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A THERMODYNAMIC MODEL FOR SCALING CONCENTRATION-
DEPENDENT SOLVENT DIFFUSIVITIES IN POLYMER MELTS

presented by
Michael John Misovich

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of the requirements for
M.S. degree in Chemical Engineering

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**A THERMODYNAMIC MODEL FOR SCALING CONCENTRATION-DEPENDENT
SOLVENT DIFFUSIVITIES IN POLYMER MELTS**

By

Michael John Misovich

A THESIS

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ABSTRACT

A THERMODYNAMIC MODEL FOR SCALING CONCENTRATION-DEPENDENT SOLVENT DIFFUSIVITIES IN POLYMER MELTS

By

Michael John Misovich

Concentration-dependent Fickian diffusion coefficients are commonly observed in systems involving polymer melts. A theoretical model to scale the changes in diffusivity with thermodynamic parameters was applied to polymer-solvent systems. The model was applied to the polystyrene-toluene system and gave good agreement with experiment above the T_{ll} transition temperature, where it is postulated that a true liquid equilibrium exists.

The group contribution thermodynamic models Analytical Solution of Groups (ASOG) and UNIQUAC Functional-Group Activity Coefficients (UNIFAC) were examined as possible models for polymer-solvent systems. When one assumption of these models involving molecular size was relaxed, they were found in good agreement with experiment and with the Flory-Huggins model in the prediction of polymer-solvent equilibria in concentrated nonpolar solutions.

TABLE OF CONTENTS

List of Tables	iv
List of Figures	v
List of Symbols	vi
Chapter 1 -- Introduction	1
Chapter 2 -- Literature Review	5
2.1 Models for Diffusivity in Polymer Melts	5
2.1.1 Empirical Models for Concentration Dependence	7
2.1.2 Free Volume Models for Diffusivity	8
2.2 Thermodynamic Models Applicable to Polymer Systems	10
2.2.1 Polymer Equilibrium	10
2.2.2 Flory-Huggins	13
2.2.3 Group Contribution Methods	14
2.3 The T_{11} Transition in Polystyrene	16
2.3.1 T_{11} Dependence on Solvent Concentration	18
2.3.2 Effects of Molecular Weight Distributions on T_{11}	19
Chapter 3 -- Model Development	22
3.1 Thermodynamic Basis for Scaling Diffusivity	22
3.2 Application of Thermodynamics to Diffusivity Modeling	26
3.2.1 Derivation of ASOG Solution	27
3.2.2 Properties of ASOG Result	31
3.3 Application of UNIFAC	35
3.4 Effects of Molecular Weight Distributions	40
3.4.1 Effects of MWD on ASOG	43
3.4.2 Effects of MWD on UNIFAC	47
3.5 Variation and Estimation of ASOG Size Parameters	49
3.5.1 Empirical Size Parameter from Maximum Diffusivity	52
3.5.2 Size Parameter from Equilibrium Measurements	54
3.5.3 Size Parameter from Flory-Huggins χ Parameter	57
3.6 Temperature Dependence of Diffusivity	58

Chapter 4 -- Model Application	60
4.1 Thermodynamic Data	60
4.2 Range of Validity of the Model	62
4.3 Diffusivity Data	64
4.3.1 Application of Concentration Dependence Models	67
4.4 Temperature and Concentration Dependence	74
4.5 Concentration Bias of D_0	86
Chapter 5 -- Conclusions and Recommendations	88
List of References	92 A

LIST OF TABLES

Table 1.	<u>T₁₁</u> Measurements for Polystyrene (Non-Flow Techniques)	17
Table 2.	Entropic and Enthalpic Activity Coefficients for the Toluene-Polystyrene System	29
Table 3.	Combinatorial and Residual Activity Coefficients for the Toluene-Polystyrene System	35
Table 4.	UNIFAC Size Parameters for Toluene-Polystyrene System	38
Table 5.	Comparison of ASOG and UNIFAC Results	40
Table 6.	Lowering of <u>T₁₁</u> by Plasticization with Toluene	62
Table 7.	Lowering of <u>T₁₁</u> by Toluene Using Equation (5)	63
Table 8.	Diffusivity of Toluene-Polystyrene Systems	65
Table 9.	D ₀ Values for Experimental Data Above <u>T₁₁</u>	77
Table 10.	Linear Regression of Arrhenius Plots for 23 Experimental Points	79
Table 11.	Uncertain Experimental Points	79
Table 12.	Linear Regression of Arrhenius Plots for 14 Experimental Points	79
Table 13.	Ratio of Extreme D ₀ Values for 23 Experimental Points	82
Table 14.	Ratio of Extreme D ₀ Values for 14 Experimental Points	82
Table 15.	Predicted D ₀ Values from 14 Point Regression Results	85

LIST OF FIGURES

Figure 1. ASOG Predictions of Diffusivity	69
Figure 2. ASOG Predictions of Diffusivity at High Solvent Concentrations	70
Figure 3. Arrhenius Plot of ASOG Predictions	75
Figure 4. Arrhenius Plot of ASOG Predictions with VSP	76
Figure 5. ASOG Correlation of Diffusivity Data	83
Figure 6. ASOG Correlation of Diffusivity Data at High Solvent Concentrations	84
Figure 7. ASOG Concentration Bias	87

LIST OF SYMBOLS

a	thermodynamic activity
a_1	thermodynamic activity of solvent
C	molar concentration
d	empirical parameter in Equation (3)
D	binary mutual diffusion coefficient
D_0	binary mutual diffusion coefficient at zero solvent concentration
D_{00}	temperature and concentration independent binary mutual diffusion coefficient
e	base of the natural logarithm
E	activation energy for diffusion
J	diffusional flux
k	Boltzmann constant: universal gas law constant per molecule
K	empirical parameter in Equation (5)
l_i	UNIFAC parameter for component i defined by Equation (47)
M_1	molecular weight of solvent
M_2	molecular weight of polymer
M_c^c	critical polymer molecular weight for entanglements
M_n^c	polymer number average molecular weight
M_w^c	polymer weight average molecular weight
N	Avogadro's number: number of molecules per mole
N_{deb}	Deborah number for diffusion
q	UNIFAC functional group surface area parameter
q_i	UNIFAC surface area parameter for component i
r_2	UNIFAC functional group size parameter
r^2	linear regression correlation coefficient
r_i	UNIFAC size parameter for component i
R	universal gas law constant per mole
R_{1inf}	ASOG size term for solvent
R_1	ASOG size term for solvent at zero solvent concentration
S_i	ASOG size parameter for component i
T	temperature
T_g	glass transition temperature of an amorphous polymer
T_{ll}^g	liquid-liquid transition temperature of an amorphous polymer
$T_{ll,i}$	liquid-liquid transition temperature of component i
u	mobility of diffusing particle per unit force
v_2	volume fraction of polymer

V_i	specific volume of component i
$w_{1,c}$	critical weight fraction of solvent required to plasticize system below its T_{11}
$w_{1,max}$	weight fraction of solvent at which maximum diffusivity occurs
w_i	weight fraction of component i
x_i	mole fraction in equation (3)
x	distance for one-dimensional diffusion
x_i	mole fraction of component i
$x_{i,max}$	mole fraction of component i at which maximum diffusivity occurs
x_n	polymer number average degree of polymerization
$x_{n,i}$	polymer fraction i number average degree of polymerization
y	ratio of polymer size parameter S_2 to solvent size parameter S_1 in ASOG model
z	coordination number in UNIFAC model

Greek Letters

γ	activity coefficient of solvent
γ_{lg}	group interaction (enthalpic) contribution to activity coefficient
γ_s	size difference (entropic) contribution to activity coefficient in
$\gamma_{1,inf}$	activity coefficient of solvent at zero solvent concentration
θ_1	UNIFAC surface area fraction of solvent
θ_m	characteristic relaxation time for system
λ_d	characteristic diffusion time for system
ψ	chemical potential
ψ_0	concentration-independent term in chemical potential

μ_1	chemical potential of solvent
ρ	mass density of system
ρ_i	mass density of component i
ϕ_1	UNIFAC segment fraction of solvent
χ_1	Flory-Huggins interaction parameter for system
n_1	weight fraction activity coefficient of solvent
n_1^{inf}	weight fraction activity coefficient of solvent at zero solvent concentration

Subscripts

1	solvent
2	polymer
2,i	polydisperse polymer fraction or species i

CHAPTER 1

INTRODUCTION

The study of diffusion of small solvent molecules in polymers is important in a wide range of applications. Among these are the permeability of plastic films and packaging materials, and the resistance of paints, coatings, rubber, and other polymer products to environmental factors. Diffusion is important in various processing steps in polymer production, e.g., plasticization and devolatilization. In these and other applications, the diffusional behavior of a solvent or other penetrant must be characterized for the particular polymer-solvent system used.

Unfortunately, the study of diffusion in these systems is complicated by several factors. Most notably, there exists no single theory capable of describing the phenomena which occur. These include viscoelastic and similar

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). Efforts have been made to characterize certain types of behavior within certain temperature or concentration ranges (Vrentas, Jarzebski, and Duda, 1975). Such work indicates that changes, often abrupt, in polymer morphology and physical properties are in some degree responsible for the unusual diffusional behavior seen in these systems.

For process design and research, criteria are needed for scaling diffusion coefficients with temperature and concentration. Industrial problems which are related include polymer devolatilization, polymer swelling, and the incorporation of polymer additives such as plasticizers. The conditions of devolatilization are well above the glass transition temperature T_g . Polystyrene is devolatilized in the temperature range 200 C to 250 C, well above its T_g of 102 C.

Another problem in analyzing these systems is the lack of reliable and complete experimental data in the literature. Much of the published data are restricted to a few common systems, e.g., polystyrene-benzene. It is often expressed in a form which may be convenient for the specific study, but which omits details which would be important or

enlightening for further research. One example of this is the practice of giving raw data for weight uptake of penetrant, but failing to include parameters such as sample thickness which would be required in order to calculate diffusion coefficients. Data on the concentration of penetrant used, along with thermodynamic partition coefficients, are vital in studying the concentration dependence of diffusivity, but are often omitted. A quite notable omission in some studies is polymer characterization parameters such as average molecular weight and polydispersity. The net effect of such missing information makes much published data of little value for studying concentration and temperature dependence of diffusion coefficients.

The goal of this thesis was to propose a simple model for diffusion in polymer melts, at temperatures sufficiently above T_g that polymer relaxations are fast compared to the experimental time. In such systems, diffusivity has been observed to be a strong function of concentration (Duda and Vrentas, 1979) as well as temperature. The model was based upon thermodynamic concepts, analogous to work which has been done in scaling diffusion coefficients in non-polymer systems. It will be particularly applicable in predicting diffusion characteristics for the processing step of devolatilization. Available literature data for solvent diffusion coefficients as a function of concentration and

temperature in a typical polymer-solvent system were used in calculating the model parameters, and also for testing the predictions of the model. This thesis concerned the following topics: scaling of solvent diffusivity with concentration and temperature, thermodynamic modeling of polymer-solvent systems at low solvent concentrations, and correlation and testing with published data.

