maximum 20 characters).

Lines 2 to J+1: For each functional group in the compound, the number of times that group occurs in the compound as a real value (ASOG-KT rules for counting groups allow fractional weighting) followed by the position in which the group appears in the list of M functional groups later in the file.

After all N sets have been completed, there are M lines, each containing a group name (maximum 7 characters). Following these, there are two sets of M lines containing the ASOG-KT interaction parameters. Each line in the first set contains the ASOG-KT temperature-independent interaction parameters, a_{ij}, for group i with each of the M groups j, in order, as real values. Each line in the second set contains the ASOG-KT temperature-dependent interaction parameters, b_{ij}, for group i with each of the M groups j, in order, as real values.

Dr. Eric A. Grulke of Michigan State University has a disk copy of this program and necessary files. Source code for the program is stored in file VSP.PAS, and the executable version of the program is stored in

file VSP.EXE. The program is executed by giving the name of the file at the DOS prompt, i.e., A:VSP (assuming the floppy drive is device A:).

Table D-2. Source Code for Program to Fit All Solvent Concentration Thermodynamic Data.

```
program asogvsp(infile,outfile,display,auxfile,input,output);
type
   setptr = ^dataset;
   dataset = record
      concen:real;
      activity:real;
      next:setptr
      end;
   modeltype = (vsp,flory,fhvsp,asogvsp);
   nametype = string(20);
   realarray = array[1..20] of real;
   intarray = array[1..20] of integer;
const
   e = 2.7182818;
   grouptablesize = 20;
   compoundtablesize = 50;
   blank = '                    ';
var
   wl,omegalexp,omegalinf,conc,act,ml,m2,m2r,chi,densityratio:real;
   omegal,tempomegal,lngl,rhol,rho2,tk:real;
   sumsqrerror:array[modeltype] of real;
   olinf,olinf2,glinf,fholinf,fhglinf,res:real;
   mean,sd:real;
   z,tstat:array[modeltype] of real;
   wlray,olray,lnglray:realarray;
   relerr:array[modeltype] of realarray;
   count,i,j,solvindex,polyindex:integer;
   npts:integer;
   stat:array[modeltype] of integer;
   rank:array[modeltype] of intarray;
   numcompounds:0..compoundtablesize;
   numgroups:0..grouptablesize;
   endofdata,found:boolean;
   concunit,actunit,rhounit,ch:char;
   heading:string(80);
   compoundname:array[1..compoundtablesize] of nametype;
   compoundgroups:array[1..compoundtablesize] of integer;
   grouptable:array[1..compoundtablesize,1..grouptablesize] of integer;
   groupcount:array[1..compoundtablesize,1..grouptablesize] of real;
   mw:array[1..compoundtablesize] of real;
   groupname:array[1..grouptablesize] of nametype;
   groupm,groupn,groupa:array[1..grouptablesize,1..grouptablesize]
                        of real;
```

Table E-2 (cont'd.).

```
   ptr,firstset,lastset,nextset:setptr;
   model:modeltype;
   infile,outfile,display,auxfile,data:text;
procedure getactunits;
begin
   writeln(display,'      a for activity');
   writeln(display,'      w for wt frac activity coef');
   writeln(display,'      x for mol frac activity coef');
end;
procedure getconcunits;
begin
   writeln(display,'      w for weight fraction solvent');
   writeln(display,'      m for mass ratio solvent/polymer');
   writeln(display,'      x for mole fraction solvent');
end;
procedure getmolecwts;
begin
   write(display,'Enter MW of polymer, MW of solvent ');
   readln(infile,m2,m1)
end;
function convertconc(conc:real;concunit:char):real;
begin
   case concunit of
      'w': convertconc:=conc;
      'x': convertconc:=conc/(conc+(m2/m1)*(1.0-conc));
      'm': convertconc:=1.0-1.0/(1.0+conc)
   end
end;
function convertact(act:real;actunit:char):real;
begin
   case actunit of
      'w': convertact:=act;
      'a': convertact:=act/w1;
      'x': convertact:=act*conc/w1;
   end
end;
function convertrho(rho:real;rhounit:char;mw:real):real;
begin
   case rhounit of
      'd': convertrho:=rho;
      'v': convertrho:=1.0/rho;
      'm': convertrho:=mw/rho;
   end
end;
procedure getcompound(solvorpoly:nametype;var index:integer);
var
   name:nametype;
   i:integer;
   getnew:boolean;
```

Table E-2 (cont'd.).

```
procedure getgroups;
var
   i,gindex:integer;
   gname:nametype;
   getnew:boolean;
procedure getgroupparams;
var
   i:integer;
begin
   if numgroups > 1
   then writeln('Enter interaction parameters m and n');
   for i:=1 to numgroups-1 do
   begin
      write('(',gname,groupname[i],') ');
      readln(groupm[numgroups,i],groupn[numgroups,i]);
   end;
   for i:=1 to numgroups-1 do
   begin
      write('(',groupname[i],gname,') ');
      readln(groupm[i,numgroups],groupn[i,numgroups]);
   end;
   groupm[numgroups,numgroups]:=0.0;
   groupn[numgroups,numgroups]:=0.0;
end;
begin
   i:=0;
   repeat
      writeln('Enter name of the next group in ',name);
      write('or return to stop entering groups ');
      readln(gname);
      if gname <> blank
      then
      begin
         i:=i+1;
         gindex:=0;
         getnew:=false;
         if numgroups > 0
         then
            repeat
               gindex:=gindex+1;
            until (groupname[gindex] = gname) or (gindex = numgroups)
         else getnew:=true;
         if (numgroups > 0) and (groupname[gindex] <> gname)
         then getnew:=true;
```

Table E-2 (cont'd.).

```
         if getnew
         then
         begin
            numgroups:=numgroups+1;
            groupname[numgroups]:=gname;
            gindex:=numgroups;
            getgroupparams;
         end;
         grouptable[index,i]:=gindex;
         write('How many are in ', name);
         readln(groupcount[index,i]);
      end;
   until gname = blank;
   compoundgroups[index]:=i;
end;
begin
   readln(infile,name);
   index:=0;
   getnew:=false;
   if numcompounds > 0
   then
      repeat
         index:=index+1;
      until (compoundname[index] = name) or (index = numcompounds)
   else getnew:=true;
   if (numcompounds > 0) and (compoundname[index] <> name)
   then getnew:=true;
   if getnew
   then
      begin
      numcompounds:=numcompounds+1;
      compoundname[numcompounds]:=name;
      index:=numcompounds;
      writeln('For ',name);
      write('Enter molecular weight of the ',solvorpoly);
      readln(mw[index]);
      getgroups;
      end;
end;
procedure generatea;
var
   i,j:integer;
begin
   for i:=1 to numgroups do
      for j:=1 to numgroups do groupa[i,j]:=
                                 exp(groupm[i,j]+groupn[i,j]/tk);
end;
```

Table E-2 (cont'd.).

```
function enthpart(w1:real):real;
type
   grouptype = array[1..grouptablesize] of real;
var
   k:integer;
   x1,x2,total:real;
   group:array[1..grouptablesize] of integer;
   num:array[1..grouptablesize] of real;
   bigx,bigxstar:grouptype;
function gamma(x:grouptype; k:integer):real;
var
   l,m:integer;
   sum,den:real;
begin
   sum:=0.0;
   for l:=1 to numgroups do sum:=sum+x[l]*groupa[k,l];
   gamma:=-ln(sum)+1.0;
   sum:=0.0;
   for l:=1 to numgroups do
   begin
      den:=0.0;
      for m:=1 to numgroups do
         den:=den+x[m]*groupa[l,m];
      sum:=sum+x[l]*groupa[l,k]/den;
   end;
   gamma:=result(gamma)-sum;
end;
begin
   x1:=w1/m1/(w1/m1+(1.0-w1)/m2r);
   x2:=1.0-x1;
   total:=0.0;
   for k:=1 to numgroups do bigxstar[k]:=0.0;
   for k:=1 to compoundgroups[solvindex] do
   begin
      group[k]:=grouptable[solvindex,k];
      num[k]:=groupcount[solvindex,k];
      bigxstar[group[k]]:=num[k];
      total:=total+bigxstar[group[k]];
   end;
   for k:=1 to numgroups do bigxstar[k]:=bigxstar[k]/total;
   total:=0.0;
   for k:=1 to numgroups do bigx[k]:=0.0;
   for k:=1 to compoundgroups[solvindex] do
      bigx[group[k]]:=x1*num[k];
   for k:=1 to compoundgroups[polyindex] do
      bigx[grouptable[polyindex,k]]:=bigx[grouptable[polyindex,k]]+
                                     x2*groupcount[polyindex,k];
   for k:=1 to numgroups do total:=total+bigx[k];
   for k:=1 to numgroups do bigx[k]:=bigx[k]/total;
```

Table E-2 (cont'd.).

```
   enthpart:=0.0;
   for k:=1 to compoundgroups[solvindex] do
      enthpart:=result(enthpart)+num[k]*(gamma(bigx,group[k])
                                        -gamma(bigxstar,group[k]));
   writeln(auxfile,'enthpart of ',wl,': ',result(enthpart));
end;
function findact(model:modeltype):real;
var
   y,phi1,phi2:real;
begin
   case model of
      vsp:
         begin
         y:=wl+(e/olinf)*(1.0-wl);
         findact:=exp((y-wl)/y)/y
         end;
      flory:
         begin
         phi1:=densityratio*wl/(densityratio*wl+(1.0-wl));
         phi2:=1.0-phi1;
         findact:=exp(ln(phi1)+chi*phi2*phi2+phi2)/wl
         end;
      fhvsp:
         begin
         y:=wl+(e*fhglinf/fholinf)*(1-wl);
         findact:=exp((y-wl)/y*(y+(y-wl)*ln(fhglinf))/y)/y;
         end;
      asogvsp:
         begin
         y:=wl+(e*glinf/olinf2)*(1.0-wl);
         findact:=exp((y-wl)/y+lngl)/y
         end;
      end
end;
procedure fitparams(var chi,olinf,olinf2,glinf,fholinf,fhglinf,res:real;
                        wlray,olray:realarray; npts:integer);
const
   delta = 0.0001;
var
   i:integer;
   res1,res2,res3,change,size:real;
   deriv,deriv2:real;
procedure findchi;
var
   i:integer;
   phi1,phi2,num,den:real;
begin
   num:=0;
   den:=0;
```

Table E-2 (cont'd.).

```
   for i:=1 to npts do
   begin
      phi2:=(1-wlray[i])/(densityratio*wlray[i]+1-wlray[i]);
      phi1:=1-phi2;
      num:=num+sqr(phi2)*(ln(wlray[i]*olray[i]/phi1)-phi2);
      den:=den+sqr(sqr(phi2));
   end;
   chi:=num/den;
end;
procedure findolinf(var res:real; olinf,glinf:real);
var
   i:integer;
   gl,wtavg,size:real;
begin
   res:=0;
   for i:=1 to npts do
   begin
      size:=e*glinf/olinf;
      wtavg:=wlray[i]+size*(1-wlray[i]);
      if glinf <> 1.0 then gl:=lnglray[i] else gl:=0.0;
      res:=res+sqr(ln(olray[i])+ln(wtavg)-size*(1-wlray[i])/wtavg-gl);
   end;
end;
procedure findolgl(var res,ol,gl:real; size:real);
var
   i:integer;
   r2,num,den,chi:real;
   rl:realarray;
begin
   num:=0;
   den:=0;
   for i:=1 to npts do
   begin
      rl[i]:=wlray[i]/(wlray[i]+size*(1-wlray[i]));
      r2:=1-rl[i];
      num:=num+sqr(r2)*(ln(wlray[i]*olray[i]/rl[i])-r2);
      den:=den+sqr(sqr(r2));
   end;
   chi:=num/den;
   gl:=exp(chi);
   ol:=e*gl/size;
   res:=0;
```

Table E-2 (cont'd.).

```
   for i:=1 to npts do
   begin
      r2:=1-rl[i];
      res:=res+(ln(wlray[i]*olray[i]/rl[i])-r2-chi*sqr(r2))
               *(1-1/rl[i]+2*chi*r2)*size/ol*(1-wlray[i])/wlray[i]
               *sqr(rl[i]);
   end;
   count:=count+1;
end;
begin
   count:=0;
   findchi;
   olinf:=densityratio*exp(1+chi);
   olinf2:=olinf;
   writeln(auxfile,'vsp');
   repeat
      findolinf(res2,olinf+delta,1.0);
      findolinf(res1,olinf-delta,1.0);
      findolinf(res3,olinf,1.0);
      deriv:=(res2-res1)/(2*delta);
      deriv2:=(res2+res1-2*res3)/sqr(delta);
      if deriv2 > 0 then change:=deriv/deriv2
                    else change:=-deriv/deriv2;
      olinf:=olinf-change;
      writeln(auxfile,res2,res1,res3,olinf,deriv,deriv2);
   until abs(change) < 0.0001*abs(olinf);
   glinf:=exp(enthpart(0.0));
   for i:=1 to npts do lnglray[i]:=enthpart(wlray[i]);
   writeln(auxfile,'asogvsp, glinf = ',glinf);
   repeat
      findolinf(res2,olinf2+delta,glinf);
      findolinf(res1,olinf2-delta,glinf);
      findolinf(res3,olinf2,glinf);
      deriv:=(res2-res1)/(2*delta);
      deriv2:=(res2+res1-2*res3)/sqr(delta);
      if deriv2 > 0 then change:=deriv/deriv2
                    else change:=-deriv/deriv2;
      olinf2:=olinf2-change;
      writeln(auxfile,res2,res1,res3,olinf2,deriv,deriv2);
   until abs(change) < 0.0001*abs(olinf2);
   size:=1;
   repeat
      findolgl(res2,fholinf,fhglinf,size+delta);
      findolgl(res1,fholinf,fhglinf,size-delta);
      findolgl(res,fholinf,fhglinf,size);
      deriv:=(res2-res1)/(2*delta);
      change:=res/deriv;
```

Table E-2 (cont'd.).

```
      if change < size
      then size:=size-change
      else size:=size/2;
      if fhglinf > fholinf then size:=e/(4*olinf);
      writeln(auxfile,size,change,deriv,res);
   until abs(change) < 0.00001*size;
   writeln(auxfile,'Total calls to fhvsp: ',count:4);
end;
procedure sortrank(error:realarray; var rank:intarray; n:integer);
var
   i,j,temp:integer;
   trank:intarray;
begin
   for i:=1 to n do trank[i]:=i;
   for i:=1 to n-1 do
      for j:=i+1 to n do
         if error[trank[i]] > error[trank[j]]
         then
         begin
            temp:=trank[i];
            trank[i]:=trank[j];
            trank[j]:=temp;
         end;
   for i:=1 to n do rank[trank[i]]:=i;
end;
procedure stattest(test:integer; rank:intarray; n:integer;
                   var stat:integer; var mean,sd,z,tstat:real);
var
   i:integer;
   t:real;
begin
   stat:=0;
   case test of
   1: begin
      for i:=1 to n do stat:=stat+i*rank[i];
      mean:=n*(n+1)*(n+1)/4;
      sd:=n*(n+1)/12*sqrt(float(n-1));
      end;
   2: begin
      for i:=1 to n-1 do stat:=stat+sqr(rank[i+1]-rank[i]);
      mean:=n*(n-1)*(n+1)/6;
      sd:=sqrt(n*(n-2)*(n+1)*(5*n*n-2*n-9)/180);
      end;
   3: begin
      for i:=1 to n-1 do stat:=stat+abs(rank[i+1]-rank[i]);
      mean:=(n-1)*(n+1)/3;
      sd:=sqrt((n-2)*(4*n*n-3*n-7)/90);
      end;
   end;
```

Table E-2 (cont'd.).

```
   z:=(stat-mean)/sd;
   t:=1/(1+0.33267*abs(z));
   tstat:=exp(-z*z/2)/sqrt(2*3.14159)*
          t*(0.4361836+t*(-0.1201676+t*0.9372980));
   if test > 1 then tstat:=1-tstat else tstat:=1-2*tstat;
end;
begin (* main program *)
   reset(infile);
   assign(data,'vsp.tab');
   reset(data);
   rewrite(outfile);
   rewrite(display);
   rewrite(auxfile);
   readln(data,numcompounds,numgroups);
   for i:=1 to numcompounds do
      begin
      readln(data,compoundgroups[i],mw[i],compoundname[i]);
      for j:=1 to compoundgroups[i] do
         readln(data,groupcount[i,j],grouptable[i,j]);
      end;
   for i:=1 to numgroups do readln(data,groupname[i]);
   for i:=1 to numgroups do
   begin
      for j:=1 to numgroups do read(data,groupm[i,j]);
      readln(data);
   end;
   for i:=1 to numgroups do
   begin
      for j:=1 to numgroups do read(data,groupn[i,j]);
      readln(data);
   end;
   repeat
      writeln(display,'Enter a heading for this data set');
      readln(infile,heading);
      writeln(outfile,heading);
      writeln(outfile);
      writeln(auxfile,heading);
      write(display,'What is the solvent? ');
      getcompound('solvent molecule    ',solvindex);
      m1:=mw[solvindex];
      write(display,'What is the polymer? ');
      getcompound('polymer repeat unit ',polyindex);
      m2r:=mw[polyindex];
      write(display,'Enter temperature in Kelvin ');
      readln(infile,tk);
      writeln(display,
                'Enter inf diln wt frac act coef, or 0 if unknown');
      readln(infile,omegalinf);
```

Table E-2 (cont'd.).

```
      if omegalinf = 0.0
      then
         begin
         writeln(display,
                   'Enter known activity or act coef, followed by:');
         getactunits;
         read(infile,act,actunit);
         while actunit = ' ' do read(infile,actunit);
         readln(infile);
         writeln(display,'Enter concentration, followed by units:');
         getconcunits;
         read(infile,conc,concunit);
         while concunit = ' ' do read(infile,concunit);
         readln(infile);
         if concunit = 'x' then getmolecwts;
         w1:=convertconc(conc,concunit);
         tempomegal:=convertact(act,actunit);
         new(firstset);
         firstset^.concen:=w1;
         firstset^.activity:=tempomegal;
         firstset^.next:=nil;
         end
      else
         begin
         writeln(display,'Enter units of activity or act coef data');
         getactunits;
         repeat read(infile,actunit); until actunit <> ' ';
         readln(infile);
         writeln(display,'Enter units of concentration data');
         getconcunits;
         repeat read(infile,concunit); until concunit <> ' ';
         readln(infile);
         firstset:=nil;
         end;
      writeln(display,'Enter polymer density or sp vol followed by');
      writeln(display,'   d for density');
      writeln(display,'   v for specific volume');
      writeln(display,'   m for molar volume');
      read(infile,rho2,rhounit);
      while rhounit = ' ' do read(infile,rhounit);
      readln(infile);
      if (concunit <> 'x') and (rhounit = 'm') then getmolecwts;
      rho2:=convertrho(rho2,rhounit,m2);
      write(display,'Enter solvent ');
      case rhounit of
         'd': write(display,'density ');
         'v': write(display,'specific volume ');
         'm': write(display,'molar volume ')
         end;
```

Table E-2 (cont'd.).

```
      readln(infile,rhol);
      rhol:=convertrho(rhol,rhounit,ml);
      densityratio:=rho2/rhol;
      repeat
         writeln(display,'Enter conc followed by activity or act coef');
         writeln(display,'or an out of range concentration to stop');
         readln(infile,conc,act);
         wl:=convertconc(conc,concunit);
         omegalexp:=convertact(act,actunit);
         endofdata:=(wl>1.0) or (wl<0.0);
         if not endofdata
         then
            begin
            nextset:=firstset;
            lastset:=firstset;
            found:=false;
            while not found do
               begin
               if nextset = nil
               then found:=true
               else
                  begin
                  found:=nextset^.concen > wl;
                  if not found
                  then
                     begin
                     lastset:=nextset;
                     nextset:=nextset^.next
                     end
                  end
               end;
            new(ptr);
            ptr^.concen:=wl;
            ptr^.activity:=omegalexp;
            ptr^.next:=nextset;
            if lastset = nextset
            then firstset:=ptr
            else lastset^.next:=ptr;
            end
      until endofdata;
      ptr:=firstset;
      npts:=0;
      while ptr <> nil do
      begin
         npts:=npts+1;
         wlray[npts]:=ptr^.concen;
         olray[npts]:=ptr^.activity;
         ptr:=ptr^.next;
      end;
```

Table E-2 (cont'd.).

```
      generatea;
      fitparams(chi,olinf,olinf2,glinf,fholinf,fhglinf,res,wlray,olray,
                npts);
      writeln(outfile,'Results of least squares fit:');
      writeln(outfile);
      write(outfile,'VSP inf diln wt frac activity coefficient: ');
      writeln(outfile,olinf:10:4);
      writeln(outfile,'Flory-Huggins chi parameter: ',chi:8:4);
      write(outfile,'FH-VSP inf diln parameters: ');
      write(outfile,' wt frac act coeff',fholinf:8:4);
      write(outfile,'  enth coeff',fhglinf:8:4); writeln(outfile);
      write(outfile,'ASOG-VSP inf diln parameters: ');
      write(outfile,' wt frac act coeff',olinf2:8:4);
      write(outfile,'  enth coeff',glinf:8:4); writeln(outfile);
      writeln(outfile);
      writeln(outfile,
           ' Wt Frac          Activity Coefficients and Percent Error');
      writeln(outfile,
               ' Solvent   Exptl   VSP           Flory-Huggins FH-VSP',
                     '        ASOG-VSP');
      writeln(outfile);
      for model := vsp to asogvsp do sumsqrerror[model]:=0.0;
      for i:=1 to npts do
      begin
         wl:=wlray[i];
         omegalexp:=olray[i];
         lngl:=lnglray[i];
         write(outfile,wl:8:3,omegalexp:8:3);
         for model := vsp to asogvsp do
            begin
            omegal:=findact(model);
            relerr[model,i]:=ln(omegal/omegalexp)*100;
            write(outfile,omegal:8:3,relerr[model,i]:6:1);
            sumsqrerror[model]:=sumsqrerror[model]+sqr(relerr[model,i]);
            end;
         if sumsqrerror[model] < 0.0 then sumsqrerror[model]:=0.0;
         writeln(outfile);
      end;
      writeln(outfile);
      write(outfile,'Standard pct err');
      for model := vsp to flory do write(outfile,
                              sqrt(sumsqrerror[model]/(npts-1)):14:1);
      if npts > 2
      then write(outfile,sqrt(sumsqrerror[fhvsp]/(npts-2)):14:1);
      write(outfile,sqrt(sumsqrerror[asogvsp]/(npts-1)):14:1);
      writeln(outfile); writeln(outfile); writeln(outfile);
```

Table E-2 (cont'd.).

```
      for model := vsp to asogvsp do
      begin
         sortrank(relerr[model],rank[model],npts);
      end;
      writeln(outfile,'Analysis of model error randomness');
      writeln(outfile);
      write(outfile,'Sum sqr rank difference test: ');
      for model := vsp to asogvsp do
          stattest(2,rank[model],npts,stat[model],mean,
                   sd,z[model],tstat[model]);
      writeln(outfile,'mean = ',mean:7:2,'  sd = ',sd:6:2);
      writeln(outfile);
      write(outfile,'Test statistic  ');
      for model := vsp to asogvsp do write(outfile,stat[model]:14);
      writeln(outfile);
      write(outfile,'Normal (Z)      ');
      for model := vsp to asogvsp do write(outfile,z[model]:14:3);
      writeln(outfile);
      write(outfile,'Reject level    ');
      for model := vsp to asogvsp do write(outfile,tstat[model]:14:6);
      writeln(outfile); writeln(outfile);
      write(outfile,'Sum abs rank difference test: ');
      for model := vsp to asogvsp do
          stattest(3,rank[model],npts,stat[model],mean,
                   sd,z[model],tstat[model]);
      writeln(outfile,'mean = ',mean:7:2,'  sd = ',sd:6:2);
      writeln(outfile);
      write(outfile,'Test statistic  ');
      for model := vsp to asogvsp do write(outfile,stat[model]:14);
      writeln(outfile);
      write(outfile,'Normal (Z)      ');
      for model := vsp to asogvsp do write(outfile,z[model]:14:3);
      writeln(outfile);
      write(outfile,'Reject level    ');
      for model := vsp to asogvsp do write(outfile,tstat[model]:14:6);
      writeln(outfile); writeln(outfile); writeln(outfile);
      if (chi >= 0.5) or (fhglinf >= sqrt(e))
      then
      begin
         writeln(outfile,'Phase separation behavior prediction');
         writeln(outfile);
         if chi >= 0.5
         then writeln(outfile,'Flory-Huggins model: ',
                      'wt frac = ',1/(1+densityratio*(2*chi-1)):5:3);
         if fhglinf >= sqrt(e)
         then writeln(outfile,'FH-VSP model:        ',
                      'wt frac = ',1/(1+fholinf/(e*fhglinf)*
                                   (2*ln(fhglinf)-1)):5:3);
      end;
```

Table E-2 (cont'd.).

```
      page(outfile);
   until eof(infile);
   rewrite(data);
   writeln(data,numcompounds,numgroups);
   for i:=1 to numcompounds do
      begin
      writeln(data,compoundgroups[i]:3,mw[i]:7:2,compoundname[i]);
      for j:=1 to compoundgroups[i] do
         writeln(data,groupcount[i,j]:5:2,grouptable[i,j]:3);
      end;
   for i:=1 to numgroups do writeln(data,groupname[i]);
   for i:=1 to numgroups do
   begin
      for j:=1 to numgroups do write(data,groupm[i,j]:12:4);
      writeln(data);
   end;
   for i:=1 to numgroups do
   begin
      for j:=1 to numgroups do write(data,groupn[i,j]:12:4);
      writeln(data);
   end;
end.
```

APPENDIX F.

Derivation of Equations in "Generalized Correlation for Solvent Activities in Polymer Solutions"

This appendix contains a more detailed derivation of the equations presented in the reprint article "Generalized Correlation for Solvent Activities in Polymer Solutions". This article was included as part of Chapter 2 of the dissertation. The major source of the equations which were used to derive the results was the ASOG model (Derr and Deal, 1969). In this appendix, equation numbers refer to the reprint article itself, beginning on page 13 of the dissertation. New equations not included in the article are numbered with a preceding letter F, e.g., F-1, F-2, etc.

Eqs 1 to 4 are taken directly from the ASOG model. Only eqs 1 and 2 are used to derive further results; eqs 3 and 4 were presented for the sake of completeness. Eq 5, actually an inequality, merely states the assumption that the solvent molecule is much smaller than the polymer molecule.

DERIVATION OF EQUATION 6

Eq 6 is the first equation which was derived. The superscript ∞ in the

equations shown refers to the limiting value of a variable as the mole fraction (or weight fraction) of solvent (component 1) approaches zero. Beginning with eq 2 and letting x_1 approach zero (x_2 will approach one)

$$R_1 = S_1 / (S_1x_1 + S_2x_2) \tag{2}$$

$$R_1^{\infty} = S_1 / (S_1(0) + S_2(1)) = S_1 / S_2 \tag{F-1}$$

then substituting this value into eq 1 to give the mole fraction activity coefficient at infinite dilution

$$\ln \gamma_1^{S} = 1 - R_1 + \ln R_1 \tag{1}$$

$$\ln \gamma_1^{S\infty} = 1 - R_1^{\infty} + \ln R_1^{\infty} = 1 - (S_1/S_2) + \ln (S_1/S_2) \tag{F-2}$$

and finally using eq 5 to eliminate one of the terms in eq F-2 gives eq 6.

$$S_1 \ll S_2 \tag{5}$$

$$\ln \gamma_1^{S\infty} = 1 + \ln (S_1/S_2) \tag{F-3}$$

$$\gamma_1^{S\infty} = \exp [1 + \ln (S_1/S_2)] = \exp(1) \cdot S_1/S_2 = e \cdot S_1/S_2 \tag{6}$$

In the article, the superscript ^{S} was suppressed since only the size component of activity was being considered. It should be pointed out that eq 1, taken from the ASOG model, leaves out a factor which appears in the athermal Flory-Huggins equation. For our purposes, this factor would equal $(1 - S_1/S_2)$, and would differ negligibly from one after the assumption of eq 5 is made. Eq 5 restricts the application of the results to binary solutions of low molecular weight solvents in high molecular weight polymers.

DERIVATION OF EQUATION 7

Eq 7 follows from the definition of mole fraction and weight fraction concentration variables and activity coefficients at infinite dilution, where x_1 approaches zero and x_2 approaches one.

$$a_1 = \gamma_1 x_1 = \Omega_1 w_1 \qquad \text{(F-4)}$$

$$\Omega_1 = \gamma_1 x_1 / w_1 \qquad \text{(F-5)}$$

$$w_1 = M_1 x_1 \; / \; (M_1 x_1 + M_2 x_2) \qquad \text{(F-6)}$$

$$\Omega_1 = \gamma_1 \; (M_1 x_1 + M_2 x_2) \; / \; M_1 \qquad \text{(F-7)}$$

$$\Omega_1^{\infty} = \gamma_1^{\infty} \; (M_1(0) + M_2(1)) \; / \; M_1 = \gamma_1^{\infty} \; M_2 \; / \; M_1 \qquad (7)$$

Eq 8 follows from substitution of eq 6 into eq 7, and eq 9 follows from substitution of eq 10 into eq 8. Eq 10 expresses the fact that the size ratio equals the ratio of molecular weights for chemically similar polymer-solvent pairs. This is the assumption which is removed by the variable size parameter concept. Instead, the effective size ratio, shown in eq 11, is given by rearrangement of eq 8, treating the size ratio as an unknown and the activity coefficient Ω_1^{∞} as a known value. Eqs 12 and 13 are transformations from weight fraction composition variables to mole fraction, analogous to eq F-6 above.

DERIVATION OF EQUATION 14

Eq 14 for the size ratio R_1 was derived in several steps, as shown below. Eq 2 was divided through by S_1, then eq 11 was substituted for S_2/S_1, and eqs 12 and 13 were substituted for x_1 and x_2. The final

expression was simplified by multiplying through by M_1/M_2.

$$R_1 = S_1 / (S_1x_1 + S_2x_2) \quad (2)$$

$$R_1 = 1 / (x_1 + (S_2/S_1)\, x_2) \quad (F\text{-}8)$$

$$S_2/S_1 = (e/\Omega_1^{\infty})\, (M_2/M_1) \quad (11)$$

$$R_1 = 1 / (x_1 + (e/\Omega_1^{\infty})\, (M_2/M_1)\, x_2) \quad (F\text{-}9)$$

$$x_1 = (M_2/M_1)\, w_1 / ((M_2/M_1)\, w_1 + w_2) \quad (12)$$

$$x_2 = w_2 / ((M_2/M_1)\, w_1 + w_2) \quad (13)$$

$$R_1 = ((M_2/M_1)\, w_1 + w_2) / ((M_2/M_1)\, w_1 + (e/\Omega_1^{\infty})\, (M_2/M_1)\, w_2) \quad (F\text{-}10)$$

$$R_1 = (w_1 + (M_1/M_2)\, w_2) / (w_1 + (e/\Omega_1^{\infty})\, w_2) \quad (14)$$

In the article, w_2 was replaced by $1\text{-}w_1$ to reinforce the fact that the expressions derived were functions of a single concentration variable. The variable w_2 has been retained in this appendix for clarity in all equations.