CHAPTER 2

LITERATURE REVIEW

2.1 Models for Diffusivity in Polymer Melts

It is generally recognized (Vrentas and Duda, 1979) that for small values of the diffusion Deborah number, the classical (Fickian) diffusion equations are applicable to polymer-solvent systems. Fickian behavior is defined as

$$J = -D \nabla C \quad (1)$$

where the flux J of a component can be described by a diffusion coefficient D times the concentration gradient (Bird, Stewart, and Lightfoot, 1960). However, the solvent diffusivity is not necessarily constant with concentration. Such behavior is likely to occur above the glass transition temperature of the system, where local relaxation of the polymer is rapid compared to the diffusion process. The

Deborah number is defined as

$$N_{deb} = \theta_m / \lambda_D \quad (2)$$

where θ_m is a characteristic relaxation time for the polymer-solvent system and λ_D is a characteristic diffusion time. Evaluation of N_{deb} is discussed in the literature (Vrentas, et al, 1975). Modulus data can be integrated numerically to evaluate λ_D , while pure component diffusivities, solvent concentration, and a characteristic sample dimension are needed to evaluate θ_m . Since it must be evaluated for the polymer-solvent system, not for the pure polymer, both concentration and temperature become important independent variables.

The presupposition that small values of N_{deb} are likely to occur above T_g must be qualified by saying that it is necessary to consider T_g of the polymer-solvent system, not that of the pure polymer. Most solvents will act as plasticizers, and lower the glass transition temperature. As solvent concentration increases, T_g will usually decrease, and the Deborah number will become small. For a model which scales diffusivity based on thermodynamics to work, it is necessary, although not sufficient, that N_{deb} must be low. If relaxation and diffusion are occurring on the same time scale, Fickian behavior will not be observed even at a single concentration. Relaxation must be much faster than diffusion in order for thermodynamic equilibrium

to occur, although fast relaxation does not guarantee equilibrium. A thermodynamically based model which correctly predicts diffusivity as a function of concentration over the entire concentration range at one temperature may thus fail at a lower temperature for low values of solvent concentration. However, it might still correctly describe diffusivity at a higher range of solvent concentrations, since N_{deb} changes with solvent concentration as mentioned above.

2.1.1 Empirical Models for Concentration Dependence

Much of the work to date in scaling diffusivity with concentration for polymers has been empirical. An exponential concentration dependence has been proposed (Kokes and Long, 1953) of the form

$$D(x) = D_0 \exp(dx) \quad (3)$$

where x represents solvent fraction, D_0 is a concentration independent diffusivity (at zero solvent concentration) and d is a characteristic constant for the system. This constant d can be related to the Flory-Huggins interaction parameter X for the system, but in general must be determined empirically.

2.1.2 Free Volume Models for Diffusivity

Theories of diffusion based upon free volume have been successfully applied to polymer-solvent systems, beginning with the work of Fujita (1961). Recent adaptations and extensions of these theories by Duda, Vrentas, and other investigators have shown good agreement with experiment in some cases (Duda, Vrentas, Ju, and Hsieh, 1982).

Free volume models for diffusivity have their roots in previous descriptions of transport properties in liquid systems. This includes models for liquid viscosity as a function of the free volume in a system (Batschinski, 1913; Doolittle and Doolittle, 1957) and models for segmental mobility in polymers (Bueche, 1953; Meares, 1958). Cohen and Turnbull (1959) and Turnbull and Cohen (1961) derive an expression for self-diffusion coefficients as a function of free volume. Their work is utilized by Fujita (1961, 1968) in describing polymer-solvent diffusion. However, the Fujita theory is not successful in describing the quantitative changes in diffusivity with concentration (Duda, et al, 1982).

The model proposed by Duda, et al (1982) shows excellent agreement with experiment for a few common polymer-solvent

systems. The theory contains parameters which describe the amount of free volume in the system, the critical amount of free volume necessary for molecular motion (jumping) of solvent to occur, and the ratio between solvent critical free volume for jumping and polymer segment (jumping unit) critical free volume for jumping. Viscosity data is utilized to predict the variation of these transport parameters with temperature and concentration. Density or specific volume data is used both in the prediction of transport properties and in the prediction of thermodynamic behavior. An overlap factor is included to account for the fact that the same free volume is available to more than one molecule.

This work has the advantage of a strong theoretical framework as compared with strictly empirical studies. Nevertheless, the lack of sufficient understanding of the diffusion process at the molecular level hampers the direct application of free volume models, since many of the parameters required are not available but must be evaluated empirically from diffusion data. Other thermodynamic and transport parameters which are required for successful application may not be available for the polymer-solvent system in question. Finally, even when all the parameters are available from the literature or through experimental correlation, the equations of the model do not clearly indicate the temperature and concentration dependence of

diffusivity, since the equations of the model contain so many independent variables. Many of these variables contain implicit concentration and temperature dependences of their own. Without explicit knowledge of these functional dependences, the prediction of expected maxima and limiting cases for a range of conditions is difficult.

2.2 Thermodynamic Models Applicable to Polymer Systems

2.2.1 Polymer Equilibrium

Amorphous polymers can be considered to exist as non-equilibrium liquids below their glass transition temperature. This state is made possible by the fact that polymer molecules do not have sufficient energy to relax into a true equilibrium conformation, even though such a state would be favored thermodynamically. Over a sufficiently long time scale, a non-equilibrium amorphous polymer will approach an equilibrium liquid state.

The determination of whether a particular polymer, or polymer-solvent system, is at equilibrium depends on the time scale of the measurement used to characterize the system. To observe equilibrium, the polymer relaxation must

be faster than the time scale of interest. Amorphous polymers generally exhibit a change in modulus (or viscosity) of several orders of magnitude within the time scale of the experiment when they are heated above T_g . This provides an indication that polymer relaxations occur quickly above T_g .

The mechanism for polymer relaxation above the glass transition is postulated to be the motion of long segments of polymer molecules, consisting of 20-50 chain atoms. This local relaxation manifests itself in a large decrease in polymer modulus and viscosity, properties which are strongly dependent upon local conditions within polymer molecules.

It has been postulated since the early 1960's that a transition or relaxation somewhat analogous to the glass transition can occur in certain amorphous polymers (Boyer, 1963; Boyer, 1966). This transition is generally referred to as the liquid-liquid transition, and the transition temperature called T_{ll} . Boyer proposes that this transition, occurring above T_g , corresponds to motion of entire polymer molecules, as opposed to T_g , which involves motion of segments of polymer molecules containing 20-50 chain atoms. The region below T_g in temperature is termed the glassy state, with the region between T_g and T_{ll} called a "fixed fluid" and the region above T_{ll} called a "true liquid" by some investigators (Ueberreiter, 1965; Gillham, Benci, and

Boyer, 1976). This terminology is meant to imply that true thermodynamic equilibrium is not achieved in amorphous polymers at T_g , but rather at T_{11} . In the "fixed fluid" region, motion of entire molecules is hindered in such a way that a true equilibrium liquid state cannot occur, although local movement of segments causes a change in properties such as viscosity from their values in the glassy state.

Although the existence of such a transition has been proposed for twenty years, the acceptance of the idea has been slow. The reasons for this lack of acceptance, along with a complete compilation of experimental evidence for T_{11} , are given by Boyer (1979). Among the experimental evidence cited are investigations using melt fusion and flow (Ueberreiter and Orthmann, 1958), dynamic melt viscosity (Onogi, Masuda, and Kitagawa, 1966), falling ball viscosity (Colborne, 1967), diffusion and solubility (Duda and Vrentas, 1968) dynamic mechanical testing (Sidorovitch, Marei, and Gashtol'd, 1970), volumetric methods (Hocker, Blake, and Flory, 1971), heat capacity measurement (Boyer, 1972), thermal diffusivity (Ueberreiter and Naghizadeh, 1972), differential scanning calorimetry (Stadnicki, Gillham, and Boyer, 1976), torsional braid analysis (Gillham, et al, 1976), representing macroscopic techniques, and electron spin resonance (Smith, Boyer, and Kumler, 1979) and carbon-13 nuclear magnetic resonance (Axelson and Mandelkern, 1978), representing molecular techniques.

The diffusion and solubility study was undertaken by Duda and Vrentas on the system n-pentane-polystyrene (1968). The results giving evidence for T_{11} were unexpected (Boyer, 1979) but show a definite change in the Arrhenius activation energy for diffusion at about 150 C, with E decreasing by a factor of three from 44 kcal/mole below T_{11} to 14 kcal/mole above T_{11} . This result is for polystyrene with a weight average molecular weight of 412,000. Equilibrium solubility also shows variation in temperature dependence at T_{11} , although the investigators admit this may be due to scatter in the data.

2.2.2 Flory-Huggins

Various models for polymer-solvent thermodynamics have been proposed. Most of these are variations on the treatment by Flory and Huggins, which treats the entropy of mixing in a roughly statistical manner, and uses an interaction parameter, χ , to model the enthalpy of mixing. The chemical potential of the solvent is given by

$$\mu_1 = RT (\ln(1 - v_2) + \chi v_2^2 + v_2) \quad (4)$$

where v_2 is the volume fraction of polymer (Flory, 1953). Evidence indicates that the entropic terms are correctly predicted by Flory-Huggins theory. The enthalpic terms are

incorrectly modeled, and much further work has led to the reinterpretation of the meaning of the interaction parameter as a free energy term (Billmeyer, 1971). The independent variable used is the volume fraction. Since most experimental data is expressed in terms of weight fraction, a more convenient measurement for solid materials, density or specific volume data is required to convert weight fraction data to a volume fraction basis.

2.2.3 Group Contribution Methods

Although not specifically designed for use with polymers, a number of recent general thermodynamic models are applicable to polymer-solvent systems. Among these are the group contribution models which have recently been proposed by various investigators. These models allow for separate modeling of both the entropic and enthalpic effects in solution. They specifically provide for the consideration of the differences in molecular size which characterize polymer-solvent systems. Finally, they are based upon other models, not including the concept of group contribution, which are firmly founded on theoretical grounds or backed by experimental verification. These other models include Wilson's correlation based upon local volume fractions (1964), the UNIQUAC model based upon local area fractions

(Abrams and Prausnitz, 1975), Staverman's combinatorial entropy (1950), and the original work of Flory and Huggins mentioned above.

The earliest group contribution model was the Analytical Solution of Groups stated by Derr and Deal (1969). This model contains an entropic term based upon Flory-Huggins theory, with an enthalpic term given by Wilson's equation. The independent variable used is mole fraction, rather than the volume fraction used by Flory-Huggins. Differences in molecular volume are accounted for by counting the number of "size groups" in a molecule. Agreement with experiment is found to be good, although a lack of data restricts application to molecules which contain only a few very common functional groups (Palmer, 1975).

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, Jones, and Prausnitz, 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. The separate entropic (combinatorial) and enthalpic (residual) terms in the model are derived

naturally from statistical thermodynamics.

Besides this advantage on theoretical grounds, UNIFAC also contains a more accurate means of modeling molecular size than ASOG. Pure component data are used to generate the size terms for each molecule, based upon the number and type of functional groups it contains. Both surface area and volume of the molecule are considered in the UNIFAC model. It is stated that the UNIFAC model is more general than UNIQUAC (Gmehling, Rasmussen, and Fredenslund, 1982), which in turn can be reduced to nearly all of the previously proposed thermodynamic models by appropriate substitutions (Abrams and Prausnitz, 1975). Despite the obvious possibilities for application in polymer systems, neither UNIFAC nor ASOG has been used in any published work.