DERIVATION OF EQUATION 15

Eq 15 is easily derived from substitution of eq 12 into eq F-5, cancelling w_1 and multiplying through by M_1/M_2.

$$\Omega_1 = \gamma_1 x_1 / w_1 \quad (F\text{-}5)$$

$$x_1 = (M_2/M_1)\, w_1 / ((M_2/M_1)\, w_1 + w_2) \quad (12)$$

$$\Omega_1 = \gamma_1\, (M_2/M_1)\, w_1 / w_1\, ((M_2/M_1)\, w_1 + w_2) \quad (F\text{-}11)$$

$$\Omega_1 = \gamma_1 / (w_1 + (M_1/M_2)\, w_2) \quad (15)$$

DERIVATION OF EQUATION 16

To derive eq 16, begin by substituting eq 14 into eq 1 (superscript S suppressed in eq 1), noting the simplification for $1-R_1$ given as eq F-12.

$$\ln \gamma_1 = 1 - R_1 + \ln R_1 \tag{1}$$

$$R_1 = (w_1 + (M_1/M_2)\, w_2) \,/\, (w_1 + (e/\Omega_1^{\infty})\, w_2) \tag{14}$$

$$1 - R_1 = (e/\Omega_1^{\infty} - M_1/M_2)\, w_2 \,/\, (w_1 + (e/\Omega_1^{\infty})\, w_2) \tag{F-12}$$

$$\ln \gamma_1 = (e/\Omega_1^{\infty} - M_1/M_2)\, w_2 \,/\, (w_1 + (e/\Omega_1^{\infty})\, w_2) + \ln (w_1 + (M_1/M_2)\, w_2) - \ln (w_1 + (e/\Omega_1^{\infty})\, w_2) \tag{F-13}$$

Take the exponential of eq F-13 and substitute it into eq 15 to produce eq F-15. Then use the assumption given by eq 17 to eliminate the molecular weight term, giving eq 16. The assumption is that the molecular weight of solvent is much smaller than that of polymer, and that Ω_1^{∞} is not too large (the solution is not too nonideal).

$$\gamma_1 = \exp [\, (e/\Omega_1^{\infty} - M_1/M_2)\, w_2 \,/\, (w_1 + (e/\Omega_1^{\infty})\, w_2) \,] \cdot (w_1 + (M_1/M_2)\, w_2) \,/\, (w_1 + (e/\Omega_1^{\infty})\, w_2) \tag{F-14}$$

$$\Omega_1 = \gamma_1 \,/\, (w_1 + (M_1/M_2)\, w_2) \tag{15}$$

$$\Omega_1 = \exp [\, (e/\Omega_1^{\infty} - M_1/M_2)\, w_2 \,/\, (w_1 + (e/\Omega_1^{\infty})\, w_2) \,] \cdot 1 \,/\, (w_1 + (e/\Omega_1^{\infty})\, w_2) \tag{F-15}$$

$$e/\Omega_1^{\infty} \gg M_1/M_2 \tag{17}$$

$$\Omega_1 = \exp [\, (e/\Omega_1^{\infty})\, w_2 \,/\, (w_1 + (e/\Omega_1^{\infty})\, w_2) \,] \,/\, (w_1 + (e/\Omega_1^{\infty})\, w_2) \tag{16}$$

CONVERGENCE OF THE ITERATION PROCEDURE FOR CALCULATING Ω_1^{∞} IN EQUATIONS 18 TO 23

Eqs 18 to 23, defining an iteration procedure for calculating Ω_1^{∞} from

a finite concentration activity value, all follow from straightforward substitution involving eq 16 and eqs 18 to 23 themselves. The convergence properties of the iteration scheme were not examined in the article, except for the comment that the "procedure converges quickly". Since the method consists of successive substitutions, a necessary condition for convergence in eq 20 is given by the magnitude of the derivative of the right hand side, i.e., $|F'(Y)| < 1$.

$$Y = \exp\left(1 - w_1^{exptl}/Y - \ln \Omega_1^{exptl}\right) = F(y) \tag{20}$$

$$F'(Y) = \exp\left(1 - w_1^{exptl}/Y - \ln \Omega_1^{exptl}\right) \cdot \left(w_1^{exptl}/Y^2\right)$$

$$= Y \cdot \left(w_1^{exptl}/Y^2\right) - w_1^{exptl}/Y \tag{F-16}$$

Since Y is calculated as the result of the exponential function, it is necessarily positive. The experimental weight fraction of solvent, w_1^{exptl}, is also a positive quantity. (If w_1^{exptl} were zero, the iteration scheme would be unnecessary since the experimental activity value would already be at infinite dilution of solvent.) Consider the first two approximations of Y, Y_0 (given by eq 21), and Y_1 (given by eq 22 with n = 1, shown here as eq F-17).

$$Y_0 = \exp\left(1 - \ln \Omega_1^{exptl}\right) \tag{21}$$

$$Y_1 = \exp\left(1 - w_1^{exptl}/Y_0 - \ln \Omega_1^{exptl}\right) \tag{F-17}$$

$$Y_1 = \exp\left(1 - \ln \Omega_1^{exptl}\right) \cdot \exp\left(- w_1^{exptl}/Y_0\right)$$

$$= Y_0 \exp\left(- w_1^{exptl}/Y_0\right) \tag{F-18}$$

Because the argument of the exponential function in eq F-18 is negative, and Y_0 is positive, $Y_1 < Y_0$ can be concluded. Identical logic applies to the general case of Y_n, leading to this result.

$$Y_0 > Y_1 > Y_2 > . \quad . \quad . > Y_{n-1} > Y_n \tag{F-19}$$

Assume that the expression for F'(Y) given by eq F-16 does not meet the necessary condition for convergence.

$$|F'(Y)| = w_1^{exptl}/Y \geq 1 \tag{F-20}$$

This expression will take on its smallest value when its denominator is largest, i.e., when Y is largest. According to eq F-19, this will occur when n equals zero on the initial iteration. For eq F-20 to hold for any value of Y, it must hold for Y_0 as shown in eq F-21. The expression for Y_0 from eq 21 can then be substituted to give eq F-22, and since the denominator is positive, the direction of inequality remains the same in eq F-23.

$$w_1^{exptl}/Y_0 \geq 1 \tag{F-21}$$

$$Y_0 = \exp\,(1 - \ln \Omega_1^{exptl}) \tag{21}$$

$$w_1^{exptl} \,/\, \exp\,(1 - \ln \Omega_1^{exptl}) \geq 1 \tag{F-22}$$

$$w_1^{exptl} \geq \exp\,(1 - \ln \Omega_1^{exptl}) \tag{F-23}$$

Working through the exponential function gives eq F-24, which can then be rearranged to eq F-25 using the definition of activity coefficient.

$$w_1^{exptl} \geq e \,/\, \Omega_1^{exptl} \tag{F-24}$$

$$w_1^{exptl} \Omega_1^{exptl} = a_1^{exptl} \geq e \tag{F-25}$$

Since the activity of a component cannot exceed unity when based on a pure component standard state, eq F-25 is a contradiction. Thus the original assumption of eq F-20 must be false, and the necessary

condition for convergence holds for the iteration scheme of successive substitutions described by eqs 18 to 23.

Eq 24 is the Flory-Huggins equation for solvent activity, and eqs 25 and 26 are definitions of the volume fraction in a binary system with no volume of mixing. When eq 24 is rearranged for χ, and eqs F-4, 16, 25 and 26 are substituted, the results are

$$\ln a_1 = \ln \phi_1 + \phi_2 + \chi \phi_2^2 \qquad (24)$$

$$\chi = (\ln a_1 - \ln \phi_1 - \phi_2) / \phi_2^2 \qquad (F\text{-}26)$$

$$a_1 = \Omega_1 w_1 \qquad (F\text{-}4)$$

$$\Omega_1 = \exp [(e/\Omega_1^{\infty}) w_2 / (w_1 + (e/\Omega_1^{\infty}) w_2)] / (w_1 + (e/\Omega_1^{\infty}) w_2) \qquad (16)$$

$$\ln a_1 = \ln \phi_1 + \phi_2 + \chi \phi_2^2 \qquad (24)$$

$$\phi_1 = (\rho_2/\rho_1) w_1 / ((\rho_2/\rho_1) w_1 + w_2) \qquad (25)$$

$$\phi_2 = w_2 / ((\rho_2/\rho_1) w_1 + w_2) \qquad (26)$$

$$\ln a_1 = \ln \phi_1 + \phi_2 + \chi \phi_2^2 \qquad (24)$$

$$\begin{aligned} \chi = [& (e/\Omega_1^{\infty}) w_2 / (w_1 + (e/\Omega_1^{\infty}) w_2) - \ln (w_1 + (e/\Omega_1^{\infty}) w_2) \\ & + \ln w_1 - \ln (\rho_2/\rho_1) w_1 + \ln ((\rho_2/\rho_1) w_1 + w_2) \\ & - w_2 / ((\rho_2/\rho_1) w_1 + w_2)] \cdot ((\rho_2/\rho_1) w_1 + w_2)^2 / w_2^2 \end{aligned} \qquad (F\text{-}27)$$

This result is simplified by grouping together all the logarithm terms as shown in eq F-28 and by dividing out individual w_2 factors as shown in eq F-29. When the factor $((\rho_2/\rho_1) w_1/w_2 + 1)^2$ is multiplied through the other three terms, eq 27 results. There is a typographical error in eq 27 of the article which shows a division by w_2 in the denominator of the logarithm term; multiplication by w_2 is correctly shown here.

$$\chi = [\ (e/\Omega_1^{\infty})\ w_2 \ /\ (w_1 + (e/\Omega_1^{\infty})\ w_2)$$
$$- w_2 \ /\ (\ (\rho_2/\rho_1)\ w_1 + w_2\ )$$
$$+ \ln\ (\ (w_1 + (\rho_1/\rho_2)\ w_2) \ /\ (w_1 + (e/\Omega_1^{\infty})\ w_2)\ )\ ]$$
$$\cdot\ (\ (\rho_2/\rho_1)\ w_1 + w_2\ )^2 \ /\ w_2^2 \qquad \text{(F-28)}$$

$$\chi = [\ (e/\Omega_1^{\infty})\ w_2 \ /\ (w_1 + (e/\Omega_1^{\infty})\ w_2)$$
$$- 1 \ /\ (\ (\rho_2/\rho_1)\ w_1/w_2 + 1\ )$$
$$+ \ln\ (\ (w_1 + (\rho_1/\rho_2)\ w_2) \ /\ (w_1 + (e/\Omega_1^{\infty})\ w_2)\ )\ ]$$
$$\cdot\ (\ (\rho_2/\rho_1)\ w_1/w_2 + 1\ )^2 \qquad \text{(F-29)}$$

$$\chi = (\ (\rho_2/\rho_1)\ w_1/w_2 + 1\ )^2 \cdot (e/\Omega_1^{\infty})\ w_2 \ /\ (w_1 + (e/\Omega_1^{\infty})\ w_2)$$
$$- (\ (\rho_2/\rho_1)\ w_1/w_2 + 1\ )$$
$$+ (\ (\rho_2/\rho_1)\ w_1/w_2 + 1\ )^2$$
$$\cdot \ln\ (\ (w_1 + (\rho_1/\rho_2)\ w_2) \ /\ (w_1 + (e/\Omega_1^{\infty})\ w_2)\ ) \qquad (27)$$

Table F-1. Equations Used in "Generalized Correlation for Solvent Activities in Polymer Solutions".

$$\ln \gamma_1^{S} = 1 - R_1 + \ln R_1 \qquad (1)$$

$$R_1 = S_1 \ /\ (S_1x_1 + S_2x_2) \qquad (2)$$

$$\ln \gamma_i^{G} = \sum_k \nu_{ki} \ln \Gamma_k - \sum_k \nu_{ki} \ln \Gamma_k^{*} \qquad (3)$$

$$\ln \Gamma_k = - \ln \sum_l X_l A_{kl} + 1 - \sum_l \frac{X_l A_{lk}}{\sum_m X_m A_{lm}} \qquad (4)$$

$$S_1 \ll S_2 \qquad (5)$$

$$\gamma_1^{S\infty} = \exp\ [1 + \ln\ (S_1/S_2)] = \exp(1) \cdot S_1/S_2 = e \cdot S_1/S_2 \qquad (6)$$

$$\Omega_1^{\infty} = \gamma_1^{\infty}\ (M_1(0) + M_2(1))\ /\ M_1 = \gamma_1^{\infty}\ M_2\ /\ M_1 \qquad (7)$$

$$\Omega_1^{\infty} = e \cdot S_1/S_2 \cdot M_2/M_1 \qquad (8)$$

Table F-1 (cont'd.).

$$\Omega_1^{\infty} = e \tag{9}$$

$$S_2/S_1 = M_2/M_1 \tag{10}$$

$$S_2/S_1 = (e/\Omega_1^{\infty})\ (M_2/M_1) \tag{11}$$

$$x_1 = (M_2/M_1)\ w_1 \ /\ ((M_2/M_1)\ w_1 + w_2) \tag{12}$$

$$x_2 = w_2 \ /\ ((M_2/M_1)\ w_1 + w_2) \tag{13}$$

$$R_1 = (w_1 + (M_1/M_2)\ w_2) \ /\ (w_1 + (e/\Omega_1^{\infty})\ w_2) \tag{14}$$

$$\Omega_1 = \gamma_1 \ /\ (w_1 + (M_1/M_2)\ w_2) \tag{15}$$

$$\Omega_1 = \exp\ [\ (e/\Omega_1^{\infty})\ w_2 \ /\ (w_1 + (e/\Omega_1^{\infty})\ w_2)\ ]\ /\ (w_1 + (e/\Omega_1^{\infty})\ w_2) \tag{16}$$

$$e/\Omega_1^{\infty} >> M_1/M_2 \tag{17}$$

$$Y = w_1^{exptl} + (e/\Omega_1^{\infty})\ w_2 \tag{18}$$

$$\Omega_1^{exptl} = \exp\ [\ (Y - w_1^{exptl})\ /\ Y\ ]\ /\ Y \tag{19}$$

$$Y = \exp\ (1 - w_1^{exptl}/Y - \ln \Omega_1^{exptl}) = F(y) \tag{20}$$

$$Y_0 = \exp\ (1 - \ln \Omega_1^{exptl}) \tag{21}$$

$$Y_n = \exp\ (1 - w_1^{exptl}/Y_{n-1} - \ln \Omega_1^{exptl}) \tag{22}$$

$$\Omega_1^{\infty} = e\ (1 - w_1^{exptl})\ /\ (Y - w_1^{exptl}) \tag{23}$$

$$\ln a_1 = \ln \phi_1 + \phi_2 + \chi\phi_2^{\,2} \tag{24}$$

$$\phi_1 = (\rho_2/\rho_1)\ w_1 \ /\ (\ (\rho_2/\rho_1)\ w_1 + w_2\ ) \tag{25}$$

$$\phi_2 = w_2 \ /\ (\ (\rho_2/\rho_1)\ w_1 + w_2\ ) \tag{26}$$

$$\chi = (\ (\rho_2/\rho_1)\ w_1/w_2 + 1\ )^2 \cdot (e/\Omega_1^{\infty})\ w_2 \ /\ (w_1 + (e/\Omega_1^{\infty})\ w_2)$$
$$- (\ (\rho_2/\rho_1)\ w_1/w_2 + 1\ )$$
$$+ (\ (\rho_2/\rho_1)\ w_1/w_2 + 1\ )^2$$
$$\cdot \ln (\ (w_1 + (\rho_1/\rho_2)\ w_2) \ /\ (w_1 + (e/\Omega_1^{\infty})\ w_2)\ ) \tag{27}$$

APPENDIX G.

Derivation of Equations in "Prediction of Solvent Activities in Polymer Solutions Using an Empirical Free Volume Correction"

This appendix contains a more detailed derivation of the equations presented in the manuscript article "Prediction of Solvent Activities in Polymer Solutions Using an Empirical Free Volume Correction". This article was included as part of Chapter 2 of the dissertation. In this appendix, equation numbers refer to the manuscript article itself, beginning on page 21 of the dissertation. New equations not included in the article are numbered with a preceding letter G, e.g., G-1, G-2, etc.

Eqs 1a and 1b are defining equations for solvent mole fraction activity coefficient size component and group interaction component and for the size component of solvent activity. Eqs 2 and 3 illustrate these definitions using the terms which make up the Flory-Huggins equation. Eqs 4 to 9 were presented as background from "Generalized Correlation for Solvent Activities in Polymer Solutions": these equations were either taken from the ASOG model (Derr and Deal, 1969) or were derived in Appendix F of this dissertation.

DERIVATION OF EQUATION 10

The first new equation in this article is eq 10, an extension of eq 9, which was derived in Appendix F. The key step in the derivation of eq 9 was assuming the activity coefficient Ω_1^{∞} was known and rearranging for the unknown size ratio S_2/S_1. The same approach is used to derive eq 10, but instead of considering only the size interaction component of solvent activity, a_1^S, the complete solvent activity consisting of both size and group interaction components is used as shown below. Eq 1a is written as a product rather than a sum of logarithms in eq G-1, then combined with the definition of weight fraction activity coefficient to give eq G-2. The conversion of weight fraction to mole fraction is made using eq G-3 to give eq G-4, which is evaluated at infinite dilution (as solvent concentration x_1 approaches zero) to give eq G-5 for the infinite dilution weight fraction activity coefficient Ω_1^{∞}.

$$\ln a_1 = \ln x_1 + \ln \gamma_1^S + \ln \gamma_1^G \qquad (1a)$$

$$a_1 = x_1 \gamma_1^S \gamma_1^G \qquad (G\text{-}1)$$

$$\Omega_1 = a_1/w_1 = x_1 \gamma_1^S \gamma_1^G / w_1 \qquad (G\text{-}2)$$

$$w_1 = M_1 x_1 / (M_1 x_1 + M_2 x_2) \qquad (G\text{-}3)$$

$$\Omega_1 = \gamma_1^S \gamma_1^G (M_1 x_1 + M_2 x_2) / M_1 \qquad (G\text{-}4)$$

$$\Omega_1^{\infty} = \gamma_1^{S\infty} \gamma_1^{G\infty} (M_1(0) + M_2(1)) / M_1 = \gamma_1^{S\infty} \gamma_1^{G\infty} M_2 / M_1 \qquad (G\text{-}5)$$

At this point, the expression for γ_1^S in the ASOG model, eq 4, is evaluated at infinite dilution and substituted into eq G-5, using the fact that S_1/S_2 is close to zero to simplify eq G-8.

$$\ln \gamma_1^{S} = 1 - R_1 + \ln R_1 \qquad (4)$$

$$\ln \gamma_1^{S\infty} = 1 - R_1^{\infty} + \ln R_1^{\infty} \qquad (G\text{-}6)$$

$$R_1 = S_1 / (S_1x_1 + S_2x_2) \qquad (5)$$

$$R_1^{\infty} = S_1 / (S_1(0) + S_2(1)) = S_1 / S_2 \qquad (G\text{-}7)$$

$$\ln \gamma_1^{S\infty} = 1 - S_1/S_2 + \ln S_1/S_2 = 1 + \ln S_1/S_2 \qquad (G\text{-}8)$$

$$\gamma_1^{S\infty} = e \cdot S_1/S_2 \qquad (G\text{-}9)$$

$$\Omega_1^{\infty} = e\, \gamma_1^{G\infty} \cdot S_1/S_2 \cdot M_2/M_1 \qquad (G\text{-}10)$$

This expression is rearranged to give the size ratio S_2/S_1 as a function of the other factors and resubstituted into eq 5. Transformations from mole fraction to weight fraction composition are used, and eq 10 is finally produced by assuming M_1/M_2 is close to zero.

$$S_2/S_1 = (e\gamma_1^{G\infty}/\Omega_1^{\infty})\ (M_2/M_1) \qquad (G\text{-}11)$$

$$R_1 = S_1 / (S_1x_1 + S_2x_2) \qquad (5)$$

$$R_1 = 1 / (x_1 + (S_2/S_1)\ x_2) \qquad (G\text{-}12)$$

$$R_1 = 1 / (x_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})\ (M_2/M_1)\ x_2) \qquad (G\text{-}13)$$

$$x_1 = (M_2/M_1)\ w_1 / ((M_2/M_1)\ w_1 + w_2) \qquad (G\text{-}14)$$

$$x_2 = w_2 / ((M_2/M_1)\ w_1 + w_2) \qquad (G\text{-}15)$$

$$R_1 = \frac{(M_2/M_1)\ w_1 + w_2}{(M_2/M_1)\ w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})\ (M_2/M_1)\ w_2} \qquad (G\text{-}16)$$

$$R_1 = \frac{w_1 + (M_1/M_2)\ w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})\ w_2} \qquad (G\text{-}17)$$

$$R_1 = \frac{w_1}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2} \qquad (10)$$

Eqs 11 and 12 illustrate how the infinite dilution group interaction

(residual) component of the activity coefficient, $\gamma_1^{G\infty}$, is derived from a functional expression for the residual component of the activity coefficient, γ_1^{G}. Eqs 13a and 13b define such a functional expression for an athermal solution, giving activity coefficients of unity at all concentrations. Eq 14a defines a Flory-Huggins type of residual interaction.

DERIVATION OF EQUATION 14B

To derive eq 14b, take w_1 as zero in eq 10, and use the resulting R_2 in eq 14a.

$$R_1^{\infty} = (0) / ((0) + (e\gamma_1^{G\infty}/\Omega_1^{\infty})\ (1)) = 0 \qquad \text{(G-18)}$$

$$R_2^{\infty} = 1 - R_1^{\infty} = 1 - 0 = 1 \qquad \text{(G-19)}$$

$$\ln \gamma_1^{G} = \chi^* R_2^{\,2} \qquad \text{(14a)}$$

$$\ln \gamma_1^{G\infty} = \chi^* (R_2^{\infty})^2 = \chi^* (1)^2 = \chi^* \qquad \text{(G-20)}$$

$$\gamma_1^{G\infty} = \exp(\chi^*) \qquad \text{(14b)}$$

Eqs 15a to 15d are the standard ASOG model equations (Derr and Deal, 1969). Eq 15e merely states that these equations are to be evaluated at $x_1 = 0$ to give the infinite dilution residual component of the activity coefficient. Eq 16 is identical to eq 16 (coincidentally) of "Generalized Correlation for Solvent Activities in Polymer Solutions" and is derived in Appendix F.

DERIVATION OF EQUATION 17

Eq 17 is analogous to eq 16, but using the more complex eqs 14a and 14b for the residual component rather than the athermal eqs 13a and 13b. The activity coefficient Ω_1 is given as the product of a size interaction component, γ_1^S, and a group interaction component, γ_1^G, i.e., eq G-2. If only the expression $x_1\gamma_1^S/w_1$ in eq G-2 is considered, the derivation of eq 16 in Appendix F applies, with the only difference in the result being the appearance of the additional factor $\gamma_1^{G\infty}$ in eq 10 for R_1. Taking the result from Appendix F with the additional factor gives eq G-21.

$$\Omega_1 = a_1/w_1 = x_1\gamma_1^S\gamma_1^G/w_1 \tag{G-2}$$

$$R_1 = \frac{w_1}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2} \tag{10}$$

$$x_1\gamma_1^S/w_1 = \frac{\exp\left[\dfrac{(e\gamma_1^{G\infty}/\Omega_1^{\infty})\,w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})\,w_2}\right]}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})\,w_2} = \frac{\Omega_1}{\gamma_1^G} \tag{G-21}$$

The factor γ_1^G in eq G-2 is given by eqs 14a and 10, generating eq G-24.

$$\ln \gamma_1^G = \chi^* R_2^2 \tag{14a}$$

$$R_1 = \frac{w_1}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2} \tag{10}$$

$$R_2 = 1 - R_1 = \frac{(e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2} \tag{G-22}$$

$$\ln \gamma_1^G = \chi^* \left[\frac{(e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2} \right]^2 \tag{G-23}$$

$$\gamma_1^G = \exp \left[\chi^* \left[\frac{(e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2} \right]^2 \right] \tag{G-24}$$

Multiplying eqs G-21 and G-24 together produces eq G-25 for Ω_1. Since the product of exponentials equals the exponential of the sum of the arguments, the expression can be simplified into eq G-26. Taking a common factor gives eq G-27, which is identical to eq 17 once the substitution $\chi^* = \ln \gamma_1^{G\infty}$ from eq 14b is made.

$$\Omega_1 = x_1 \gamma_1^S \gamma_1^G / w_1$$

$$= \frac{\exp \left[\frac{(e\gamma_1^{G\infty}/\Omega_1^{\infty})\, w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})\, w_2} \right] \cdot \exp \left[\chi^* \left[\frac{(e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2} \right]^2 \right]}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})\, w_2} \tag{G-25}$$

$$\Omega_1 = \frac{\exp \left[\frac{(e\gamma_1^{G\infty}/\Omega_1^{\infty})\, w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})\, w_2} + \chi^* \left[\frac{(e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2} \right]^2 \right]}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})\, w_2} \tag{G-26}$$

$$\Omega_1 = \frac{\exp \left[\frac{(e\gamma_1^{G\infty}/\Omega_1^{\infty})\, w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})\, w_2} \left[1 + \chi^* \left[\frac{(e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2} \right] \right] \right]}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})\, w_2} \tag{G-27}$$

$$\Omega_1 = \frac{\exp \left[\frac{(e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2} \left[1 + \frac{(e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2} \ln \gamma_1^{G\infty} \right] \right]}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty})w_2} \tag{17}$$

Eq 18 is a statistical formula for standard error in the expression $\ln a_1$ which is generally available in statistics texts discussing

analysis of variance.

Table G-1. Equations Used in "Prediction of Solvent Activities in Polymer Solutions Using an Empirical Free Volume Correction".

$$\ln a_1 = \ln x_1 + \ln \gamma_1^S + \ln \gamma_1^G \quad (1a)$$

$$\ln a_1 = \ln a_1^S + \ln \gamma_1^G \quad (1b)$$

$$\ln a_1^S = \ln (x_1 \gamma_1^S) = 1 - \phi_1 + \ln \phi_1 \quad (2)$$

$$\gamma_1^G = \chi \phi_2^2 \quad (3)$$

$$\ln \gamma_1^S = 1 - R_1 + \ln R_1 \quad (4)$$

$$R_1 = S_1 / (S_1 x_1 + S_2 x_2) \quad (5)$$

$$\gamma_1^\infty = e \frac{S_1}{S_2} \quad (6)$$

$$a_1 = \Omega_1 w_1 \quad (7)$$

$$\Omega_1^\infty = e \quad (8)$$

$$R_1 = \frac{w_1}{w_1 + (e/\Omega_1^\infty) w_2} \quad (9)$$

$$R_1 = \frac{w_1}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^\infty) w_2} \quad (10)$$

$$\gamma_1^G = f(w_1) \quad (11)$$

$$\gamma_1^{G\infty} = f(0) \quad (12)$$

$$\gamma_1^G = \gamma_1^{G\infty} = 1 \quad (13a)$$

$$\ln \gamma_1^G = \ln \gamma_1^{G\infty} = 0 \quad (13b)$$

$$\ln \gamma_1^G = \chi^* R_2^2 \quad (14a)$$

$$\gamma_1^{G\infty} = \exp (\chi^*) \quad (14b)$$

$$\ln \gamma_1^G = \sum_k \nu_{ki} (\ln \Gamma_k - \ln \Gamma_k^*) \quad (15a)$$

Table G-1 (cont'd.).

$$\ln \Gamma_k = - \ln \sum_l X_l A_{kl} + 1 - \sum_l \frac{X_l A_{lk}}{\sum_m X_m A_{lm}} \tag{15b}$$

$$\ln \Gamma_k^* = \ln \Gamma_k (x_1 = 1) \tag{15c}$$

$$X_k = \sum_i x_i \nu_{ki} \Big/ \sum_j \sum_l x_j \nu_{lj} \tag{15d}$$

$$\ln \gamma_1^{G\infty} = \ln \gamma_1^{G} (x_1 = 0) \tag{15e}$$

$$\Omega_1 = \frac{\exp \{ (e/\Omega_1^{\infty}) w_2 / [w_1 + (e/\Omega_1^{\infty}) w_2] \}}{w_1 + (e/\Omega_1^{\infty}) w_2} \tag{16}$$

$$\Omega_1 = \frac{\exp \left[\dfrac{(e\gamma_1^{G\infty}/\Omega_1^{\infty}) w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty}) w_2} \left[1 + \dfrac{(e\gamma_1^{G\infty}/\Omega_1^{\infty}) w_2}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty}) w_2} \ln \gamma_1^{G\infty} \right] \right]}{w_1 + (e\gamma_1^{G\infty}/\Omega_1^{\infty}) w_2} \tag{17}$$

$$s = \left[\frac{\sum (\ln a_1^{pred} - \ln a_1^{exptl})^2}{(n - d)} \right]^{1/2} \tag{18}$$

APPENDIX H.

Derivation of Equations in "Normalization and Bounding Properties Inherent in Solution of Groups Activity Coefficient Models"

This appendix contains a more detailed derivation of the equations presented in the manuscript article "Normalization and Bounding Properties Inherent in Solution of Groups Activity Coefficient Models". This article was included as part of Chapter 3 of the dissertation. In this appendix, equation numbers refer to the manuscript article itself, beginning on page xx of the dissertation. New equations not included in the article are numbered with a preceding letter H, e.g., H-1, H-2, etc.

Eq 1 is the ASOG definition of group mole fraction X_k taken for a binary solution whose molecules contain two distinct functional groups. Eqs 2 to 4 are the ASOG equations for calculation of the group interaction (residual) component of the activity coefficient, γ_1^G, from group mole fractions, X_k, and group interaction parameters, A_{kl}, with group activity coefficients, Γ_k and Γ_k^i, as intermediate results.

$$X_k = \frac{n_{k1}x_1 + n_{k2}x_2}{(n_{11}+n_{21})x_1 + (n_{12}+n_{22})x_2} \qquad (1)$$

$$\ln \gamma_i^G = n_{1i}(\ln \Gamma_1 - \ln \Gamma_1^i) + n_{2i}(\ln \Gamma_2 - \ln \Gamma_2^i) \qquad (2)$$

$$\ln \Gamma_k = -\ln(X_1A_{k1} + X_2A_{k2}) + 1 - \frac{X_1A_{1k}}{X_1A_{11}+X_2A_{12}} - \frac{X_2A_{2k}}{X_1A_{21}+X_2A_{22}} \qquad (3)$$

$$\ln \Gamma_k^{\,i} - \ln \Gamma_k \quad (x_i - 1) \tag{4}$$

Eqs 5 and 6 merely define size-weighted fraction composition variables, c_i, and group ratio variables, g_i, neither of which depends on the size of the unit chosen to measure the functional group composition of a molecule. To derive eq 7, begin with eq 5 for c_i. Eqs H-1 and H-2 are eq 5 with i set to 1 and j set to 2. Similarly, eqs H-3 and H-4 are derived from the group ratio definition of eq 6. When eq H-1 is divided by eq H-3, and eq H-2 is divided by eq H-4, eqs H-5 and H-6 result. When eq 1 is written with k equal to 1 as eq H-7, it is evident that the right hand side of eq 7 equals the sum of the right hand sides of eqs H-5 and H-6. The left hand sides of these equations must follow the same relationship, resulting in eq 7.

$$c_i = \frac{(n_{1i}+n_{2i})x_i}{(n_{11}+n_{21})x_1 + (n_{12}+n_{22})x_2} \tag{5}$$

$$c_1 = \frac{(n_{11}+n_{21})x_1}{(n_{11}+n_{21})x_1 + (n_{12}+n_{22})x_2} \tag{H-1}$$

$$c_2 = \frac{(n_{12}+n_{22})x_2}{(n_{11}+n_{21})x_1 + (n_{12}+n_{22})x_2} \tag{H-2}$$

$$g_i = n_{2i} / n_{1i} \tag{6}$$

$$1 + g_1 = (n_{11} + n_{21}) / n_{11} \tag{H-3}$$

$$1 + g_2 = (n_{12} + n_{22}) / n_{12} \tag{H-4}$$

$$\frac{c_1}{1+g_1} = \frac{n_{11}x_1}{(n_{11}+n_{21})x_1 + (n_{12}+n_{22})x_2} \tag{H-5}$$

$$\frac{c_2}{1+g_2} = \frac{n_{12}x_2}{(n_{11}+n_{21})x_1 + (n_{12}+n_{22})x_2} \tag{H-6}$$

$$X_k = \frac{n_{k1}x_1 + n_{k2}x_2}{(n_{11}+n_{21})x_1 + (n_{12}+n_{22})x_2} \qquad (1)$$

$$X_1 = \frac{n_{11}x_1 + n_{12}x_2}{(n_{11}+n_{21})x_1 + (n_{12}+n_{22})x_2} \qquad (H\text{-}7)$$

$$X_1 = \frac{c_1}{1 + g_1} + \frac{c_2}{1 + g_2} \qquad (7)$$

Eq 8 follows immediately from eq 2 when both sides are divided by n_{1i} and the ratio n_{2i}/n_{1i} is replaced by g_i.

$$\ln \gamma_i^G = n_{1i}(\ln \Gamma_1 - \ln \Gamma_1^i) + n_{2i}(\ln \Gamma_2 - \ln \Gamma_2^i) \qquad (2)$$

$$\frac{\ln \gamma_i^G}{n_{1i}} = (\ln \Gamma_1 - \ln \Gamma_1^i) + g_i(\ln \Gamma_2 - \ln \Gamma_2^i) \qquad (8)$$

The derivation of eq 9 is algebraically lengthy, but follows directly from combining eqs 3, 4, 7, and 8. Begin with the expression for group activity coefficient given by eq 3, and substitute the expression given by eq 7 for group mole fraction X_1, and use $1-X_1$ for X_2.