2.3 The T_{11} Transition in Polystyrene

Most of the experimental evidence accumulated on T_{11} indicates that the absolute temperature is inversely proportional to number average molecular weight, below a critical molecular weight. This critical molecular weight represents the point at which chain entanglements begin to affect viscous flow. Above the critical molecular weight, T_{11} increases without limit as number average molecular

weight increases. However, for experimental techniques which do not involve viscous flow, T_{11} dependence on molecular weight does not change about the critical value. Diffusion measurements are a particular example of such a technique (Boyer, 1979). In this case, T_{11} is expected to approach a limiting value at infinite molecular weight, in the same manner as T_g does.

Other published results give various values for T_{11} . Some of these are summarized in Table 1.

TABLE 1
 T_{11} Measurements for Polystyrene (Non-Flow Techniques)

Temperature (degrees C)	Molecular Weight	Reference
150	412,000 (M_w)	Duda and Vrentas, 1968
154-170	51,000 (M_w^n)	Hocker, et al, 1971
167	136,000 (M_n^n)	Boyer, 1979

Boyer estimates T_{11} for high molecular weight polystyrene to be 435-440 K, or about 162-167 C. Using the correlated data of Gillham, et al (1976), T_{11} at 75,000 number average molecular weight should be about 1.5 C below the infinite molecular weight value. This would place T_{11} for the polystyrene used in the diffusion study at about 160-165 C, about ten degrees above the range where the transition in diffusivity occurred. Boyer states that the reason for the low T_{11} given by Duda and Vrentas was possible plasticization of the polystyrene by the n-pentane used as penetrant. This hypothesis will be discussed in detail when

concentration dependence of T_{11} is considered below. Other explanations include the use of an integral diffusivity by Duda and Vrentas, thereby enhancing the variation in diffusivity due to concentration since different equilibrium solubilities were found at different temperatures. Also, the fact that none of the samples used in any diffusion studies were monodisperse can cause T_{11} to occur over a broad range of temperature, especially if the weight distribution includes polymer both above and below the critical molecular weight (Gillham, et al, 1976).

2.3.1 T_{11} Dependence on Solvent Concentration

To put this discussion on a more quantitative basis, it is useful to correlate T_{11} with system composition in the same way that it was related to molecular weight of polymer above. Experimental results (Gillham, et al, 1976) indicate that T_{11} can be modeled by an equation of the form

$$T_{11} = T_{11,1}w_1 + T_{11,2}w_2 + Kw_1w_2 \quad (5)$$

where subscripts 1 and 2 refer to the component T_{11} values and weight fractions, and K is an empirical constant. The system studied is polystyrene and m-bis(m-phenoxyphenoxy)benzene. Although the authors do not state that K must be negative, their results always show it

as such. This implies that a simplified form of (5) could be used to give an approximate result, an upper bound on T_{11}

$$T_{11} < T_{11,1}w_1 + T_{11,2}w_2 \quad (6)$$

Rearranging this to solve for weight fraction of solvent gives

$$w_{1,c} < (T_{11,2} - T_{11}) / (T_{11,2} - T_{11,1}) \quad (7)$$

which is an upper bound on the critical weight fraction required to reduce the mixture transition temperature to T_{11} .

$T_{11,2}$ is taken for the pure polymer used. The value of $T_{11,1}$ for the solvent used in analyzing Gillham's data is the boiling point of the solvent at 1 mm Hg pressure.

2.3.2 Effects of Molecular Weight Distributions on T_{11}

As mentioned above in the section on T_{11} , the molecular weight dependence for monodisperse polymer is fairly well known. Below the critical molecular weight for entanglements, about 30,000-40,000 for polystyrene, (Gillham, et al, 1976), T_{11} is a linear function of the reciprocal of the molecular weight. The same dependence is

observed in polydisperse samples, provided that all of the polymer species present are below M_c .

Above M_c , for monodisperse samples, the behavior of T_{11} depends upon the experimental technique used for measurement. When techniques involving viscous flow are used, T_{11} increases without limit as molecular weight increases. However, other experimental techniques show T_{11} asymptotically reaching a limiting value as molecular weight increases. The discrepancy between various techniques is believed to be due to the effect of entanglements on the experimental techniques involved. Bulk flow is greatly affected by entanglements, and the concentration of entanglements will increase as polymer molecular weight increases. On the other hand, thermal or diffusional properties are dependent mostly on local conditions encountered by the diffusing flux. For example, diffusion of a solvent through a polymer depends on the local viscosity, however that may be defined, rather than on the overall solution viscosity. The predominant effect of entanglements above M_c is thereby not observed in non-bulk flow measurements. In particular, this is the case for diffusional measurements.

When polydisperse samples of polymer are tested, with some species both above and below M_c , more than one T_{11} transition is observed (Gillham, et al, 1976). This

conclusion is reached by observation of T_{11} by torsional braid analysis, a technique dependent upon viscous flow. The same authors do not state what effect will be seen in a non-flow technique. Assuming that the entanglement mechanism is correct in explaining the differences in T_{11} observed by different experiments, it is likely that only a single T_{11} will be observed for a polydisperse sample with species both above and below M_c . This follows from the hypothesis that the presence and concentration of entanglements have no effect on non-flow properties, and from the observed molecular weight dependence of T_{11} measured by non-flow properties, which does not change above M_c but continues to approach its limiting value. Analogy with T_g dependence in polydisperse samples, which is also not affected by the presence of both high and low weight polymer, indicates that T_{11} will depend on the number average molecular weight in the same manner as it did below M_c .

CHAPTER 3

MODEL DEVELOPMENT

3.1 Thermodynamic Basis for Scaling Diffusivity

There is a well-developed theory relating diffusivity to thermodynamic measurements, although it has seldom been applied to polymers. The earliest application was found in calculating diffusivities in ionic solutions (Onsager and Fuoss, 1932). The classical, Fickian diffusion flux is written

$$J = -D (dC/dx) \quad (8)$$

for a one-dimensional system. This characterization of the flux assumes thermodynamic ideality exists, since in reality it is the gradient of the chemical potential μ , rather than the concentration C , which is the driving force for diffusional transport. The following steps will allow the

flux to be written in a manner which accounts for thermodynamic non-ideality.

The corrected equation for the flux is given by

$$J = -(Cu/N)(d\psi/dx) \quad (9)$$

where C is the molar concentration of diffusing particles, u is the mobility of the diffusing particle per unit force, and N is Avogadro's number (Jost, 1960). Next, the chemical potential ψ can be related to activity a by

$$\psi = \psi_0 + RT \ln a \quad (10)$$

Since ψ_0 is not a function of concentration, only of temperature, the derivative above can be rewritten in terms of the activity

$$d\psi/dx = RT (d \ln a/dx) \quad (11)$$

so that

$$J = -CukT (d \ln a/dx) \quad (12)$$

and by the chain rule

$$J = -CukT (d \ln a/dC) (dC/dx) \quad (13)$$

Noting that dC/C is equal to $d \ln C$, the final equation for the flux can be written

$$J = -ukT \left(\frac{d \ln a}{d \ln C} \right) \left(\frac{dC}{dx} \right) \quad (14)$$

Defining the concentration-independent part of the diffusivity

$$D_0 = ukT \quad (15)$$

gives as the final result for the diffusivity

$$D = D_0 \left(\frac{d \ln a}{d \ln C} \right) \quad (16)$$

or in terms of the mole fraction x_1 of solvent with activity a_1

$$D = D_0 \left(\frac{d \ln a_1}{d \ln x_1} \right) \quad (17)$$

assuming that solution molar density does not change with changes in concentration, so that

$$d \ln C = d \ln \phi + d \ln x = d \ln x \quad (18)$$

Solution molar density will change with concentration in actual polymer-solvent systems, but the assumption made above will hold approximately, if the solvent concentration does not vary widely.

It is also possible to write this result in terms of the activity coefficient γ_1 since

$$a_1 = y_1 x_1 \quad (19)$$

$$\ln a_1 = \ln y_1 + \ln x_1 \quad (20)$$

$$d \ln a_1 / d \ln x_1 = d \ln y_1 / d \ln x_1 + d \ln x_1 / d \ln x_1 \quad (21)$$

$$= 1 + (d \ln y_1 / d \ln x_1) \quad (22)$$

Therefore

$$D = D_0 (1 + d \ln y_1 / d \ln x_1) \quad (23)$$

Application of this result to polymer-solvent systems presupposes the existence of activity data for the solvent in the polymer over a range of concentrations and temperatures. Such data is scanty and incomplete. However, studies have shown that using a diffusivity based upon thermodynamic activity results in a much smaller variation in D (actually D_0) with concentration than a Fickian diffusivity based upon concentration gradients (Morrison, 1967). This implies that the use of thermodynamic activity in scaling diffusivity is effective in lumping much of the concentration dependence of diffusivity into the activity term. In general, such activity data is not available, thus preventing the direct application of (17) or (23). Attempts have been made to couple these thermodynamic results with some of the empirical modeling of diffusivity with concentration discussed in section 2.1.1 above (Kuppers and Reid, 1960), but this work gives no new information, but

merely allows the calculating of activity data from diffusivity data or vice versa.

In conclusion, it has been shown that diffusivity can be modeled as a function of concentration provided that some thermodynamic activity data can be found or generated. Such data is difficult to obtain experimentally for polymer-solvent systems; hence, to apply equation (17) or (23), further thermodynamic modeling is necessary.

3.2 Application of Thermodynamics to Diffusivity Modeling

In the following sections, the discussion of thermodynamics was intended to apply the models (ASOG and UNIFAC) to a typical polymer-solvent system for which thermodynamic data would be of use in predicting the variation of diffusivity with concentration. The system toluene(1)-polystyrene(2) was used, since there was some experimental diffusivity data available. This allowed the results of the thermodynamic modeling to be checked.

In applying the thermodynamic models to diffusivity calculations, a number of simplifying assumptions were initially made. The polymer was assumed monodisperse, so that effects of molecular weight distribution did not arise.

Constant temperature was assumed in developing the concentration dependence of diffusivity. In later sections, these assumptions were relaxed.

3.2.1 Derivation of ASOG Solution

In the ASOG model, the two contributions to the activity coefficient are y_1^s , the entropic part, and y_1^g , the enthalpic part (the superscript g refers to "group interaction"). Since the polymer and solvent were quite similar chemically, the enthalpic part was expected to be small. This corresponded to the idea of an athermal solution. On the other hand, the entropic contribution was large, due to the size differences between polymer and solvent molecules.

The entropic contribution was given by

$$\ln y_1^s = 1 - R_1 - \ln R_1 \quad (24)$$

where R_1 was the size term for component 1 (toluene). This was in turn given by

$$R_1 = S_1 / (S_1 x_1 + S_2 x_2) \quad (25)$$

The S_i terms were the number of size groups found in molecule i , and the x terms were the mole fractions of

components 1 or 2 within the solution. For the purposes of this example, the number of size groups in a molecule was equal to the number of carbon atoms it contained. For toluene, this was seven; for polystyrene, there were eight carbon atoms per repeat group in the polymer chain. S_i terms could then be written as

$$S_1 = 7 \quad (26)$$

$$S_2 = 8x_n \quad (27)$$

where x_n was the degree of polymerization of the polymer. Since the polymer was assumed monodisperse, this was a constant value for every polymer molecule, and no averaging was required.