$$\ln \Gamma_k = -\ln(X_1A_{k1} + X_2A_{k2}) + 1 - \frac{X_1A_{1k}}{X_1A_{11}+X_2A_{12}} - \frac{X_2A_{2k}}{X_1A_{21}+X_2A_{22}} \qquad (3)$$

$$X_1 = \frac{c_1}{1 + g_1} + \frac{c_2}{1 + g_2} \qquad (7)$$

$$X_2 = 1 - X_1 = 1 - \frac{c_1}{1 + g_1} + \frac{c_2}{1 + g_2} \qquad (H\text{-}8)$$

$$\ln \Gamma_k = - \ln \left[\left(\frac{c_1}{1+g_1} + \frac{c_2}{1+g_2} \right) A_{k1} + \left(1 - \frac{c_1}{1+g_1} + \frac{c_2}{1+g_2} \right) A_{k2} \right]$$

$$+ 1 - \frac{\left(\frac{c_1}{1+g_1} + \frac{c_2}{1+g_2} \right) A_{1k}}{\left(\frac{c_1}{1+g_1} + \frac{c_2}{1+g_2} \right) A_{11} + \left(1 - \frac{c_1}{1+g_1} + \frac{c_2}{1+g_2} \right) A_{12}}$$

$$- \frac{\left(1 - \frac{c_1}{1+g_1} + \frac{c_2}{1+g_2} \right) A_{2k}}{\left(\frac{c_1}{1+g_1} + \frac{c_2}{1+g_2} \right) A_{21} + \left(1 - \frac{c_1}{1+g_1} + \frac{c_2}{1+g_2} \right) A_{22}} \qquad \text{(H-9)}$$

The first step in reducing the complexity of H-9 is the calculation of the pure component 1 basis group activity coefficient, $\ln \Gamma_k^{\,1}$, defined as the group activity coefficient $\ln \Gamma_k$ taken with the mole fraction of component 1 equal to one. Substituting $x_1 = 1$ and $x_2 = 0$ into eqs H-1 and H-2 gives results for the size-weighted fractions c_i, which can then be used in eqs 7 and H-8 for X_k. These group mole fractions can be substituted into eq 3, giving $\ln \Gamma_k^{\,1}$ which simplifies to eq H-15.

$$c_1 = \frac{(n_{11}+n_{21})(1)}{(n_{11}+n_{21})(1) + (n_{12}+n_{22})(0)} = 1 \qquad \text{(H-10)}$$

$$c_2 = \frac{(n_{12}+n_{22})(0)}{(n_{11}+n_{21})(1) + (n_{12}+n_{22})(0)} = 0 \qquad \text{(H-11)}$$

$$X_1 = \frac{1}{1+g_1} + \frac{0}{1+g_2} = \frac{1}{1+g_1} \qquad \text{(H-12)}$$

$$X_2 = 1 - X_1 = 1 - \frac{1}{1+g_1} = \frac{g_1}{1+g_1} \qquad \text{(H-13)}$$

$$\ln \Gamma_k^{\,1} = -\ln\left[\left(\frac{1}{1+g_1}\right)A_{k1} + \left(\frac{g_1}{1+g_1}\right)A_{k2}\right] + 1 - \frac{\left(\frac{1}{1+g_1}\right)A_{1k}}{\left(\frac{1}{1+g_1}\right)A_{11} + \left(\frac{g_1}{1+g_1}\right)A_{12}} - \frac{\left(\frac{g_1}{1+g_1}\right)A_{2k}}{\left(\frac{1}{1+g_1}\right)A_{21} + \left(\frac{g_1}{1+g_1}\right)A_{22}} \qquad \text{(H-14)}$$

$$\ln \Gamma_k^{\,1} = -\ln\left[\frac{A_{k1} + A_{k2}g_1}{1+g_1}\right] + 1 - \frac{A_{1k}}{A_{11} + A_{12}g_1} - \frac{A_{2k}g_1}{A_{21} + A_{22}g_1} \qquad \text{(H-15)}$$

Since eq 2 for the calculation of the activity coefficient requires the difference $\ln \Gamma_k - \ln \Gamma_k^{\,1}$, not the individual terms, this difference can be calculated by combining eqs H-9 and H-15, cancelling and combining several terms in the process.

$$\ln \Gamma_k - \ln \Gamma_k^1 = \ln \left[\frac{A_{k1} + A_{k2} g_1}{\left(c_1 + \frac{1 + g_1}{1 + g_2} c_2\right) A_{k1} + \left(1 + g_1 - c_1 - \frac{1 + g_1}{1 + g_2} c_2\right) A_{k2}} \right.$$

$$+ \frac{A_{1k}}{A_{11} + A_{12} g_1} - \frac{\left(c_1 + \frac{1 + g_1}{1 + g_2} c_2\right) A_{1k}}{\left(c_1 + \frac{1 + g_1}{1 + g_2} c_2\right) A_{11} + \left(1 + g_1 - c_1 - \frac{1 + g_1}{1 + g_2} c_2\right) A_{12}}$$

$$+ \frac{A_{2k} g_1}{A_{21} + A_{22} g_1} - \left. \frac{\left(1 + g_1 - c_1 - \frac{1 + g_1}{1 + g_2} c_2\right) A_{2k}}{\left(c_1 + \frac{1 + g_1}{1 + g_2} c_2\right) A_{21} + \left(1 + g_1 - c_1 - \frac{1 + g_1}{1 + g_2} c_2\right) A_{22}} \right] \qquad \text{(H-16)}$$

Multiply out terms in the expressions so that the composition variables are principal factors rather than the interaction parameters, giving eq H-17. Then eliminate c_1 for c_2, using $c_2 = 1 - c_1$, to give eq H-18.

$$\ln \Gamma_k - \ln \Gamma_k^{1} =$$

$$\ln \left[\frac{A_{k1} + A_{k2}g_1}{A_{k2}(1 + g_1) + (A_{k1} - A_{k2})\, c_1 + (A_{k1} - A_{k2}) \left(\frac{1 + g_1}{1 + g_2}\right) c_2} \right]$$

$$+ \frac{A_{1k}}{A_{11} + A_{12}g_1} - \frac{A_{1k}\, c_1 + A_{1k} \left(\frac{1 + g_1}{1 + g_2}\right) c_2}{A_{12}(1 + g_1) + (A_{11} - A_{12})\, c_1 + (A_{11} - A_{12}) \left(\frac{1 + g_1}{1 + g_2}\right) c_2}$$

$$+ \frac{A_{2k}g_1}{A_{21} + A_{22}g_1} - \frac{A_{2k}(1 + g_1) - A_{2k}\, c_1 - A_{2k} \left(\frac{1 + g_1}{1 + g_2}\right) c_2}{A_{22}(1 + g_1) + (A_{21} - A_{22})\, c_1 + (A_{21} - A_{22}) \left(\frac{1 + g_1}{1 + g_2}\right) c_2}$$

(H-17)

$$\ln \Gamma_k - \ln \Gamma_k^{1} = \ln \left[\frac{A_{k1} + A_{k2}g_1}{A_{k1} + A_{k2}g_1 + (A_{k1} - A_{k2}) \left(\frac{1 + g_1}{1 + g_2} - 1\right) c_2} \right]$$

$$+ \frac{A_{1k}}{A_{11} + A_{12}g_1} - \frac{A_{1k} + A_{1k} \left(\frac{1 + g_1}{1 + g_2} - 1\right) c_2}{A_{11} + A_{12}g_1 + (A_{11} - A_{12}) \left(\frac{1 + g_1}{1 + g_2} - 1\right) c_2}$$

$$+ \frac{A_{2k}g_1}{A_{21} + A_{22}g_1} - \frac{A_{2k}g_1 - A_{2k} \left(\frac{1 + g_1}{1 + g_2} - 1\right) c_2}{A_{21} + A_{22}g_1 + (A_{21} - A_{22}) \left(\frac{1 + g_1}{1 + g_2} - 1\right) c_2}$$

(H-18)

Multiply the numerator and denominator of some of the terms by $(1+g_2)$ to eliminate fractional factors and simplify the result.

$$\ln \Gamma_k - \ln \Gamma_k^{\,1} = \ln \left[\frac{(1 + g_2)(A_{k1} + A_{k2}g_1)}{(1 + g_2)(A_{k1} + A_{k2}g_1) + (A_{k2} - A_{k1})(g_2 - g_1)\, c_2} \right]$$

$$+ \frac{A_{1k}}{A_{11} + A_{12}g_1} - \frac{(1 + g_2)A_{1k} - A_{1k}(g_2 - g_1)\, c_2}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})(g_2 - g_1)\, c_2}$$

$$+ \frac{A_{2k}g_1}{A_{21} + A_{22}g_1} - \frac{(1 + g_2)A_{2k}g_1 + A_{2k}(g_2 - g_1)\, c_2}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})(g_2 - g_1)\, c_2} \qquad \text{(H-19)}$$

Eq H-19 defines the group activity coefficient differences which can be used in eq 8 to find the normalized residual activity coefficient for component 1. The algebra of this derivation is again quite involved. Begin by taking i equal to 1 in eq 8, to give eq H-20. Then substitute eq H-19 into eq H-20 twice, once each with k having the value 1 and 2.

$$\frac{\ln \gamma_i^{\,G}}{n_{1i}} = (\ln \Gamma_1 - \ln \Gamma_1^{\,i}) + g_1(\ln \Gamma_2 - \ln \Gamma_2^{\,i}) \qquad (8)$$

$$\frac{\ln \gamma_1^{\,G}}{n_{11}} = (\ln \Gamma_1 - \ln \Gamma_1^{\,1}) + g_1(\ln \Gamma_2 - \ln \Gamma_2^{\,1}) \qquad \text{(H-20)}$$

$$\frac{\ln \gamma_1^G}{n_{11}} = \ln \left[\frac{(1 + g_2)(A_{11} + A_{12}g_1)}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})(g_2 - g_1)\, c_2} \right]$$

$$+ \frac{A_{11}}{A_{11} + A_{12}g_1} - \frac{(1 + g_2)A_{11} - A_{11}\,(g_2 - g_1)\, c_2}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})\,(g_2 - g_1)\, c_2}$$

$$+ \frac{A_{21}g_1}{A_{21} + A_{22}g_1} - \frac{(1 + g_2)A_{21}g_1 + A_{21}\,(g_2 - g_1)\, c_2}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})\,(g_2 - g_1)\, c_2}$$

$$+ g_1 \ln \left[\frac{(1 + g_2)(A_{21} + A_{22}g_1)}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})(g_2 - g_1)\, c_2} \right]$$

$$+ \frac{A_{12}g_1}{A_{11} + A_{12}g_1} - \frac{g_1(1 + g_2)A_{12} - A_{12}g_1\,(g_2 - g_1)\, c_2}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})\,(g_2 - g_1)\, c_2}$$

$$+ \frac{A_{22}g_1^2}{A_{21} + A_{22}g_1} - \frac{(1 + g_2)A_{22}g_1^2 + A_{22}g_1\,(g_2 - g_1)\, c_2}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})\,(g_2 - g_1)\, c_2} \qquad \text{(H-21)}$$

Several of the terms in eq H-21 have the same denominator and can be combined into eq H-22. Common factors can be removed to give eq H-23.

$$\frac{\ln \gamma_1^G}{n_{11}} = \ln \left[\frac{(1 + g_2)(A_{11} + A_{12}g_1)}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})(g_2 - g_1)\, c_2} \right]$$

$$+ g_1 \ln \left[\frac{(1 + g_2)(A_{21} + A_{22}g_1)}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})(g_2 - g_1)\, c_2} \right]$$

$$+ \frac{A_{11} + A_{12}g_1}{A_{11} + A_{12}g_1} - \frac{(1 + g_2)(A_{11} + A_{12}g_1) - (g_2 - g_1)(A_{11} + A_{12}g_1)c_2}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})\,(g_2 - g_1)\, c_2}$$

$$+ \frac{g_1(A_{21} + A_{22}g_1)}{A_{21} + A_{22}g_1}$$

$$- \frac{(1 + g_2)g_1(A_{21} + A_{22}g_1) + (g_2 - g_1)(A_{21} + A_{22}g_1)c_2}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})\,(g_2 - g_1)\, c_2} \qquad \text{(H-22)}$$

$$\frac{\ln \gamma_1^G}{n_{11}} = \ln \left[\frac{(1 + g_2)(A_{11} + A_{12}g_1)}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})(g_2 - g_1)\, c_2} \right]$$

$$+ g_1 \ln \left[\frac{(1 + g_2)(A_{21} + A_{22}g_1)}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})(g_2 - g_1)\, c_2} \right]$$

$$+ 1 - \frac{(1 + g_2)(A_{11} + A_{12}g_1) - (g_2 - g_1)(A_{11} + A_{12}g_1)c_2}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})\,(g_2 - g_1)\, c_2}$$

$$+ g_1 - \frac{(1 + g_2)g_1(A_{21} + A_{22}g_1) + (g_2 - g_1)(A_{21} + A_{22}g_1)c_2}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})\,(g_2 - g_1)\, c_2} \qquad \text{(H-23)}$$

The terms 1 and g_1 can be combined with the complicated terms following them to produce eq H-24. Simplifying the numerators of these terms gives eq H-25, and combining common factors in the last two terms gives eq H-26.

$$\frac{\ln \gamma_1^G}{n_{11}} = \ln \left[\frac{(1 + g_2)(A_{11} + A_{12}g_1)}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})(g_2 - g_1)\, c_2} \right]$$

$$+ g_1 \ln \left[\frac{(1 + g_2)(A_{21} + A_{22}g_1)}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})(g_2 - g_1)\, c_2} \right]$$

$$+ \frac{(A_{12} - A_{11})\,(g_2 - g_1)\, c_2 + (g_2 - g_1)(A_{11} + A_{12}g_1)c_2}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})\,(g_2 - g_1)\, c_2}$$

$$+ \frac{(A_{22} - A_{21})\, g_1\, (g_2 - g_1)\, c_2 - (g_2 - g_1)(A_{21} + A_{22}g_1)c_2}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})\,(g_2 - g_1)\, c_2} \qquad \text{(H-24)}$$

$$\frac{\ln \gamma_1^G}{n_{11}} = \ln \left[\frac{(1 + g_2)(A_{11} + A_{12}g_1)}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})(g_2 - g_1)\, c_2} \right]$$

$$+ g_1 \ln \left[\frac{(1 + g_2)(A_{21} + A_{22}g_1)}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})(g_2 - g_1)\, c_2} \right]$$

$$+ \frac{A_{12}\,(1 + g_1)(g_2 - g_1)\, c_2}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})\,(g_2 - g_1)\, c_2}$$

$$- \frac{A_{21}\,(1 + g_1)(g_2 - g_1)\, c_2}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})\,(g_2 - g_1)\, c_2} \qquad \text{(H-25)}$$

$$\frac{\ln \gamma_1^G}{n_{11}} = \ln \left[\frac{(1 + g_2)(A_{11} + A_{12}g_1)}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})(g_2 - g_1)\, c_2} \right]$$

$$+ g_1 \ln \left[\frac{(1 + g_2)(A_{21} + A_{22}g_1)}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})(g_2 - g_1)\, c_2} \right]$$

$$+ (1 + g_1)(g_2 - g_1)\, c_2 \cdot$$

$$\left(\frac{A_{12}}{(1 + g_2)(A_{11} + A_{12}g_1) + (A_{12} - A_{11})\,(g_2 - g_1)\, c_2} \right.$$

$$\left. - \frac{A_{21}}{(1 + g_2)(A_{21} + A_{22}g_1) + (A_{22} - A_{21})\,(g_2 - g_1)\, c_2} \right) \qquad \text{(H-26)}$$

Further simplification is provided by replacing A_{11} and A_{22} with 1 to give eq H-27. This is allowed because the interaction parameter of a group with itself, A_{kk}, is always defined as unity .This equation is identical to eq 9 except that eq H-27 gives the ratio $\ln \gamma_1^G / n_{11}$ for component 1, while eq 9 gives the ratio $\ln \gamma_i^G / n_{1i}$ for the general case of component i. Eq 9 can be derived without detailed calculation by consideration of the variables involved in eq H-27. When molecular components 1 and 2 are interchanged, subscripts which depend on the

assignment of molecular components will interchange: ln γ_1^G with ln γ_2^G, n_{11} with n_{12}, g_1 with g_2, and c_1 with c_2. The remaining subscripts depend on assignment of functional groups and are not affected by changes in the assignment of molecular components. Eq 9 follows from eq H-27 by changing subscript 1 to i and subscript 2 to j in each of the variables where subscripts interchange when molecular components are interchanged. This completes the derivation of eq 9.

$$\frac{\ln \gamma_1^G}{n_{11}} = \ln \left[\frac{(1 + g_2)(1 + A_{12}g_1)}{(1 + g_2)(1 + A_{12}g_1) + (A_{12} - 1)(g_2 - g_1)\, c_2} \right]$$

$$+ g_1 \ln \left[\frac{(1 + g_2)(A_{21} + g_1)}{(1 + g_2)(A_{21} + g_1) + (1 - A_{21})(g_2 - g_1)\, c_2} \right]$$

$$+ (1 + g_1)(g_2 - g_1)\, c_2 \cdot$$

$$\left(\frac{A_{12}}{(1 + g_2)(1 + A_{12}g_1) + (A_{12} - 1)\,(g_2 - g_1)\, c_2} \right.$$

$$\left. - \frac{A_{21}}{(1 + g_2)(A_{21} + g_1) + (1 - A_{21})\,(g_2 - g_1)\, c_2} \right) \qquad \text{(H-27)}$$

$$\frac{\ln \gamma_i^G}{n_{1i}} = \ln \frac{(1 + g_j)(1 + A_{12}g_i)}{(1 + g_j)(1 + A_{12}g_i) + (g_j - g_i)(A_{12} - 1)c_j}$$

$$+ g_i \ln \frac{(1 + g_j)(A_{21} + g_i)}{(1 + g_j)(A_{21} + g_i) + (g_j - g_i)(1 - A_{21})c_j}$$

$$+ (1 + g_i)(g_j - g_i)c_j \cdot$$

$$\left(\frac{A_{12}}{(1 + g_j)(1 + A_{12}g_i) + (g_j - g_i)(A_{12} - 1)c_j} \right.$$

$$\left. - \frac{A_{21}}{(1 + g_j)(A_{21} + g_i) + (g_j - g_i)(1 - A_{21})c_j} \right) \qquad (9)$$

Eqs 10 and 11 are definitions of transformed interaction parameters, which are used to derive eq 12, a simplified form of eq H-27. Begin by dividing each of the four terms of eq H-27 by the first term in the denominator of that particular term to give eq H-28. The transformed interaction parameters given by eqs 10 and 11 can immediately be substituted in several places to given eq H-29.

$$\frac{\ln \gamma_1^G}{n_{11}} = \ln \left[\frac{1}{1 + \frac{(A_{12} - 1)(g_2 - g_1)\, c_2}{(1 + g_2)(1 + A_{12} g_1)}} \right]$$

$$+ g_1 \ln \left[\frac{1}{1 + \frac{(1 - A_{21})(g_2 - g_1)\, c_2}{(1 + g_2)(A_{21} + g_1)}} \right]$$

$$+ (1 + g_1)(g_2 - g_1)\, c_2 \cdot$$

$$\left(\frac{A_{12} / [(1 + g_2)(1 + A_{12} g_1)]}{1 + \frac{(A_{12} - 1)\,(g_2 - g_1)\, c_2}{(1 + g_2)(1 + A_{12} g_1)}} \right.$$

$$\left. - \frac{A_{21} / [(1 + g_2)(A_{21} + g_1)]}{1 + \frac{(1 - A_{21})\,(g_2 - g_1)\, c_2}{(1 + g_2)(A_{21} + g_1)}} \right) \qquad \text{(H-28)}$$

$$B_{12} = \frac{(g_2 - g_1)(A_{12} - 1)}{(1 + g_2)(1 + A_{12} g_1)} \qquad (10)$$

$$B_{21} = \frac{(g_2 - g_1)(1 - A_{21})}{(1 + g_2)(A_{21} + g_1)} \qquad (11)$$

$$\frac{\ln \gamma_1^G}{n_{11}} = -\ln (1 + B_{12}c_2) - g_1 \ln (1 + B_{21}c_2) + (1 + g_1)(g_2 - g_1)\, c_2 \cdot \left(\frac{A_{12} / [(1 + g_2)(1 + A_{12}g_1)]}{1 + B_{12}c_2} - \frac{A_{21} / [(1 + g_2)(A_{21} + g_1)]}{1 + B_{21}c_2} \right) \qquad \text{(H-29)}$$

Further rearrangement of the final terms of eq H-29 results in eq H-30. Eqs H-31 and H-32 indicate how the final terms can be rewritten to become eq 12.

$$\frac{\ln \gamma_1^G}{n_{11}} = -\ln (1 + B_{12}c_2) - g_1 \ln (1 + B_{21}c_2) + c_2 / (1 + g_2) \cdot \left(\frac{A_{12} (1 + g_1)(g_2 - g_1) / (1 + A_{12}g_1)}{1 + B_{12}c_2} - \frac{A_{21} (1 + g_1)(g_2 - g_1) / (A_{21} + g_1)}{1 + B_{21}c_2} \right) \qquad \text{(H-30)}$$

$$(1 + g_2)B_{12} + (g_2 - g_1) = \frac{(g_2 - g_1)(A_{12} - 1)}{(1 + A_{12}g_1)} + \frac{(g_2 - g_1)(1 + A_{12}g_1)}{(1 + A_{12}g_1)} = \frac{(g_2 - g_1)(1 + g_1)\, A_{12}}{(1 + A_{12}g_1)} \qquad \text{(H-31)}$$

$$(g_2 - g_1) - (1 + g_2)g_1B_{12} = \frac{(g_2 - g_1)(A_{21} + g_1)}{(A_{21} + g_1)} - \frac{g_1(g_2 - g_1)(1 - A_{21})}{(A_{21} + g_1)}$$

$$= \frac{(g_2 - g_1)(1 + g_1)\, A_{21}}{(A_{21} + g_1)} \qquad \text{(H-32)}$$

$$\frac{\ln \gamma_1^G}{n_{11}} = - \ln (1 + B_{12}c_2) - g_1 \ln (1 + B_{21}c_2)$$

$$+ \frac{c_2}{1+g_2} \left(\frac{(g_2-g_1) + (1+g_2)B_{12}}{1 + B_{12}c_2} - \frac{(g_2-g_1) - (1+g_2)g_1B_{21}}{1 + B_{21}c_2} \right) \qquad (12)$$

Eq 13 results from taking c_2 equal to one in eq 12. Eqs 14 and 15 define a second set of transformed interaction parameters which are used in deriving eq 16. Steps of this derivation are given as eqs H-33 to H-36.

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = - \ln (1 + B_{12}) - g_1 \ln (1 + B_{21})$$

$$+ \frac{1}{1+g_2} \left(\frac{(g_2-g_1) + (1+g_2)B_{12}}{1 + B_{12}} - \frac{(g_2-g_1) - (1+g_2)g_1B_{21}}{1 + B_{21}} \right) \qquad (13)$$

$$C_{12} = 1 + B_{12} \qquad (14)$$

$$C_{21} = 1 + B_{21} \qquad (15)$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = - \ln C_{12} - g_1 \ln C_{21}$$

$$+ \frac{1}{1+g_2} \left(\frac{(g_2-g_1) + (1+g_2)B_{12}}{C_{12}} - \frac{(g_2-g_1) - (1+g_2)g_1B_{21}}{C_{21}} \right) \qquad \text{(H-33)}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - g_1 \ln C_{21}$$
$$+ \frac{1}{1+g_2}\left(\frac{(g_2-g_1) + (1+g_2)(C_{12}-1)}{C_{12}} - \frac{(g_2-g_1) - (1+g_2)g_1(C_{21}-1)}{C_{21}}\right)$$

(H-34)

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - g_1 \ln C_{21} + \frac{(g_2-g_1) - (1+g_2)}{(1+g_2)C_{12}} + \frac{(1+g_2)C_{12}}{(1+g_2)C_{12}}$$
$$- \frac{(g_2-g_1) + (1+g_2)g_1}{(1+g_2)C_{21}} + \frac{(1+g_2)g_1C_{21}}{(1+g_2)C_{21}}$$

(H-35)

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - g_1 \ln C_{21} - \frac{(1+g_1)}{(1+g_2)C_{12}} + 1 - \frac{g_2 + g_1g_2}{(1+g_2)C_{21}} + g_1$$

(H-36)

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - g_1 \ln C_{21} - \frac{1+g_1}{1+g_2}\left(\frac{1}{C_{12}} + \frac{g_2}{C_{21}}\right) + (1+g_1) \qquad (16)$$

A sufficient condition for eq 16 to result in a value of zero is given by eq 17. This is proved by substitution in eq H-37 below. Eqs 18 to 20 result when g_1 or g_2 or both take on specific values. Eqs H-38 to H-44 show these derivations from eq 16.

$$C_{12} = C_{21} = 1 \qquad (17)$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln 1 - g_1 \ln 1 - \frac{1+g_1}{1+g_2}\left(\frac{1}{1} + \frac{g_2}{1}\right) + (1+g_1)$$

$$= -0 - g_1(0) - \frac{1+g_1}{1+g_2}(1+g_2) + (1+g_1)$$

$$= -(1+g_1) + (1+g_1) = 0 \qquad (H-37)$$

$$g_1 = 0 \tag{H-38}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - 0 \ln C_{21} - \frac{1+0}{1+g_2}\left(\frac{1}{C_{12}} + \frac{g_2}{C_{21}}\right) + (1+0) \tag{H-39}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - \frac{1}{1+g_2}\left(\frac{1}{C_{12}} + \frac{g_2}{C_{21}}\right) + 1 \tag{18}$$

$$g_2 = 0 \tag{H-40}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - g_1 \ln C_{21} - \frac{1+g_1}{1+0}\left(\frac{1}{C_{12}} + \frac{0}{C_{21}}\right) + (1+g_1) \tag{H-41}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - g_1 \ln C_{21} + (1+g_1)\left(1 - \frac{1}{C_{12}}\right) \tag{19}$$

$$g_1 = 0 \tag{H-38}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - 0 \ln C_{21} - \frac{1+0}{1+g_2}\left(\frac{1}{C_{12}} + \frac{g_2}{C_{21}}\right) + (1+0) \tag{H-39}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - \frac{1}{1+g_2}\left(\frac{1}{C_{12}}\right) - \frac{g_2}{1+g_2}\left(\frac{1}{C_{21}}\right) + 1 \tag{H-42}$$

$$g_2 \to \infty \tag{H-43}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - (0)\left(\frac{1}{C_{12}}\right) - (1)\left(\frac{1}{C_{21}}\right) + 1 \tag{H-44}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - \frac{1}{C_{21}} + 1 \tag{20}$$

Eq 21 defines the interaction parameter in terms of molar volumes and interaction energies. Eqs 22 and 23 result when eqs 14 and 15 are differentiated with respect to A_{12} and A_{21} respectively to give eqs H-45 and H-46.

$$C_{12} = \frac{(1 + g_1)(1 + A_{12}g_2)}{(1 + g_2)(1 + A_{12}g_1)} \tag{14}$$

$$\frac{dC_{12}}{dA_{12}} = \frac{(1 + g_1)}{(1 + g_2)} \frac{(1 + A_{12}g_1)(g_2) - (1 + A_{12}g_2)(g_1)}{(1 + A_{12}g_1)(1 + A_{12}g_2)}$$

$$= \frac{(1 + g_1)}{(1 + g_2)} \frac{g_2 - g_1}{(1 + A_{12}g_1)(1 + A_{12}g_2)} \tag{H-45}$$

$$C_{21} = \frac{(1 + g_1)(A_{21} + g_2)}{(1 + g_2)(A_{21} + g_1)} \tag{15}$$

$$\frac{dC_{21}}{dA_{21}} = \frac{(1 + g_1)}{(1 + g_2)} \frac{(A_{21} + g_1)(1) - (A_{21} + g_2)(1)}{(A_{21} + g_1)(A_{21} + g_2)}$$

$$= \frac{(1 + g_1)}{(1 + g_2)} \frac{g_1 - g_2}{(A_{21} + g_1)(A_{21} + g_2)} \tag{H-46}$$

Since A_{12}, A_{21}, g_1, and g_2 are all nonnegative, eqs H-45 and H-46 show that C_{kl} are monotone increasing (or decreasing) functions of A_{kl} dependent upon the sign of $g_2 - g_1$. This implies that the minima and maxima of A_{kl} are also the minima and maxima of the functions $C_{kl}(A_{kl})$. Eq 21 restricts A_{kl} to take on positive values. Therefore, limits on the values of C_{kl} can be given by taking A_{kl} equal to zero and approaching infinity in eqs 14 and 15.

$$A_{12} = 0 \tag{H-47}$$

$$A_{21} \to \infty \tag{H-48}$$

$$C_{12} = \frac{(1 + g_1)(1 + (0)g2)}{(1 + g_2)(1 + (0)g_1)} = \frac{(1 + g_1)}{(1 + g_2)} \tag{H-49}$$

$$C_{21} = \frac{(1 + g_1)(A_{21} + g_2)}{(1 + g_2)(A_{21} + g_1)} = \frac{(1 + g_1)}{(1 + g_2)} \frac{(A_{21} + g_2)}{(A_{21} + g_1)} = \frac{(1 + g_1)}{(1 + g_2)} (1) \tag{H-50}$$

$$A_{12} \to \infty \tag{H-51}$$

$$A_{21} = 0 \tag{H-52}$$

$$C_{12} = \frac{(1 + g_1)(1 + A_{12}g_2)}{(1 + g_2)(1 + A_{12}g_1)} = \frac{(1 + g_1)(1/A_{12} + g_2)}{(1 + g_2)(1/A_{12} + g_1)} = \frac{(1 + g_1)\, g_2}{(1 + g_2)\, g_1} \tag{H-53}$$

$$C_{21} = \frac{(1 + g_1)((0) + g_2)}{(1 + g_2)((0) + g_1)} = \frac{(1 + g_1)\, g_2}{(1 + g_2)\, g_1} \tag{H-54}$$

Eqs H-49, H-50, H-53, and H-54 express the limits on C_{k1}, which can be succintly written as eqs 22 and 23.

$$\frac{1+g_1}{1+g_2} < C_{12}\ ,\ C_{21} < \frac{1+g_1}{1+g_2}\,\frac{g_2}{g_1} \text{ when } g_2 > g_1 \tag{22}$$

$$\frac{1+g_1}{1+g_2}\,\frac{g_2}{g_1} < C_{12}\ ,\ C_{21} < \frac{1+g_1}{1+g_2} \text{ when } g_2 < g_1 \tag{23}$$

Eqs H-55 and H-56 are derived by differentiating eq 16 with respect to one of the C_{k1} while the other is held constant. Since the function will increase when its derivative is positive, eqs 24 and 25 result when the right hand sides of eqs H-55 and H-56 are set greater than zero.

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - g_1 \ln C_{21} - \frac{1+g_1}{1+g_2}\left(\frac{1}{C_{12}} + \frac{g_2}{C_{21}}\right) + (1+g_1) \tag{16}$$

$$\frac{\delta}{\delta C_{12}}\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty}\Bigg|_{C_{21}} = -\frac{1}{C_{12}} - \frac{1+g_1}{1+g_2}\left(\frac{-1}{C_{12}^2}\right) = \frac{1}{C_{12}}\left(\frac{1+g_1}{1+g_2}\,\frac{1}{C_{12}} - 1\right) \tag{H-55}$$

$$\frac{\delta}{\delta C_{21}}\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty}\Bigg|_{C_{12}} = -\frac{g_1}{C_{21}} - \frac{1+g_1}{1+g_2}\left(\frac{-g_2}{C_{21}^2}\right) = \frac{1}{C_{21}}\left(\frac{1+g_1}{1+g_2}\,\frac{g_2}{C_{21}} - g_1\right) \tag{H-56}$$

$$\frac{1}{C_{12}}\left(\frac{1+g_1}{1+g_2}\frac{1}{C_{12}} - 1\right) > 0 \qquad \text{(H-57)}$$

$$\frac{1+g_1}{1+g_2}\frac{1}{C_{12}} - 1 > 0 \qquad \text{(H-58)}$$

$$\frac{1+g_1}{1+g_2}\frac{1}{C_{12}} > 1 \qquad \text{(H-59)}$$

$$\frac{1+g_1}{1+g_2} > C_{12} \qquad \text{(24)}$$

$$\frac{1}{C_{21}}\left(\frac{1+g_1}{1+g_2}\frac{g_2}{C_{21}} - g_1\right) > 0 \qquad \text{(H-60)}$$

$$\frac{1+g_1}{1+g_2}\frac{g_2}{C_{21}} - g_1 > 0 \qquad \text{(H-61)}$$

$$\frac{1+g_1}{1+g_2}\frac{g_2}{C_{21}} > g_1 \qquad \text{(H-62)}$$

$$\frac{1+g_1}{1+g_2}\frac{g_2}{g_1} > C_{21} \qquad \text{(25)}$$

The permissible domain of C_{kl} values given by eqs 22 and 23 is such that either eq 24 will always be satisfied and eq 25 will never be satisfied, or the opposite will occur. When $g_2 > g_1$, bounds are given by eq 22. Eq 24 will never be satisfied so the function takes on its maximum at the minimum possible C_{12} value; at the same time, eq 25 will always be satisfied so the function takes on its maximum at the maximum possible C_{21} value. These values where the function takes on its maximum are given by eqs 26 and 27. When $g_2 < g_1$, bounds are given by eq 23. Eq 24 will always be satisfied so the function takes on its maximum at the

maximum possible C_{12} value; at the same time, eq 25 will never be satisfied so the function takes on its maximum at the minimum possible C_{21} value. This is the opposite of the case when $g_2 > g_1$. However, the bounds of eq 23 are also the opposite of the bounds of eq 22, so eqs 26 and 27 hold regardless of the sign of $g_2 - g_1$. When the objective is to minimize the function, the logic reverses and eqs 28 and 29 must hold.

$$C_{12} = \frac{1+g_1}{1+g_2} \tag{26}$$

$$C_{21} = \frac{1+g_1}{1+g_2}\,\frac{g_2}{g_1} \tag{27}$$

$$C_{12} = \frac{1+g_1}{1+g_2}\,\frac{g_2}{g_1} \tag{28}$$

$$C_{21} = \frac{1+g_1}{1+g_2} \tag{29}$$

Eqs 30 and 31 result from substitution of either eqs 26 and 27, or eqs 28 and 29, into eq 16.