The enthalpic (group interaction) activity coefficient was found by calculating the mole fractions of functional groups within the solution, then applying the Wilson equation to these values. Standard values of interaction parameters are given for various combinations of functional groups. These coefficients were normalized by subtracting off a standard-state group interaction activity coefficient found in the same way, but based upon the functional group composition of each pure component (Palmer, 1975). For the system toluene-polystyrene, these enthalpic coefficients were negligible compared to the entropic coefficients, as discussed above, and were not included in later calculations. The logarithms of entropic coefficients were

from two to four orders of magnitude larger than the logarithms of enthalpic coefficients at nearly all concentrations of solvent. At very high concentrations of solvent, where both coefficients were small, the entropic coefficients were still larger. Table 2 gives typical values of these coefficients at various solvent concentrations.

TABLE 2
Entropic and Enthalpic Activity Coefficients
for the Toluene-Polystyrene System

Weight Fraction Toluene	$\ln y_1$	
	Entropic	Enthalpic
0.000	-5.72	0.00607
0.001	-5.12	0.00606
0.01	-3.51	0.00601
0.1	-1.40	0.00547
0.5	-0.20	0.00278
0.9	-0.00546	0.000217
0.99	-0.000050	0.000003

Applying this simplifying assumption, it was possible to derive a closed form expression for the derivative which was required to scale diffusivity with concentration, using equation (17) or (23) above. Substituting equation (25) into (24) gave

$$\begin{aligned} \ln y_1 = & 1 - S_1 / (S_1 x_1 + S_2 (1 - x_1)) \\ & + \ln (S_1 / (S_1 x_1 + S_2 (1 - x_1))) \end{aligned} \quad (28)$$

The next step was to take the derivative of this with respect to x

$$\begin{aligned} d \ln y_1 / dx_1 = & S_1(S_1 - S_2) / (S_1 + (S_1 - S_2)x_1)^2 \\ & - (S_1 - S_2) / (S_2 + (S_1 - S_2)x_1) \end{aligned} \quad (29)$$

Rearranging terms gave

$$d \ln y_1 / dx_1 = (S_1 - S_2)^2(1 - x_1) / (S_2 + (S_1 - S_2)x_1)^2 \quad (30)$$

To reduce the number of variables on the right hand side, the numerator and denominator of the expression were divided through by S_1 , and the substitution $y = S_2/S_1$ was made.

$$d \ln y_1 / dx_1 = (1 - y)^2(1 - x_1) / (y + (1 - y)x_1)^2 \quad (31)$$

To get the derivative expressed in (23), the chain rule was applied.

$$\begin{aligned} d \ln y_1 / d \ln x_1 &= (d \ln y_1 / dx_1)(dx_1 / d \ln x_1) \\ &= x_1(d \ln y_1 / dx_1) \end{aligned} \quad (32)$$

Substituting (31) into (32)

$$d \ln y_1 / d \ln x_1 = (1 - y)^2 x_1 (1 - x_1) / (y + (1 - y)x_1)^2 \quad (33)$$

The final result came from substituting (33) into (22)

$$d \ln a_1 / d \ln x_1 = \frac{y^2 + 2y(1 - y)x_1 + (1 - y)^2 x_1}{y^2 + 2y(1 - y)x_1 + (1 - y)^2 x_1^2} \quad (34)$$

Equation (34) gives the value of the derivative, based upon the ASOG model, as a function of solvent mole fraction x_1

and polymer-solvent size ratio y .

3.2.2 Properties of ASOG Result

Some properties of this result could be noted immediately. At zero solvent mole fraction (pure polymer) or zero polymer mole fraction (pure solvent), the numerator and denominator became identical, and the value of the derivative was 1. Furthermore, the expressions in both the numerator and denominator were always positive. Since these differed in only their third terms, and since mole fractions lie between zero and one, the denominator must always be less than or equal to the numerator. This provided a simple proof that the derivative was always greater than or equal to 1, so it took on its minimum values at solvent mole fractions of 0 or 1, the only values of concentration at which the derivative was exactly equal to 1.

A good deal of algebra was required to find the maximum value of the derivative and the mole fraction at which it occurred. The expression in (34) above could be differentiated with respect to mole fraction, and the resulting expression set equal to zero. This gave the following quadratic equation for the extremal (maximal) value of mole fraction

$$\begin{aligned}
 (1 - (y - 1)^4 + 2y(y - 1)^3)x_1^2 \\
 + (1 - 2y^2(y - 1)^2)x_1 \\
 + y^2(y - 1)^2 = 0
 \end{aligned}
 \tag{35}$$

When this quadratic equation was solved for mole fraction, one of the roots was larger than 1, and one lay in the range between zero and one. The larger root was discarded, since mole fraction cannot be greater than one. The mole fraction at which the derivative is largest was

$$x_{1,\max} = y / (y + 1) \tag{36}$$

where y was the ratio of the number of size groups in the polymer molecule to the number of size groups in the solvent molecule. Since y was generally large for polymer-solvent systems, the derivative had its maximum at a mole fraction of solvent which approached one. This was difficult to reconcile with the result above which stated that the derivative had a minimum at a mole fraction of one.

The result was both clearer to understand and to apply when the independent variable was transformed from mole fraction to weight fraction, which is more appropriate for polymer systems. Letting the molecular weights be represented by M_1 (solvent) and M_2 (polymer), the weight fraction is defined

$$w_1 = x_1 M_1 / (x_1 M_1 + x_2 M_2) = x_1 / (x_1 + x_2 (M_2/M_1)) \quad (37)$$

The mole fraction of polymer at the maximum could be found from (36)

$$x_{2,\max} = 1 - (y / (y + 1)) = 1 / (y + 1) \quad (38)$$

The maximal weight fraction was calculated directly by substituting (36) and (38) into (37)

$$w_{1,\max} = y / (y + M_2/M_1) \quad (39)$$

For systems composed of similar functional groups in similar proportions, e.g., toluene-polystyrene, the ratio of molecular weights is approximately equal to the ratio of molecular sizes, y , according to the ASOG theory. This gave a final result of

$$w_{1,\max} = y / (y + y) = y / 2y = 0.5 \quad (40)$$

The maximum value of the derivative could now be found by substituting (36) into (34)

$$\begin{aligned} & (d \ln a_1 / d \ln x_1)_{x_{1,\max}} = \\ & \frac{y^2 + 2y(1 - y)y/(y + 1) + (1 - y)^2 y/(y + 1)}{y^2 + 2y(1 - y)y/(y + 1) + (1 - y)^2 y^2/(y + 1)^2} \end{aligned} \quad (41)$$

which reduced to

$$\left(\frac{d \ln a_1}{d \ln x_1} \right)_{x_1, \max} = (y + 1)^2 / 4y \quad (42)$$

or in the limit of large y

$$\left(\frac{d \ln a_1}{d \ln x_1} \right)_{x_1, \max} = y / 4 \quad (43)$$

The ASOG model led to several definite conclusions regarding the thermodynamics of polymer-solvent systems. Expressing these in terms of diffusivity, as given by equation (17), these conclusions were:

1) Diffusivity as a function of concentration was convex upward. The maximum value occurred at a weight fraction of 0.5 for systems in which the polymer and solvent contained similar proportions of functional groups.

2) The ratio of the maximum value of the diffusivity (at weight fraction of 0.5) to its minimum value (at weight fraction zero of solvent) was one-fourth the ratio of the molecular sizes of polymer and solvent. For similar polymer-solvent systems, this was one-fourth the ratio of the molecular weights.

3) These results assumed no enthalpic interaction between polymer and solvent molecules. Such interactions produced effects which were roughly three orders of magnitude lower

than the entropic activity coefficients derived above, in the nonpolar system studied here. The solution was athermal to an excellent approximation.

3.3 Application of UNIFAC

The UNIFAC model could be applied in a similar way. Since UNIFAC was somewhat more complex than ASOG, it was simpler to numerically calculate the activity coefficients and the required derivative using a digital computer, rather than attempt to find a closed form solution such as (34) above. As was true with the ASOG model, the enthalpic (residual) contribution to the activity coefficient was several orders of magnitude less than the entropic (combinatorial) contribution and could be neglected. Table 3 gives these values.

TABLE 3
Combinatorial and Residual Activity Coefficients
for the Toluene-Polystyrene System

Weight Fraction	$\ln y_1$	
Toluene	Combinatorial	Residual
0.001	-4.99	0.0109
0.01	-3.30	0.00401
0.1	-1.30	0.00050
0.5	-0.165	0.000082
0.9	-0.00430	0.000027
0.99	-0.000040	0.000021

The combinatorial activity coefficient is given by

$$\ln y_1 = \ln(\theta_1/x_1) + (z/2)q_1 \ln(\theta_1/\theta_1) + l_1 - (\theta_1/x_1)(x_1 l_1 + x_2 l_2) \quad (44)$$

for a binary mixture (Fredenslund, et al, 1975). θ is the area fraction

$$\theta_1 = q_1 x_1 / (q_1 x_1 + q_2 x_2) \quad (45)$$

and θ is the segment fraction (similar to volume fraction)

$$\theta_1 = r_1 x_1 / (r_1 x_1 + r_2 x_2) \quad (46)$$

The parameters q_i and r_i are analogous to the size parameters of the ASOG model. They are pure component parameters which measure molecular surface areas (q) and molecular van der Waals volumes (r). These are calculated by summing individual q and r terms for each functional group, over all the functional groups in a molecule. Since each functional group has an individual set of parameters q and r , the UNIFAC model should be somewhat more accurate than the ASOG model, which essentially counts the number of carbon atoms in a molecule to determine its size.

The terms l_i in (44) are given by

$$l_i = (z/2)((r_i - q_i) - (r_i - l)) \quad (47)$$

and z , the coordination number, is arbitrarily set

$$z = 10$$

(48)

The authors of the UNIQUAC model find that numerical results for activity coefficients are insensitive to choice of z as long as a reasonable value of z is chosen (between 6 and 12) (Abrams and Prausnitz, 1975). This assumption should apply to UNIFAC as well. However, some of the parameters used in evaluating the residual (enthalpic) activity coefficient are dependent on the value of z , and the authors of UNIQUAC warn against varying z arbitrarily (Fredenslund, et al, 1975). Since the system studied here was approximately athermal, a restriction on z for that reason need not apply. The original UNIQUAC paper does not state explicitly, but does show as an appendix, that the size parameters q and r also depend on the value of coordination number z which is chosen, implying that if z is varied, q and r for each functional group must be recalculated from van der Waals radii and surface areas. Here, z was taken as a constant equal to 10.

Pure component size parameters could be calculated for toluene and polystyrene by adding the functional group contributions. These are tabulated by several authors, and the most recent tables were used in this work (Gmehling, et al, 1982). Toluene consists of five ACH groups and one ACCH3 group. Each polystyrene repeat unit consists of 5 ACH groups, one ACCH group, and one CH2 group. Table 4 gives

the size parameters applicable to these groups.