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - g_1 \ln C_{21} - \frac{1+g_1}{1+g_2}\left(\frac{1}{C_{12}} + \frac{g_2}{C_{21}}\right) + (1+g_1) \tag{16}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty}_{\max} = -\ln \frac{1+g_1}{1+g_2} - g_1 \ln \left(\frac{1+g_1}{1+g_2}\,\frac{g_2}{g_1}\right) - \frac{1+g_1}{1+g_2}\left(\frac{1+g_2}{1+g_1} + g_2\,\frac{1+g_2}{1+g_1}\,\frac{g_1}{g_2}\right) + (1+g_1) \tag{H-63}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty}_{max} = (1+g_1)\ln\frac{1+g_2}{1+g_1} + g_1 \ln\frac{g_1}{g_2}$$

$$- (1+g_1) + (1+g_1) \qquad \text{(H-64)}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty}_{max} = (1+g_1)\ln\frac{1+g_2}{1+g_1} + g_1 \ln\frac{g_1}{g_2} \qquad \text{(30)}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty}_{min} = -\ln\left(\frac{1+g_1}{1+g_2}\,\frac{g_2}{g_1}\right) - g_1 \ln\frac{1+g_1}{1+g_2}$$

$$- \frac{1+g_1}{1+g_2}\left(\frac{1+g_2}{1+g_1}\,\frac{g_1}{g_2} + g_2\,\frac{1+g_2}{1+g_1}\right) + (1+g_1) \qquad \text{(H-65)}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty}_{min} = -\ln\left(\frac{1+g_1}{1+g_2}\,\frac{g_2}{g_1}\right) - g_1 \ln\frac{1+g_1}{1+g_2}$$

$$- \frac{g_1}{g_2} - g_2 + (1+g_1) \qquad \text{(H-66)}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty}_{min} = (1+g_1)\ln\frac{1+g_2}{1+g_1} + \ln\frac{g_1}{g_2} + (g_2-g_1)\left(\frac{1}{g_2} - 1\right) \qquad \text{(31)}$$

Eqs 32 and 33 are generated by inverting eqs 14 and 15 to express the A_{kl} as functions of C_{kl}.

$$C_{12} = \frac{(1 + g_1)(1 + A_{12}g_2)}{(1 + g_2)(1 + A_{12}g_1)} \qquad \text{(14)}$$

$$\frac{(1 + g_2)}{(1 + g_1)} C_{12} = \frac{(1 + A_{12}g_2)}{(1 + A_{12}g_1)} \qquad \text{(H-67)}$$

$$\frac{(1 + g_2)}{(1 + g_1)} C_{12} + A_{12}g_1 \frac{(1 + g_2)}{(1 + g_1)} C_{12} = 1 + A_{12}g_2 \qquad \text{(H-68)}$$

$$\frac{(1 + g_2)}{(1 + g_1)} C_{12} - 1 = A_{12}g_2 - A_{12}g_1 C_{12} \frac{(1 + g_2)}{(1 + g_1)} \qquad \text{(H-69)}$$

$$(1 + g_2)\, C_{12} - (1 + g_1) = A_{12}\, g_2(1 + g_1) - A_{12}\, g_1(1 + g_2)\, C_{12} \qquad \text{(H-70)}$$

$$A_{12} = \frac{(1 + g_2)C_{12} - (1 + g_1)}{g_2(1 + g_1) - g_1(1 + g_2)C_{12}} \qquad (32)$$

$$C_{21} = \frac{(1 + g_1)(A_{21} + g_2)}{(1 + g_2)(A_{21} + g_1)} \qquad (15)$$

$$\frac{(1 + g_2)}{(1 + g_1)}\, C_{21} = \frac{(A_{21} + g_2)}{(A_{21} + g_1)} \qquad \text{(H-71)}$$

$$A_{21}\, \frac{(1 + g_2)}{(1 + g_1)}\, C_{21} + g_1\, \frac{(1 + g_2)}{(1 + g_1)}\, C_{21} = (A_{21} + g_2) \qquad \text{(H-72)}$$

$$g_1\, \frac{(1 + g_2)}{(1 + g_1)}\, C_{21} - g_2 = A_{21} - A_{21}\, \frac{(1 + g_2)}{(1 + g_1)}\, C_{21} \qquad \text{(H-72)}$$

$$g_1 (1 + g_2)\, C_{21} - g_2 (1 + g_1) = A_{21} (1 + g_1) - A_{21} (1 + g_2)\, C_{21} \qquad \text{(H-73)}$$

$$A_{21} = \frac{g_1(1 + g_2)C_{21} - g_2(1 + g_1)}{(1 + g_1) - (1 + g_2)C_{21}} \qquad (33)$$

Table H-1. Equations Used in "Normalization and Bounding Properties Inherent in Solution of Groups Activity Coefficient Models"

$$X_k = \frac{n_{k1}x_1 + n_{k2}x_2}{(n_{11}+n_{21})x_1 + (n_{12}+n_{22})x_2} \qquad (1)$$

$$\ln \gamma_i^{\,G} = n_{1i}(\ln \Gamma_1 - \ln \Gamma_1^{\,i}) + n_{2i}(\ln \Gamma_2 - \ln \Gamma_2^{\,i}) \qquad (2)$$

$$\ln \Gamma_k = -\ln(X_1A_{k1} + X_2A_{k2}) + 1 - \frac{X_1A_{1k}}{X_1A_{11}+X_2A_{12}} - \frac{X_2A_{2k}}{X_1A_{21}+X_2A_{22}} \qquad (3)$$

$$\ln \Gamma_k^{\,i} = \ln \Gamma_k\, (x_i = 1) \qquad (4)$$

$$c_i = \frac{(n_{1i}+n_{2i})x_i}{(n_{11}+n_{21})x_1 + (n_{12}+n_{22})x_2} \qquad (5)$$

$$g_i = n_{2i} / n_{1i} \tag{6}$$

$$X_1 = \frac{c_1}{1 + g_1} + \frac{c_2}{1 + g_2} \tag{7}$$

$$\frac{\ln \gamma_i^G}{n_{1i}} = (\ln \Gamma_1 - \ln \Gamma_1^i) + g_i(\ln \Gamma_2 - \ln \Gamma_2^i) \tag{8}$$

$$\begin{aligned}\frac{\ln \gamma_i^G}{n_{1i}} = \ln & \frac{(1 + g_j)(1 + A_{12}g_i)}{(1 + g_j)(1 + A_{12}g_i) + (g_j - g_i)(A_{12} - 1)c_j} \\ & + g_i \ln \frac{(1 + g_j)(A_{21} + g_i)}{(1 + g_j)(A_{21} + g_i) + (g_j - g_i)(1 - A_{21})c_j} \\ & + (1 + g_i)(g_j - g_i)c_j \cdot \\ & \left(\frac{A_{12}}{(1 + g_j)(1 + A_{12}g_i) + (g_j - g_i)(A_{12} - 1)c_j} \right. \\ & \left. - \frac{A_{21}}{(1 + g_j)(A_{21} + g_i) + (g_j - g_i)(1 - A_{21})c_j} \right)\end{aligned} \tag{9}$$

$$B_{12} = \frac{(g_2 - g_1)(A_{12} - 1)}{(1 + g_2)(1 + A_{12}g_1)} \tag{10}$$

$$B_{21} = \frac{(g_2 - g_1)(1 - A_{21})}{(1 + g_2)(A_{21} + g_1)} \tag{11}$$

$$\begin{aligned}\frac{\ln \gamma_1^G}{n_{11}} = & - \ln (1 + B_{12}c_2) - g_1 \ln (1 + B_{21}c_2) \\ & + \frac{c_2}{1+g_2} \left(\frac{(g_2-g_1) + (1+g_2)B_{12}}{1 + B_{12}c_2} - \frac{(g_2-g_1) - (1+g_2)g_1B_{21}}{1 + B_{21}c_2} \right)\end{aligned} \tag{12}$$

$$\begin{aligned}\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = & - \ln (1 + B_{12}) - g_1 \ln (1 + B_{21}) \\ & + \frac{1}{1+g_2} \left(\frac{(g_2-g_1) + (1+g_2)B_{12}}{1 + B_{12}} - \frac{(g_2-g_1) - (1+g_2)g_1B_{21}}{1 + B_{21}} \right)\end{aligned} \tag{13}$$

$$C_{12} = 1 + B_{12} = \frac{(1 + g_1)(1 + A_{12}g_2)}{(1 + g_2)(1 + A_{12}g_1)} \tag{14}$$

$$C_{21} = 1 + B_{21} = \frac{(1 + g_1)(A_{21} + g_2)}{(1 + g_2)(A_{21} + g_1)} \tag{15}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - g_1 \ln C_{21} - \frac{1+g_1}{1+g_2}\left(\frac{1}{C_{12}} + \frac{g_2}{C_{21}}\right) + (1+g_1) \tag{16}$$

$$C_{12} = C_{21} = 1 \tag{17}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - \frac{1}{1+g_2}\left(\frac{1}{C_{12}} + \frac{g_2}{C_{21}}\right) + 1 \tag{18}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - g_1 \ln C_{21} - (1+g_1)\left(1 - \frac{1}{C_{12}}\right) \tag{19}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty} = -\ln C_{12} - \frac{1}{C_{21}} + 1 \tag{20}$$

$$A_{ij} = \frac{v_j}{v_i} \exp\left[-\frac{(\lambda_{ij} - \lambda_{ii})}{RT}\right] \tag{21}$$

$$\frac{1+g_1}{1+g_2} < C_{12}\,,\ C_{21} < \frac{1+g_1}{1+g_2}\frac{g_2}{g_1} \text{ when } g_2 > g_1 \tag{22}$$

$$\frac{1+g_1}{1+g_2}\frac{g_2}{g_1} < C_{12}\,,\ C_{21} < \frac{1+g_1}{1+g_2} \text{ when } g_2 < g_1 \tag{23}$$

$$\frac{1+g_1}{1+g_2} > C_{12} \tag{24}$$

$$\frac{1+g_1}{1+g_2}\frac{g_2}{g_1} > C_{21} \tag{25}$$

$$C_{12} = \frac{1+g_1}{1+g_2} \tag{26}$$

$$C_{21} = \frac{1+g_1}{1+g_2}\,\frac{g_2}{g_1} \tag{27}$$

$$C_{12} = \frac{1+g_1}{1+g_2}\,\frac{g_2}{g_1} \tag{28}$$

$$C_{21} = \frac{1+g_1}{1+g_2} \tag{29}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty}_{max} = (1+g_1)\ln\frac{1+g_2}{1+g_1} + g_1 \ln\frac{g_1}{g_2} \tag{30}$$

$$\left(\frac{\ln \gamma_1^G}{n_{11}}\right)^{\infty}_{min} = (1+g_1)\ln\frac{1+g_2}{1+g_1} + \ln\frac{g_1}{g_2} + (g_2-g_1)\left(\frac{1}{g_2} - 1\right) \tag{31}$$

$$A_{12} = \frac{(1 + g_2)C_{12} - (1 + g_1)}{g_2(1 + g_1) - g_1(1 + g_2)C_{12}} \tag{32}$$

$$A_{21} = \frac{g_1(1 + g_2)C_{21} - g_2(1 + g_1)}{(1 + g_1) - (1 + g_2)C_{21}} \tag{33}$$

APPENDIX I.

Derivation of Equations in "A Diffusion Coefficient Model for Polymer Devolatilization"

This appendix contains a more detailed derivation of the equations presented in the reprint article "A Diffusion Coefficient Model for Polymer Devolatilization". This article was included as part of Chapter 4 of the dissertation. In this appendix, equation numbers refer to the manuscript article itself, beginning on page 21 of the dissertation. New equations not included in the article are numbered with a preceding letter I, e.g., I-1, I-2, etc.

Eqs 1 to 5 were taken from previously published work (Duda, Vrentas, Ju, and Liu, 1982) and are not derived here.

DERIVATION OF EQUATION 6

The first new equation is eq 6. It was derived from the expression for the activity of solvent developed in Chapter 2 of this dissertation. Definitions from Chapter 2 are given as eqs I-1 and I-2, and are differentiated with respect to mole fraction to give eqs I-3 and I-4. The second factor on the right hand side of eq I-3 is given as a function of the size ratio S_2/S_1 and mole fraction x_1 in eq I-5, which

is combined with eq I-4 to give eq I-6 for the derivative of the logarithm of activity coefficient, ln γ_1, with respect to mole fraction x_1. Eq I-7 uses the chain rule is used to express the derivative d ln γ_1 / d ln x_1 in terms of the derivative in eq I-6, which is substituted to give eq I-8. The definition of activity in used in eq I-9 to produce an expression for the derivative d ln a_1 / d ln x_1 in eq I-10.

$$\ln \gamma_1 = 1 - R_1 - \ln R_1 \tag{I-1}$$

$$R_1 = S_1 / (S_1 x_1 + S_2 x_2) = 1 / (x_1 + (S_2/S_1)\, x_2) \tag{I-2}$$

$$\frac{d \ln \gamma_1}{dx_1} = \frac{dR_1}{dx_1} (1 - \frac{1}{R_1}) \tag{I-3}$$

$$\frac{dR_1}{dx_1} = \frac{1}{(x_1 + (S_2/S_1)\, x_2)^2} \cdot (1 - \frac{S_2}{S_1}) \tag{I-4}$$

$$1 - \frac{1}{R_1} = 1 - (x_1 + \frac{S_2}{S_1} x_2) = (1 - \frac{S_2}{S_1})(1 - x_1) \tag{I-5}$$

$$\frac{d \ln \gamma_1}{dx_1} = \frac{1}{(x_1 + (S_2/S_1)\, x_2)^2} \cdot (1 - \frac{S_2}{S_1})(1 - \frac{S_2}{S_1})(1 - x_1)$$

$$= \frac{[1 - (S_2/S_1)]^2 (1 - x_1)}{(x_1 + (S_2/S_1)\, x_2)^2} = \frac{[1 - (S_2/S_1)]^2 (1 - x_1)}{[(S_2/S_1) + [1 - (S_2/S_1)] x_1]^2} \tag{I-6}$$

$$\frac{d \ln \gamma_1}{d \ln x_1} = \frac{d \ln \gamma_1}{dx_1} \cdot \frac{dx_1}{d \ln x_1} = x_1 \frac{d \ln \gamma_1}{dx_1} \tag{I-7}$$

$$\frac{d \ln \gamma_1}{d \ln x_1} = \frac{[1 - (S_2/S_1)]^2 x_1 (1 - x_1)}{[(S_2/S_1) + [1 - (S_2/S_1)] x_1]^2} \tag{I-8}$$

$$\frac{d \ln a_1}{d \ln x_1} = \frac{d \ln \gamma_1 x_1}{d \ln x_1} = \frac{d \ln \gamma_1}{d \ln x_1} + \frac{d \ln x_1}{d \ln x_1} = 1 + \frac{d \ln \gamma_1}{d \ln x_1} \qquad \text{(I-9)}$$

$$= 1 + \frac{[1 - (S_2/S_1)]^2 x_1 (1 - x_1)}{[(S_2/S_1) + [1 - (S_2/S_1)]x_1]^2}$$

$$= 1 + \frac{[1 - (S_2/S_1)]^2 x_1 - [1 - (S_2/S_1)]^2 x_1^2}{(S_2/S_1)^2 + 2(S_2/S_1)[1 - (S_2/S_1)]x_1 + [1 - (S_2/S_1)]^2 x_1^2}$$

$$= \frac{(S_2/S_1)^2 + [1 + (S_2/S_1)][1 - (S_2/S_1)]x_1}{(S_2/S_1)^2 + 2(S_2/S_1)[1 - (S_2/S_1)]x_1 + [1 - (S_2/S_1)]^2 x_1^2} \qquad \text{(I-10)}$$