TABLE 4
UNIFAC Size Parameters for Toluene-Polystyrene system

Functional Group	r	q
ACH	0.5313	0.400
ACCH3	1.2663	0.968
ACCH	0.8121	0.348
CH2	0.6744	0.540

The appropriate r and q values for toluene(1)-polystyrene(2) system were

$$r_1 = 5(0.5313) + 1.2663 = 3.9228 \quad (49)$$

$$q_1 = 5(0.400) + 0.968 = 2.968 \quad (50)$$

$$r_2 = (5(0.5313) + 0.8121 + 0.6744)x_n = 4.1430 x_n \quad (51)$$

$$q_2 = (5(0.400) + 0.348 + 0.540)x_n = 2.888 x_n \quad (52)$$

These parameters were used in the system of equations (44)-(48) above. The result of solving these equations was a value for the activity coefficient. These equations were easily solved using a computer program, and the activity coefficients generated were numerically differentiated using a simple finite difference approximation. This gave the desired result, which was a numerical value for the derivative $d \ln a_1 / d \ln x_1$ which appeared in (17) above, the fundamental expression for diffusivity as a function of concentration.

Numerical results generated by UNIFAC were found to agree both qualitatively and quantitatively with the analytic

results from the ASOG model given by (34) above. The weight fraction of solvent at which the derivative was maximum occurred at about 0.47 in the numerical UNIFAC model, comparable to the maximal weight fraction of 0.50 from the ASOG model according to (40). Actually, the more general ASOG result was equation (39). Equation (40) then resulted by approximating the ratio of molecular weights by the ratio of size groups. Both this approximation and the less accurate representation of molecular size by the ASOG concept of size groups contributed to the difference between UNIFAC and ASOG results. The fact that this difference was slight indicated that the simpler ASOG model worked nearly as well as UNIFAC. The maximum value of the derivative, predicted by ASOG to be $y/4$, is about 0.22y in the numerical results from UNIFAC. Once again, this agreement indicated that the two models were consistent with each other, and that the simpler ASOG model was about as accurate as the more complex UNIFAC model for the toluene-polystyrene system. Some typical results for polystyrene-toluene with polymer molecular weight 75,000 are given in Table 5.

TABLE 5
Comparison of ASOG and UNIFAC Results

Weight Fraction	$d \ln a_1 / d \ln x_1$	
Toluene	ASOG	UNIFAC
0.001	1.812	1.811
0.01	9.849	9.830
0.1	74.41	69.24
0.4	197.8	178.7
0.5	204.3	180.3
0.8	133.9	111.6
0.9	74.90	65.99

3.4 Effects of Molecular Weight Distributions

Throughout the discussion so far, polymer molecular weight was a relevant parameter in the predictions of the ASOG and UNIFAC models of activity coefficients, and in the predicted T_{11} transition temperature. Little had been said about the effect of polydisperse polymer samples upon the stated results. The results given so far were applicable to monodisperse polymer. Unfortunately, no experimental data is available for solvent diffusivity as a function of concentration in monodisperse polymer. Before further development of the diffusivity model was attempted, the effect of polydispersity upon the predictions of the thermodynamic models had to be analyzed, so that these predictions could be compared on a more sound basis to existing experimental data for polydisperse systems. A

discussion of the effects of molecular weight distributions was vital for testing of the model, and its application to practical problems.

The goal of this section was to describe as completely and correctly as possible the molecular weight distribution dependent features of the diffusivity model developed above. At the same time, an attempt was made to use as few parameters of the weight distribution as possible. We hoped the model could describe the thermodynamics of polydisperse systems with only a few molecular weight distribution descriptors.

As is the case with many of the thermodynamic models used for prediction of activity coefficients, both the ASOG and UNIFAC models allow for an indefinite number of components in the mixture. Equations (25) and (44)-(46) are applicable to binary systems only, but generalized forms are available. These generalized equations have a sound basis in theory, since both ASOG and UNIFAC consider a solution to consist of functional groups rather than individual molecular components. It is the functional groups and their concentrations which are "counted" in order to determine activity coefficients under ASOG and UNIFAC.

A solution consisting of solvent (toluene) and polydisperse polymer (polystyrene) could be treated as a multicomponent

system containing solvent, along with a number of polymer species of differing molecular weights (or molecular sizes). The mole fraction of solvent would remain the same as in an assumed binary system of solvent and monodisperse polymer with the number average molecular weight of the actual polydisperse system. However, there now would be a mole fraction for each polymer species present in the solution. This was defined by the equation

$$x_{2,i} = x_2 x_i \quad (53)$$

where x_2 was the mole fraction of polymer in an assumed binary system of solvent and monodisperse polymer with the number average molecular weight of the actual polydisperse polymer. The mole fraction of polymer species i among all polymer species present was x_i . $x_{2,i}$ represented the mole fraction of polymer species i within the overall polymer-solvent system. The following identities hold for the mole fraction quantities defined here.

$$x_1 + x_2 = 1 \quad (54)$$

$$\sum x_i = 1 \quad (55)$$

Combining (53)-(55) verified that the solvent mole fraction plus all of the polymer species mole fractions summed to one.

$$x_1 + \sum x_{2,i} = 1 \quad (56)$$

The x_i mole fractions are readily available from an experimental or theoretical molecular weight distribution. In practice, these will generally be polymer fractions containing several different molecular weight species as opposed to individual polymer species. As long as the fractions are not very broad in weight distribution, approximating a set of molecular species as a single fraction with molecular weight equal to the number average molecular weight of that fraction would not introduce large errors. A limiting case of this treatment would be approximating the entire set of polymer species as a single monodisperse polymer with number average molecular weight. In this case, equation (56) would reduce to equation (54), and the multicomponent system reduced to a binary system, for which the results of ASOG and UNIFAC are already available in equations (34) and (44)-(52) above.

3.4.1 Effects of MWD on ASOG

To apply ASOG to a multicomponent system, solving for activity coefficient of solvent, the equations relating to only solvent parameters did not change.

$$\ln y_1 = 1 - R_1 - \ln R_1$$

$$S_1 = 7$$

However, the equations which contained polymer parameters (component 2) must be generalized. Equation (17) for the solvent size term became

$$R_1 = S_1 / (S_1 x_1 + \sum S_{2,i} x_{2,i}) \quad (57)$$

where the size parameter of polymer fraction i was defined by the generalized form of equation (19).

$$S_{2,i} = 8x_{n,i} \quad (58)$$

The new variable $x_{n,i}$ represented the degree of polymerization of monodisperse polymer species i , or the number-average degree of polymerization of polydisperse polymer fraction i .

This system of equations was considerably more complex than the original system (16)-(19) since it contained $i+1$ mole fractions and size parameters as compared to two mole fractions and size terms in the original system. Fortunately, there were some simplifications that could be made regarding the summation term in (57). First, the definition of polymer mole fraction within the system (53) was substituted into (57) yielding

$$R_1 = S_1 / (S_1 x_1 + \sum S_{2,i} x_2 x_i) \quad (59)$$

Then x_2 was removed from the summation since it was a constant with respect to the summation variable i , and size parameter $S_{2,i}$ was replaced by its definition (58)

$$R_1 = S_1 / (S_1 x_1 + x_2 \sum 8x_{n,i} x_i) \quad (60)$$

Now the summation defined the number average degree of polymerization for the entire polymer sample taken as a whole.

$$x_n = \sum x_{n,i} x_i \quad (61)$$

This final substitution transformed (60) to

$$R_1 = S_1 / (S_1 x_1 + x_2 (8x_n)) \quad (62)$$

The factor $8x_n$ was identical to the the size parameter S_2 for a fictitious binary system of solvent and monodisperse polymer with the number average molecular weight of the actual polydisperse polymer. This was seen by comparison to equation (19) used above for the calculations on a binary system. This means that (62) was identical to

$$R_1 = S_1 / (S_1 x_1 + S_2 x_2)$$

which defined the solvent size term for the binary system.

The system of equations (16), (18), (57), and (58), represented the multicomponent system toluene plus i

fractions of polystyrene. The analysis of equations (59)-(62) just proved that this system reduced to the system (16)-(19), which represented a binary system of toluene and monodisperse polystyrene with molecular weight equal to the number average molecular weight of the polydisperse polystyrene in the multicomponent system. Therefore, all results derived from (16)-(19) were also applicable to the multicomponent system (16), (18), (57), and (58). In particular, equation (34) held for the multicomponent system!

The conclusion of this work was simple yet vital. Using the ASOG model for activity coefficients, in order to model diffusivity, it was permissible to treat a polydisperse polymer sample as though it were a sample of monodisperse polymer with the number average molecular weight of the actual polydisperse sample.

This result was a consequence of the fact that wherever a molecular weight dependent parameter occurred in equation (57), it was always multiplied by the mole fraction associated with it. The summation in (57) weighted each degree of polymerization by its mole fraction, which produced a number average degree of polymerization across the entire sample.

3.4.2 Effects of MWD on UNIFAC

To determine whether the UNIFAC model also allows the same conclusion, all that need be done was to check the generalized UNIFAC model for a multicomponent system. If in every equation where a molecular weight dependent parameter occurs, it was weighted by the mole fraction associated with it, and summed over all mole fractions, no further proof was required.

The generalized UNIFAC model consisted of the following equations, analogous to (44)-(46).

$$\ln y_1 = \ln(\phi_1/x_1) + (z/2)q_1 \ln(\theta_1/\phi_1) + l_1 - (\phi_1/x_1) \sum x_i l_i \quad (63)$$

$$\theta_1 = q_1 x_1 / (q_1 x_1 + \sum q_{2,i} x_{2,i}) \quad (64)$$

$$\phi_1 = r_1 x_1 / (r_1 x_1 + \sum r_{2,i} x_{2,i}) \quad (65)$$

Equations (48)-(50) remained as defined above, while equations (51) and (52) were modified to give volumes and surface areas in terms of the number average molecular weight of each fraction.

$$r_{2,i} = (5(0.5313) + 0.8121 + 0.6744) x_{n,i} \quad (66)$$

$$q_{2,i} = (5(0.400) + 0.348 + 0.540) x_{n,i} \quad (67)$$

The equation for the solvent term l_1 remained as given in

(47). Each polymer fraction had its own $l_{2,i}$ term given by

$$l_{2,i} = ((r_{2,i} - q_{2,i}) - (r_{2,i} - 1)) \quad (68)$$

Equations (66) and (67) were the only ones which contained the molecular weight dependent terms $x_{n,i}$ explicitly. These equations defined $r_{2,i}$ and $q_{2,i}$, which were used, in turn, in (68) to define $l_{2,i}$, in (64) to define θ_1 , and in (65) to define ϕ_1 . The terms $l_{2,i}$ were used in (63) in defining the activity coefficient itself.

Starting with (63), the activity coefficient depended upon molecular weight dependent parameters ϕ_1 , θ_1 , and $l_{2,i}$ only. (64) showed that θ_1 contained a summation of $q_{2,i}$ times $x_{2,i}$, which by the previous discussion resulted in a number averaging of $q_{2,i}$. Since $q_{2,i}$ was indeed proportional to a number average quantity, the summation in the definition of θ_1 reduced to a single number average term over the whole polymer sample. Similarly, ϕ_1 contained a summation of $r_{2,i}$, which reduced to a single number average term over the whole polymer sample. Equations (64) and (65) thereby reduced to (45) and (46). The only remaining parameter in (63) to be considered was $l_{2,i}$. It appeared in a summation in (63), but itself was defined in terms of the number average quantities $r_{2,i}$ and $q_{2,i}$ in (68). Once again, since the summation in (63) was weighted by mole fractions $x_{2,i}$, it could be reduced to a single term involving the number average over the whole

polydisperse sample. (63)-(65) then became identical to (44)-(46). The UNIFAC model, like the ASOG model, treated a multicomponent solvent-polydisperse polymer system like a binary system of solvent and monodisperse polymer with the number average molecular weight of the polydisperse polymer.

The important conclusion of this section was that the only parameter necessary to apply the thermodynamic ASOG and UNIFAC models to a polydisperse polymer in solution was the number average molecular weight. Nothing else, not even polydispersity was required. The exact experimental distribution or form of theoretical distribution used in characterizing the polymer was irrelevant. The results found previously for monodisperse polymer also applied to polydisperse polymer samples.

3.5 Variation and Estimation of ASOG Size Parameters

The diffusivity model developed and described so far consists of equation (17) or (23) giving a chemical potential driving force for diffusion in a concentration dependence factor. The derivative factor giving the concentration dependence could be modelled by either ASOG or UNIFAC activity coefficient equations, (34) or the set (44)-(48). The only information required for these was

number average molecular weight and relevant molecular structure parameters. Numerical calculations showed that the quantitative difference between the UNIFAC and ASOG predictions was negligible. Since ASOG is a simpler, albeit more naive model, it made more practical sense to apply it by using equation (34) to predict the concentration dependence of diffusivities.

A specific observation about the model seemed relevant to improving its behavior. For the toluene-polystyrene system, ASOG predicted maximum diffusivity at solvent weight fraction 0.5; UNIFAC at solvent weight fraction 0.47. ASOG predicted symmetric behavior about this maximum; UNIFAC nearly symmetric behavior. Such behavior was not observed in the experimental data, as will be discussed at length in Chapter 4. Rather, the experimental data showed a maximum at lower weight fractions of solvent.

Corrections could be designed for the model so as to increase the accuracy of its predictive ability. The parameters in the model which directly affected concentration dependence were y , the polymer-solvent size ratio, and M_2 , the value chosen for the polymer molecular weight. D_0 did not directly affect concentration dependence as it represented the zero-concentration diffusivity, but was not affected by changes in concentration. To change the concentration dependence

within the model required modifications to the size parameter ratio γ or to the polymer molecular weight M_2 .

In section 3.4, the behavior of the ASOG and UNIFAC models for polydisperse polymers was studied. It was shown that the correct method for modeling polydisperse polymer-solvent thermodynamics using these models was to use M_n , the number average molecular weight, as M_2 , the polymer molecular weight parameter. Varying from this result would affect the predictions of the model, since it would substantially change the relationship between mole fraction and weight fraction. Changing M_2 would violate the theoretical basis of ASOG and UNIFAC. Justification for using an "effective molecular weight" rather than M_n is scant. Although the use of M_n could be disputed as being an artifact of the ASOG and UNIFAC models, there was no physical basis for such a dispute.

The size parameters, as reflected by the parameter γ in (34), were a more likely candidate for a correction. A dispute with the ASOG and UNIFAC definition of the size parameters would be justifiable on certain physical grounds. Specifically, the summation of size groups (or functional group volumes and areas) which was applicable to small molecules may have failed to correctly describe molecular size in polymer molecules, which tend to assume conformations such as random coils in melts and solutions.

The idea of varying the size parameter could be placed on firmer, quantitative theoretical ground by carefully considering some of the assumptions made in the ASOG derivation. The original basis for setting the size parameter y equal to the ratio of molecular weights was that polymer and solvent molecules composed of similar types and proportions of functional groups would occupy volumes proportional to their molecular weights. This implied that the densities of polymer and solvent were identical, which was known not to be the case for polystyrene-toluene (and most other polymer-solvent systems composed of similar functional groups). The density of polystyrene was greater than that of toluene, meaning that polystyrene had a smaller specific volume than toluene. Assuming that y was equal to the ratio of molecular weights yielded a value for polymer specific volume which was too large, hence the size parameter ratio y must be reduced.

3.5.1 Empirical Size Parameter from Maximum Diffusivity

Before discussing a theoretical basis for a correction to polymer size, it was useful to observe some of the consequences. The weight fraction of maximal diffusivity was indeed affected by changes in the parameter y , as given by equation (39). Decreasing y would decrease the maximal

weight fraction, which is observed in the experimental data. (The ASOG result of maximal weight fraction 0.5, equation (40), came from approximating y by the ratio of the molecular weights.) The maximum value of the derivative (equal to the ratio of the maximum diffusivity to the minimum, zero concentration diffusivity) would also be changed in equations (42) and (43).

The maximum diffusivity observed in the experimental data could be used as an empirical predictor for the value of y to use in the model. The parameter y could easily be generated for a given maximal weight fraction by rearrangement of (39) to

$$y = M_2 w_{1,\max} / M_1 (1 - w_{1,\max}) \quad (69)$$

When the maximal weight fraction was one-half, (67) gave $y = M_2/M_1$ as expected.

This modification to the model was empirical because it required the knowledge of the position of the maximum in the experimental data. Knowing this, equation (69) forced y to take on the correct value so that this maximum would be reproduced identically by equation (39). It was noteworthy that this modification to the ASOG model produced consistent results with the expected decrease in y due to the density argument presented above, as will be shown in detail in Chapter 4.

3.5.2 Size Parameter from Equilibrium Measurements

A quantitative means of determining the variation in the size parameter independent of the known maximum in the diffusivity curve could be derived strictly from a single equilibrium measurement of the infinite dilution weight fraction activity coefficient, n_1^{inf} . Defining this in terms of the mole fraction activity coefficient used here, y_1 ,

$$a_1 = y_1 x_1 = n_1 w_1 =$$

$$n_1 x_1 M_1 / (x_1 M_1 + x_2 M_2) \quad (70)$$

and solving for n_1

$$n_1 = y_1 (x_1 M_1 + x_2 M_2) / M_1 \quad (71)$$

then taking the infinite dilution limit as x_1 goes to zero

$$n_1^{\text{inf}} = y_1^{\text{inf}} M_2 / M_1 \quad (72)$$

Applying (24) and (25) with x_1 approaching zero, and with $S_1 \ll S_2$

$$R_1^{\text{inf}} = S_1 / (S_1(0) + S_2(1)) = S_1 / S_2 \quad (73)$$

$$\ln y_1^{\text{inf}} = 1 - S_1/S_2 + \ln(S_1/S_2) \quad (74)$$

$$\ln y_1^{\text{inf}} = 1 + \ln(S_1/S_2) \quad (75)$$

This resulted in an infinite dilution mole fraction activity coefficient

$$y_1 = \exp(1 + \ln(S_1/S_2)) = e \cdot (S_1/S_2) \quad (76)$$

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

Considering the expression (72) for the infinite dilution weight fraction activity coefficient, a final result was

$$n_1^{\text{inf}} = e(S_1/S_2)(M_2/M_1) \quad (77)$$

Beginning with the simplest but least correct case, assume that the size parameter ratio y (equal to S_2/S_1) was equal to the ratio of molecular weights M_2/M_1 . The size parameter and molecular weight terms cancel, giving

$$n_1^{\text{inf}} = e \quad (78)$$

The prediction of (78) will be discussed in detail in Chapter 4, but in brief, observed experimental values for the polystyrene-toluene system (Vrentas, Duda, and Hsieh, 1983) indicate that n_1^{inf} is larger than given by (78).

A corrected value of y can be found given an experimental measurement of activity coefficient. It follows from rearrangement of (77) along with the definition of y that

$$y = (e/n_1^{\text{inf}})(M_2/M_1) \quad (79)$$

Noting that the experimental activity coefficients were larger than e allows the conclusion

$$y < M_2/M_1 \quad (80)$$

which was consistent with both the empirical evidence (maximum in the diffusivity curve) and theoretical evidence (higher density of polymer as compared to solvent) that the size parameter y must be reduced.

The weight fraction of maximum diffusivity could be predicted directly from the infinite dilution activity coefficient by substituting the result (79) into (39)

$$\begin{aligned} w_{1,\text{max}} &= y / (y + M_2/M_1) \\ &= \frac{(e/n_1^{\text{inf}})(M_2/M_1)}{(e/n_1^{\text{inf}})(M_2/M_1) + M_2/M_1} \\ &= e / (e + n_1^{\text{inf}}) \end{aligned} \quad (81)$$

In conclusion, the variation of the size parameter y was not

merely justified in fitting the experimental diffusivity data, but actually necessary in order to correctly explain the differences in density between polymer and solvent as well as to correlate equilibrium data for the infinite dilution weight fraction activity coefficient of solvent. A decrease in the size parameter y was consistent with the observed maximum in the diffusivity curves at solvent weight fraction less than 0.50, with the density of polystyrene being larger than toluene, and with the observed infinite dilution weight fraction activity coefficient for toluene in polystyrene larger than $e = 2.718$.

3.5.3 Size Parameter from Flory-Huggins χ Parameter

The size parameter y was computed above from diffusivity data (maximum weight fraction) and from thermodynamic data (infinite dilution activity coefficient). It was possible to use a result (Vrentas, et al, 1983) giving infinite dilution activity coefficient in terms of polymer and solvent parameters in the calculation of y values without using activity data. This result is

$$n_1^{\text{inf}} = (V_1/V_2) \exp(1 + \chi) \quad (82)$$

where V_1 and V_2 are specific volumes of solvent and polymer. These could also be replaced by densities

$$n_1^{\text{inf}} = (\varphi_2/\varphi_1) \exp(1 + X) \quad (83)$$

Combining equation (83) with (79) gave the following result for y

$$y = (\varphi_1/\varphi_2) \exp(-X) \cdot (M_2/M_1) \quad (84)$$

This result allowed y to be evaluated a priori without any experimental data, as long as a value for X and the density data were known.

3.6 Temperature Dependence of Diffusivity

The temperature dependence of diffusivity could also be modelled and checked against the given data. The fundamental equation which had been used thus far to scale diffusivity with concentration is equation (17), which was valid at constant temperature. In applying (17) to give the concentration dependence of diffusivity, using either the ASOG or UNIFAC models, data for each temperature given could be modelled independently. It is possible to scale diffusivity with temperature, by assuming that the zero concentration diffusivity D_0 varies according to an Arrhenius-type expression.

$$D_0 = D_{00} \exp(-E/RT) \quad (85)$$

In this expression, E represents the activation energy for diffusion, and D_{00} is a temperature and concentration independent diffusivity. The relation of (85) to (15) is given by the fact that mobility u is expected to have an exponential dependence on absolute temperature T . The explicit linear dependence on temperature in (15) is essentially negligible in comparison to the implicit exponential dependence of mobility on temperature. Only the exponential factor need be included in (85).