When eq I-10 is multiplied through by x_2 to give eq I-11, the left hand side matches eq 6. The right hand side must be transformed from size ratio and mole fraction variables to infinite dilution activity coefficient Ω_1^{∞} and weight fraction variables. Eqs I-12 and I-13 provide the concentration variable transformations, giving eq I-14 when the substitutions are made in eq I-11 and numerator and denominator are multiplied through by the square of the denominator of I-12. Inspection of the denominator of eq I-14 shows it to be a perfect square as written in eq I-15 and simplified in eq I-16, while the numerator is simplified by multiplying out some terms in eq I-15, then cancelling in eq I-16.

$$x_2 \frac{d \ln a_1}{d \ln x_1} = \frac{(S_2/S_1)^2 x_2 + [1 + (S_2/S_1)][1 - (S_2/S_1)]x_1 x_2}{(S_2/S_1)^2 + 2(S_2/S_1)[1 - (S_2/S_1)]x_1 + [1 - (S_2/S_1)]^2 x_1^2} \qquad \text{(I-11)}$$

$$x_1 = (M_2/M_1)w_1 \,/\, [(M_2/M_1)w_1 + w_2] \qquad \text{(I-12)}$$

$$x_2 = w_2 \,/\, [(M_2/M_1)w_1 + w_2] \qquad \text{(I-13)}$$

$$x_2 \frac{d \ln a_1}{d \ln x_1} = \frac{(S_2/S_1)^2 w_2[(M_2/M_1)w_1 + w_2] + [1 + (S_2/S_1)][1 - (S_2/S_1)](M_2/M_1)w_1w_2}{(S_2/S_1)^2[(M_2/M_1)w_1 + w_2]_2 + 2(S_2/S_1)[1 - (S_2/S_1)](M_2/M_1)w_1[(M_2/M_1)w_1 + w_2] + [1 - (S_2/S_1)]^2[(M_2/M_1)w_1]^2} \tag{I-14}$$

$$x_2 \frac{d \ln a_1}{d \ln x_1} = \frac{(S_2/S_1)^2 w_2(M_2/M_1)w_1 + (S_2/S_1)^2 w_2^2 + (M_2/M_1)w_1w_2 - (S_2/S_1)^2(M_2/M_1)w_1w_2}{[(S_2/S_1)[(M_2/M_1)w_1 + w_2] + [1 - (S_2/S_1)](M_2/M_1)w_1]^2} \tag{I-15}$$

$$x_2 \frac{d \ln a_1}{d \ln x_1} = \frac{(S_2/S_1)^2 w_2^2 + (M_2/M_1)w_1w_2}{[(S_2/S_1)w_2 + (M_2/M_1)w_1]^2} \tag{I-16}$$

When the result for the size ratio from Chapter 2, eq I-17, is substituted into eq I-16, eq I-18 results. Multiplication of numerator and denominator by $(M_1/M_2)^2$ gives eq I-19. When the assumption $M_1 \ll M_2$ is made in eq I-19, eq 6 results.

$$S_2/S_1 = (e/\Omega_1^{\infty})(M_2/M_1) \tag{I-17}$$

$$x_2 \frac{d \ln a_1}{d \ln x_1} = \frac{(e/\Omega_1^{\infty})^2(M_2/M_1)^2 w_2^2 + (M_2/M_1)w_1w_2}{[(e/\Omega_1^{\infty})(M_2/M_1)w_2 + (M_2/M_1)w_1]^2} \tag{I-18}$$

$$x_2 \frac{d \ln a_1}{d \ln x_1} = \frac{(e/\Omega_1^{\infty})^2 w_2^2 + (M_1/M_2)w_1w_2}{[(e/\Omega_1^{\infty})w_2 + w_1]^2} \tag{I-19}$$

$$\frac{\rho_2 \hat{V}_2 \rho_1}{RT} \left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,p} = x_2 \frac{d \ln a_1}{d \ln x_1} = \left[\frac{\frac{e}{\Omega_1^{\infty}} w_2}{w_1 + \frac{e}{\Omega_1^{\infty}} w_2} \right]^2 \qquad (6)$$

Eq 7 results directly from substitution of eq 6 into eq 2, then substitution of that result into eq 1.

DERIVATION OF EQUATION 10

Eqs 8 and 9 define parameter groups which appear in eq 3. When eqs 8 and 9 are used in eq 3, it becomes eq I-20. Substitution of eqs I-20 and 4 into eq 7 results in eq 10.

$$\frac{\hat{V}_{FH}}{\gamma} = \frac{K_{11}}{\gamma} w_1 (K_{21} + T - T_{g1}) + \frac{K_{12}}{\gamma} w_2 (K_{22} + T - T_{g2}) \qquad (3)$$

$$A_1 = \frac{K_{11}}{\gamma} w_1 (K_{21} + T - T_{g1}) \qquad (8)$$

$$A_2 = \frac{K_{12}}{\gamma} w_2 (K_{22} + T - T_{g2}) \qquad (9)$$

$$\frac{\hat{V}_{FH}}{\gamma} = A_1 w_1 + A_2 w_2 \qquad (I\text{-}20)$$

$$D_{01} = D_0 \exp(-E/RT) \qquad (4)$$

$$D = D_{01}\left[\frac{\frac{e}{\Omega_1^{\infty}} w_2}{w_1 + \frac{e}{\Omega_1^{\infty}} w_2}\right]^2 \exp\left[\frac{-\gamma(w_1\hat{V}_1^{*} + w_2\xi\hat{V}_2^{*})}{\hat{V}_{FH}}\right] \tag{7}$$

$$D = D_0\left[\frac{\frac{e}{\Omega_1^{\infty}} w_2}{w_1 + \frac{e}{\Omega_1^{\infty}} w_2}\right]^2 \exp\left[-\frac{w_1\hat{V}_1^{*} + w_2\xi\hat{V}_2^{*}}{A_1w_1 + A_2w_2} - \frac{E}{RT}\right] \tag{10}$$

DERIVATION OF EQUATIONS 12, 12A, 12B, 12C

Eq 11 is a Taylor (or Maclaurin) expansion of the function $D(w_1)$ about the point w_1 equal to zero. Eq 12c results when w_1 is taken as zero (w_2 will then equal one) in eq 10, as shown in eq I-21. For simplicity of derivation, define F_1 and F_2 to be the two factors in eq 10 which are functions of w_1, allowing eq 10 to be rewritten as eq I-24, and eq 11, the partial derivative of eq 10 with respect to w_1, to be written as eq I-25. The derivatives of F_1 and F_2 themselves are given and simplified in eqs I-26 and I-27, and substituted back into eq I-25 to give eq I-28. Removing common factors results in eq I-29, and recognition of the leading factor as the right hand side of eq I-24 gives eq I-30. When w_1 is taken as zero, eqs I-31 and I-32 result, simplifying the expression for the derivative to eq I-33. Comparison of eq I-33 with eqs 11, 12, 12a, 12b, and 12c shows the set of equations to be identical.

$$D = D_0 \left(\frac{\frac{e}{\Omega_1^\infty} w_2}{0 + \frac{e}{\Omega_1^\infty} \cdot 1} \right)^2 \exp \left[- \frac{0 \cdot \hat{V}_1^* + 1 \cdot \xi \hat{V}_2^*}{A_1 \cdot 0 + A_2 \cdot 1} - \frac{E}{RT} \right] \tag{I-21}$$

$$D(0) = D_0 \exp \left[- \left(\frac{E}{RT} + \frac{\xi \hat{V}_2^*}{A_2} \right) \right] \tag{12c}$$

$$F_1 = \left(\frac{\frac{e}{\Omega_1^\infty} w_2}{w_1 + \frac{e}{\Omega_1^\infty} w_2} \right) \tag{I-22}$$

$$F_2 = \exp \left[- \frac{w_1 \hat{V}_1^* + w_2 \xi \hat{V}_2^*}{A_1 w_1 + A_2 w_2} - \frac{E}{RT} \right] \tag{I-23}$$

$$D = D_0 \, F_1^2(w_1) \, F_2(w_1) \tag{I-24}$$

$$\frac{\partial D}{\partial w_1} = D_0 \left[F_1^2 \frac{\partial F_2}{\partial w_1} + F_2 \cdot 2 F_1 \frac{\partial F_1}{\partial w_1} \right] \tag{I-25}$$

$$\frac{\partial F_2}{\partial w_1} = F_2 \cdot \frac{(w_1 \hat{V}_1^* + w_2 \xi \hat{V}_2^*)(A_1 - A_2) - (A_1 w_1 + A_2 w_2)(\hat{V}_1^* - \xi \hat{V}_2^*)}{(A_1 w_1 + A_2 w_2)^2}$$

$$= F_2 \cdot \frac{A_1 \xi \hat{V}_2^* (w_1 + w_2) - A_2 \hat{V}_1^* (w_1 + w_2)}{(A_1 w_1 + A_2 w_2)^2}$$

$$= F_2 \cdot \frac{A_1 \xi \hat{V}_2^* - A_2 \hat{V}_1^*}{(A_1 w_1 + A_2 w_2)^2} \tag{I-26}$$

$$\frac{\partial F_1}{\partial w_1} = \frac{(w_1 + (e/\Omega_1^{\infty})w_2)\,(-(e/\Omega_1^{\infty})) - (e/\Omega_1^{\infty})w_2\,(1 - (e/\Omega_1^{\infty}))}{(w_1 + (e/\Omega_1^{\infty})w_2)^2}$$

$$= \frac{-(e/\Omega_1^{\infty})(w_1 + w_2)}{(w_1 + (e/\Omega_1^{\infty})w_2)^2} = \frac{-(e/\Omega_1^{\infty})}{(w_1 + (e/\Omega_1^{\infty})w_2)^2} = -\frac{F_1^2}{(e/\Omega_1^{\infty})} \qquad \text{(I-27)}$$

$$\frac{\partial D}{\partial w_1} = D_0 \left[F_1^2 F_2 \cdot \frac{A_1\xi\hat{V}_2^* - A_2\hat{V}_1^*}{(A_1w_1 + A_2w_2)^2} - F_2 \cdot \frac{2F_1^3}{(e/\Omega_1^{\infty})}\right] \qquad \text{(I-28)}$$

$$\frac{\partial D}{\partial w_1} = D_0 F_1^2 F_2 \cdot \left[\frac{A_1\xi\hat{V}_2^* - A_2\hat{V}_1^*}{(A_1w_1 + A_2w_2)^2} - \frac{2F_1}{(e/\Omega_1^{\infty})}\right] \qquad \text{(I-29)}$$

$$\frac{\partial D}{\partial w_1} = D(w_1) \cdot \left[\frac{A_1\xi\hat{V}_2^* - A_2\hat{V}_1^*}{(A_1w_1 + A_2w_2)^2} - \frac{2F_1(w_1)}{(e/\Omega_1^{\infty})}\right] \qquad \text{(I-30)}$$

$$\left.\frac{\partial D}{\partial w_1}\right|_{w_1=0} = D(0) \cdot \left[\frac{A_1\xi\hat{V}_2^* - A_2\hat{V}_1^*}{(A_1\cdot 0 + A_2\cdot 1)^2} - \frac{2F_1(0)}{(e/\Omega_1^{\infty})}\right] \qquad \text{(I-31)}$$

$$F_1(0) = (e/\Omega_1^{\infty})^2 / [0 + (e/\Omega_1^{\infty})\cdot 1]^2 = (e/\Omega_1^{\infty})^2 / (e/\Omega_1^{\infty})^2 = 1 \qquad \text{(I-32)}$$

$$\left.\frac{\partial D}{\partial w_1}\right|_{w_1=0} = D(0) \cdot \left[\frac{A_1\xi\hat{V}_2^* - A_2\hat{V}_1^*}{A_2^2} - \frac{2}{(e/\Omega_1^{\infty})}\right] \qquad \text{(I-33)}$$

$$D(w_1) = D\Big|_{w_1=0} + \left.\frac{\partial}{\partial w_1}\right|_{T,w_1=0} (w_1 - 0) \qquad (11)$$

$$D(w_1) = D(0)\,[1 + (K_1 - K_2)\,w_1] \qquad (12)$$

$$D(0) = D_0 \exp\left[-\left(\frac{E}{RT} + \frac{\xi\hat{V}_2^*}{A_2}\right)\right] \qquad (12c)$$

$$K_1 = \frac{A_1\xi\hat{V}_2^* - A_2\hat{V}_1^*}{A_2^2} \qquad (12a)$$

$$K_2 = 2 \Big/ \frac{e}{\Omega_1^{\infty}} \tag{12b}$$

Eq 13 is the commonly used WLF equation for viscosity, as applied by Duda, Vrentas, Ju, and Liu (1982).

Table I-1. Equations Used in "A Diffusion Coefficient Model for Polymer Devolatilization".

$$D = D_1 \frac{\rho_2 \hat{V}_2 \rho_1}{RT} \left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,p} \tag{1}$$

$$D_1 = D_{01} \exp\left[\frac{-\gamma(w_1 \hat{V}_1^{*} + w_2 \xi \hat{V}_2^{*})}{\hat{V}_{FH}}\right] \tag{2}$$

$$\frac{\hat{V}_{FH}}{\gamma} = \frac{K_{11}}{\gamma} w_1 (K_{21} + T - T_{g1}) + \frac{K_{12}}{\gamma} w_2 (K_{22} + T - T_{g2}) \tag{3}$$

$$D_{01} = D_0 \exp(-E/RT) \tag{4}$$

$$\frac{\rho_2 \hat{V}_2 \rho_1}{RT} \left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,p} = (1 - \phi_1)^2 (1 - 2\chi\phi_1) \tag{5}$$

$$\frac{\rho_2 \hat{V}_2 \rho_1}{RT} \left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,p} = x_2 \frac{d \ln a_1}{d \ln x_1} = \left(\frac{\frac{e}{\Omega_1^{\infty}} w_2}{w_1 + \frac{e}{\Omega_1^{\infty}} w_2} \right)^2 \tag{6}$$

$$D = D_{01}\left[\frac{\frac{e}{\Omega_1^{\infty}} w_2}{w_1 + \frac{e}{\Omega_1^{\infty}} w_2}\right]^2 \exp\left[\frac{-\gamma(w_1\hat{V}_1^{*} + w_2\xi\hat{V}_2^{*})}{\hat{V}_{FH}}\right] \tag{7}$$

$$A_1 = \frac{K_{11}}{\gamma} w_1 (K_{21} + T - T_{g1}) \tag{8}$$

$$A_2 = \frac{K_{12}}{\gamma} w_2 (K_{22} + T - T_{g2}) \tag{9}$$

$$D = D_0\left[\frac{\frac{e}{\Omega_1^{\infty}} w_2}{w_1 + \frac{e}{\Omega_1^{\infty}} w_2}\right]^2 \exp\left[-\frac{w_1\hat{V}_1^{*} + w_2\xi\hat{V}_2^{*}}{A_1w_1 + A_2w_2} - \frac{E}{RT}\right] \tag{10}$$

$$D(w_1) = D\Big|_{w_1=0} + \frac{\partial}{\partial w_1}\Big|_{T,w_1=0} (w_1 - 0) \tag{11}$$

$$D(w_1) = D(0)\,[1 + (K_1 - K_2)\, w_1] \tag{12}$$

$$K_1 = \frac{A_1\xi\hat{V}_2^{*} - A_2\hat{V}_1^{*}}{A_2^2} \tag{12a}$$

$$K_2 = 2 \Big/ \frac{e}{\Omega_1^{\infty}} \tag{12b}$$

$$D(0) = D_0 \exp\left[-\left(\frac{E}{RT} + \frac{\xi\hat{V}_2^{*}}{A_2}\right)\right] \tag{12c}$$

$$\ln \eta_1 = \ln A_1 + \frac{\xi\hat{V}_1^{*}/K_{11}}{K_{21} + T - T_{g1}} \tag{13}$$

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