Combining (17) with (85) allowed diffusivity to be written as a function of concentration and temperature, with only two parameters, D_{00} and E , to be fitted.

$$D = D_{00} \exp(-E/RT) (d \ln a_1 / d \ln x_1) \quad (86)$$

To check whether the Arrhenius expression (85) correctly modelled the temperature dependence of diffusivity, it was transformed into

$$\ln D_0 = \ln D_{00} - E/RT \quad (87)$$

If equation (85) holds, and values of $\ln D_0$ are plotted versus $1/T$, the points should lie on a straight line.

CHAPTER 4

MODEL APPLICATION

4.1 Thermodynamic Data

Since the application of ASOG and UNIFAC group contribution thermodynamic models to diffusivity scaling produced results which were consistent, the next check of their validity was in comparison to experimental data. The predictions of these models should be checked for consistency with existing thermodynamic data before applying them to diffusion data.

Experimental data for infinite dilution weight fraction activity coefficient have been tabulated (Vrentas, et al, 1983) for the polystyrene-toluene system. These data cover a temperature range from 100-200 C, and show a variation in n_1^{inf} values in the range of 4-8. The study itself suggests a value of about 4.8 based on the Flory-Huggins equation at

110 C.

The original ASOG model, with size parameter y given by the ratio of molecular weight of polymer to solvent, predicted an infinite dilution weight fraction activity coefficient of $e = 2.718$ according to equation (78). This result was not expected to be accurate due to the previously discussed flaws in the ASOG treatment of polymer size, although it was within the proper order of magnitude.

Equation (77) gives the general result when the size parameter is not fixed by molecular weight. It states that n_1^{inf} is inversely proportional to the size parameter $y = S_2/S_1$. A value for y could then be calculated from known densities and Flory-Huggins parameter X . At 110 C, the density of toluene is 0.778 g/cm^3 (Prausnitz, Eckert, Orye, and O'Connell, 1967), while the density of polystyrene is 1.023 g/cm^3 (Fox and Loshaek, 1955). Duda, et al (1983) give X for polystyrene-toluene as 0.28-0.30. The resulting y value from equation (84) was $y = (0.557-0.568)M_2/M_1$, which gave n_1^{inf} in the range 4.73-4.83, which is the experimentally observed value of Duda, et al (1983). The model with variable size parameter was successful in predicting equilibrium activity coefficient.

4.2 Range of Validity of the Model

As mentioned previously, the postulated mechanism for T_{11} is thermodynamic equilibrium between polymer molecules. Since the diffusivity model proposed here depends upon the existence of equilibrium, it should be valid under conditions where the polymer-solvent system is above T_{11} . The T_{11} transition is a function of both temperature and concentration. It occurs at approximately 160-165 C in pure polystyrene, and will decrease in temperature as the concentration of solvent increases. Equation (7) was applied to give a quantitative prediction of the decrease in T_{11} , using 160-165 C as $T_{11,2}$ for pure polystyrene, and using -27 C, the boiling point of toluene at 1 mm Hg pressure, for $T_{11,1}$. Substituting these values into equation (7) gave the upper bounds on toluene weight fraction in Table 6.

TABLE 6
Lowering of T_{11} by Plasticization with Toluene

Temperature (degrees C)	Weight Fraction Toluene
160	0.000-0.026
140	0.107-0.130
110	0.267-0.286

These ranges were upper bounds, as mentioned above, and for nonzero K in (5), the actual weight fraction of toluene required to lower T_{11} to a given temperature would be

somewhat less than the predicted amount from (7). Although data for the toluene-polystyrene system was not available, an estimate could be made by using the K value for the system studied, -60 C. Equation (5) was then applied and gave the results in Table 7

TABLE 7
Lowering of T_{11} by Toluene Using Equation (5)

Temperature (degrees C)	Weight Fraction Toluene
160	0.000-0.020
140	0.083-0.102
110	0.214-0.231

These results may be closer to the actual concentrations of toluene required than the upper bounds given in Table 6. As was indicated in the tables, the amount of change was not large. Both sets of results were consistent with previously reported T_{11} values for polystyrene-toluene systems of various concentrations (Ueberreiter, 1965). The conclusion that the high concentration data represented conditions in the toluene-polystyrene system above T_{11} even at temperatures below T_{11} of pure polymer was justified. The thermodynamic models for predicting diffusivities would be applicable to all conditions of temperature and concentration above the transition values given in Tables 6 and 7.

4.3 Diffusivity Data

The equations could be tested by comparing them to data for diffusivities as functions of temperature and solvent concentration. Such data is incredibly sparse in the literature. Although many studies of polymer-solvent diffusion have been undertaken, few have studied the scaling of diffusivity with concentration. Only recently has data been published describing the variation of diffusivity, and most of this has been limited to its variation with temperature. Good experimental data is available for solvent diffusivity as a function of solvent weight fraction and temperature (Duda, et al, 1982).

The following procedure was used in modeling the data. At a given temperature, the concentration dependence of diffusivity was assumed to be given by the term $d \ln a_1 / d \ln x_1$. The value of $d \ln a_1 / d \ln x_1$ itself came from the thermodynamic models. A single experimental point was chosen to correlate D_0 , using equation (17) along with the known value of $d \ln a_1 / d \ln x_1$ at the solvent concentration of the data point used. This value of D_0 was then used to generate a curve of diffusivity as a function of concentration, at the given temperature. The procedure could be repeated at every temperature for which

experimental data was available.

The reported data was tabulated in Table 8.

TABLE 8
Diffusivity of Toluene-Polystyrene Systems

Temperature (degrees C)	Wt. Frac. Toluene	Diffusivity x 10 ⁹ (cm**2/sec)
110.0	0.020	1.90
	0.056	26.3
	0.095	129
	0.146	512
	0.230	1000
	0.329	1180
	0.431	921
	0.498	805
	0.584	541
	0.598	520
	0.655	369
	0.658	428
140.0	0.011	20.1
	0.033	82.0
	0.066	259
	0.090	538
	0.110	732
	0.130	1230
160.0	0.013	172
	0.023	343
	0.058	966
170.0	0.004	217
	0.006	277
	0.018	507
	0.048	1090
178.0	0.005	347
	0.014	697
	0.014	637
	0.016	656
	0.041	1200

Equations (39) and (40) predicted a maximum value for the diffusion coefficient as a function of concentration. Only at low temperatures (below 140 C) does the range of toluene concentration go much above five weight percent, and only the data at 110 C shows a range of concentration large

enough so that the diffusivity values begin to decrease with concentration. Although the molecular weight of the polystyrene is not specified in the paper from which the data was taken, it was assumed to be consistent with other samples used by the same authors previously. The weight-average molecular weight is given as 275,000. Number-average molecular weight was required for the ASOG and UNIFAC models presented here; however, it is not available for the published data. Consistency with other samples of polystyrene within this author's experience would place the polydispersity between three and four, and yielded an estimate of 75,000 for the number-average molecular weight of the polystyrene used in the experiments for which data is given here.

Although the range of concentration in the data is not very broad, there is no disadvantage in modeling devolatilization using this data. This is because devolatilization occurs at low concentrations of solvent (or other small molecule). Data below five weight percent of toluene should be sufficient for analyzing the accuracy of the ASOG and UNIFAC models within the range of concentration encountered during devolatilization.

4.3.1 Application of Concentration Dependence Models

The thermodynamic models were expected to apply in the case where equilibrium existed between molecules. Temperatures and concentration ranges above T_{11} were used as the source of experimental points for the purpose of correlating the data.

One experimental data point gave diffusivity at a particular concentration and temperature. Knowing solvent concentration, the ASOG model allowed the calculation of $d \ln a_1 / d \ln x_1$ by equation (34) provided that y was known. In the section above, ASOG predicted equilibrium results more accurately when y was not assumed equal to M_2/M_1 . Here, comparisons were also made of the prediction of diffusivity using equations (69) or (79) to give y . The known value of maximum diffusivity was used to give y using (69); the published values of Duda, et al (1983) were used to give y using (79). Having the value of $d \ln a_1 / d \ln x_1$ allowed calculation of D_0 by equation (17). A complete list of D_0 values is given in Table 9, section 4.4. A curve of diffusivity as a function of concentration at that particular temperature could then be generated since D_0 had been found, and since the functional form of (34) could give $d \ln a_1 / d \ln x_1$ at any value of solvent concentration.

In generating the curves in Figures 1 and 2, the experimental data points used in evaluating D_0 were the lowest concentration points given, such that the system was known to be above T_{11} according to the results given in Tables 6 and 7. The lowest concentration was chosen because it allowed testing of the models under a worst-case situation. Small variations in experimental accuracy could lead to large changes in predicted results, since fewer significant figures of precision were available at low concentrations. Also, it was anticipated that in applying the models presented here, low concentration data would generally be extrapolated to higher concentrations. This is due to the experimental difficulties inherent in diffusivity studies at high concentrations. Since the D values expected for use in devolatilization studies are in the parts per million (ppm) range of solvent concentration, D_0 was most appropriately modeled using low concentration data.

Qualitative agreement with experiment was seen to be good at all temperatures. The theoretically derived curves had the correct trend of increase in diffusivity with concentration, and in the case of the 110 C data in Figure 2, the correct shape. The 110 C data are the only data which extend high enough into the concentration range to test the theoretical prediction of maxima in the diffusivity curves. These data went through a maximum at roughly 35 weight percent toluene, certainly in agreement with the predictions of maxima by the

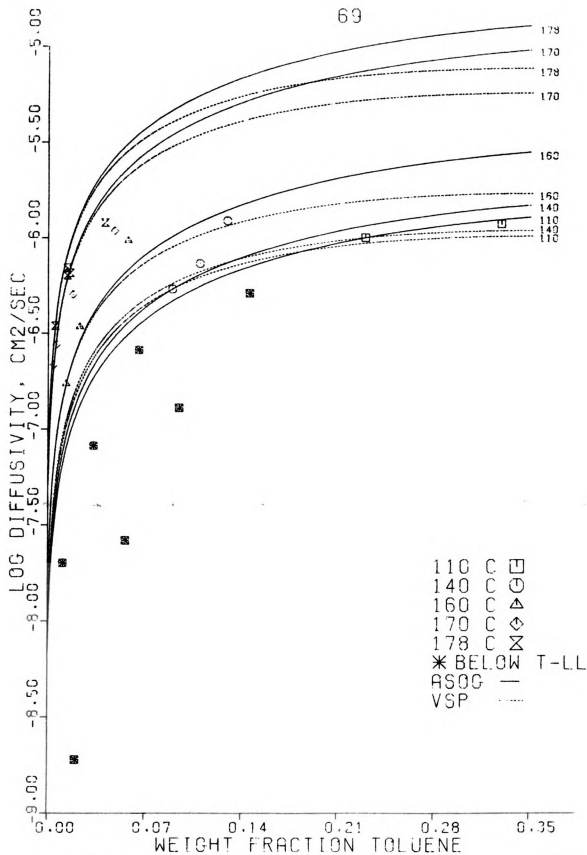


FIGURE 1. ASOG PREDICTIONS OF DIFFUSIVITY

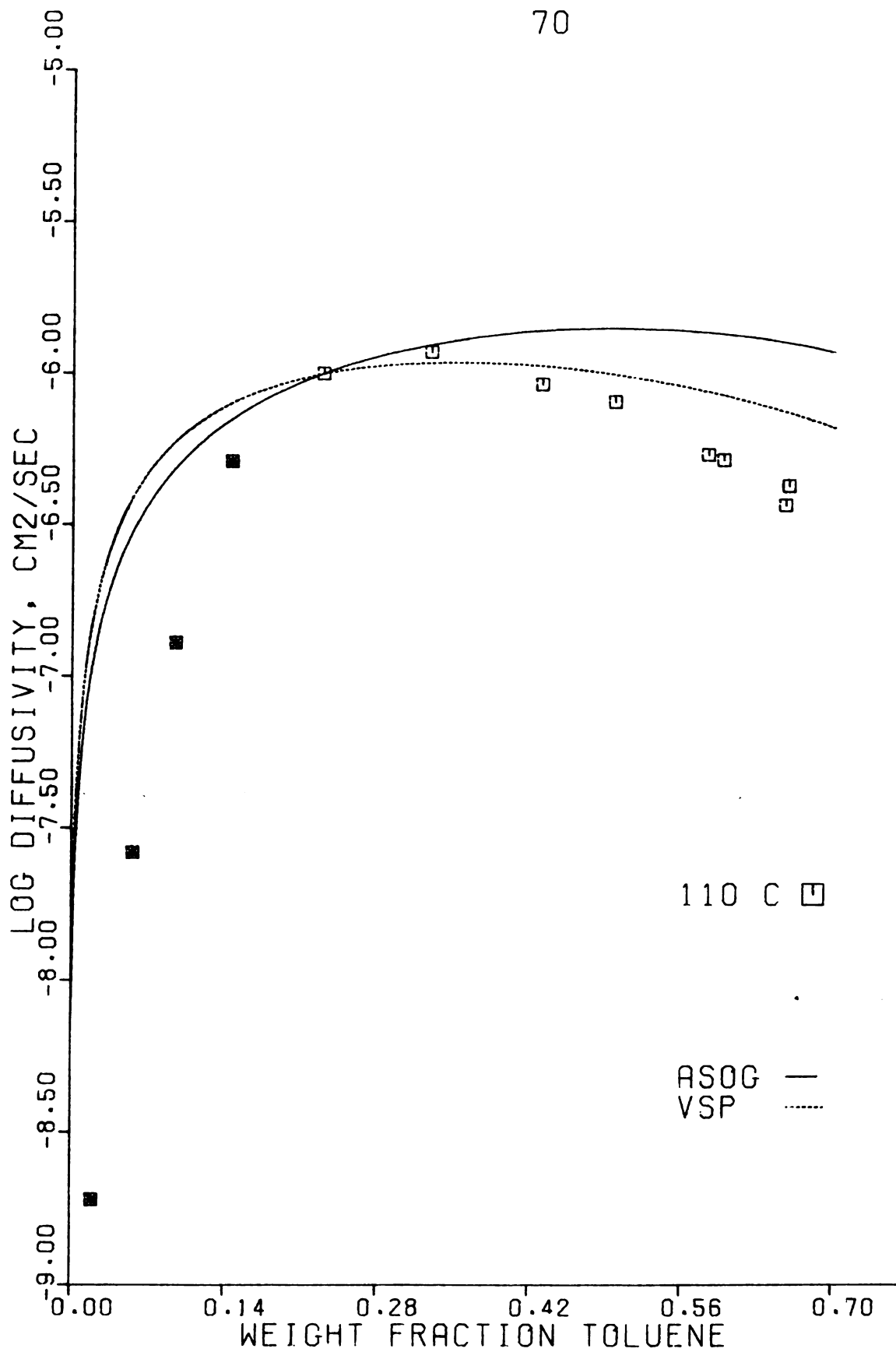


FIGURE 2. ASOG PREDICTIONS OF DIFFUSIVITY
AT HIGH SOLVENT CONCENTRATIONS

ASOG and UNIFAC models.

Quantitative agreement with experiment was generally good to excellent within the concentration and temperature ranges above T_{11} , where the model was expected to apply. The points below T_{11} are labeled as such in Figures 1 and 2. These experimental points were in the "fixed fluid" region below T_{11} , where thermodynamic equilibrium may not be reached. The model was not expected to apply to such data points, and Figures 1 and 2 indicate, in general, that this was true. The experimental points below T_{11} were not in agreement with the predictions of the model. Some of this data differed from the predictions by as much as two orders of magnitude. The experimental points above the T_{11} transition, where the model was expected to apply, fell within roughly a factor of two of the predictions for all data points available.

Figures 1 and 2 included curves for the model based on a size factor $y = M_2/M_1$, as well as based on a size factor given by (69), using a known value of 0.35 for the maximum concentration. Although both of these agreed well with the experimental data in a qualitative way, Figure 2 showed that the variable size parameter (VSP) model (y given by (69)) had better quantitative agreement at and above the concentration of maximum diffusivity. Substituting n_1^{inf} equal to 5 into equation (79) gave $w_{1,\text{max}}$ equal to 0.35,

exactly consistent with the maximum in the diffusivity curve as a function of concentration at 110 C. Furthermore, the trend in the activity coefficient data shows an increase with temperature. Since y is inversely proportional to n_1^{inf} , y will decrease with temperature. This implies that the maximum diffusivity will occur at lower concentration of solvent as temperature increases, a result which is consistent with experimental observation (Chalykh and Vasenin, 1966; Rehage, Ernst, and Fuhrmann, 1970). Since equation (79) was consistent with equation (69) in generating a value for the size parameter ratio y , the results in Figures 1 and 2 which are labeled VSP apply to y values predicted by either the empirical method of correlating the weight fraction of maximum diffusivity or the semi-theoretical method based upon equilibrium activity coefficient.

There was some arbitrariness involved in choosing the initial data point for testing of the data. This was not a real problem, as could be seen by examining the form of equation (17), which was the same as equation (86) at constant temperature. The derivative $d \ln a_1 / d \ln x_1$ was a function of composition only, not of temperature, since the ASOG and UNIFAC results both indicated athermal solution behavior. Since (17) was a function of composition only, the diffusivity isotherms should differ by only the ratio of their D_0 values, a constant factor, at any given

concentration. Curves which differ everywhere by a constant factor will appear as vertical translations of one another in the semilog plots of Figures 1 and 2.

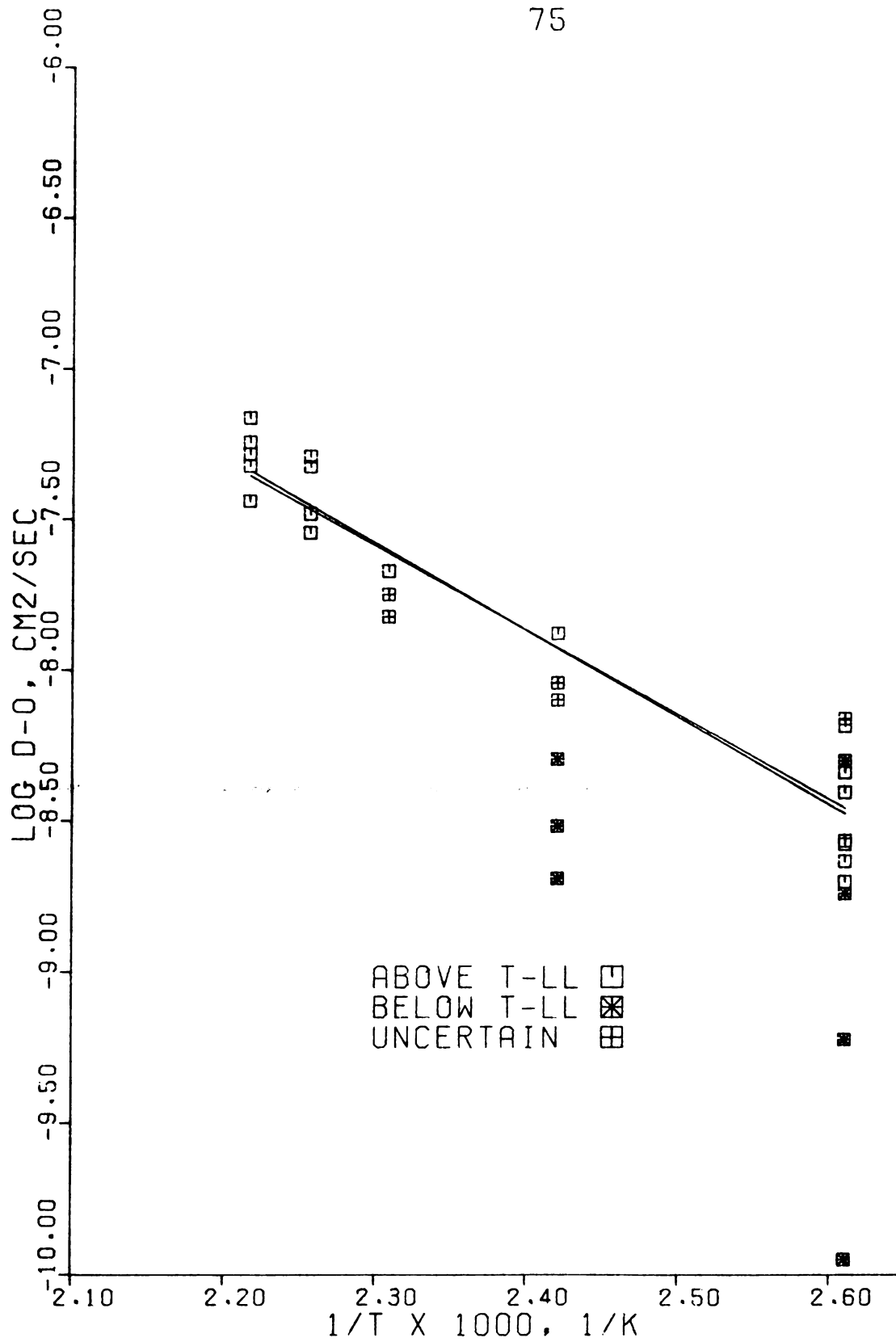
A careful visual examination of the experimental data plotted on those figures showed that the low concentration data above the T_{11} transition would fall on such curves, but that the low temperature, low concentration data would not. This argument served to eliminate the low temperature, low concentration data a priori from the valid range of (17) or (86). It did not however, decisively prove the validity of these equations without the evidence given above with reference to Figures 1 and 2, which indicated that the model did indeed fit the experimental data. The condition that the semilog plots of diffusion isotherms be vertical translations of one another was a necessary condition, but not a sufficient condition, for equation (17) to hold.

If a different experimental point were chosen for correlating D_0 as described above, the result would be a shifting of the diffusivity isotherm in the vertical direction. As mentioned above, the testing of the model was done as a worst-case analysis. No effort was made to choose the "best" experimental point for correlating the data. Choosing a different point for correlating D_0 would not affect the agreement shown by Figures 1 and 2, so long as the point chosen was within the temperature and

concentration range above the T_{11} transition. In the case where several experimental points were available at a given temperature, application of the model might include some type of regression or "best fit" criterion to generate an initial D_0 value. Section 4.4 describes such a procedure and its results. No matter which data point was used for correlating D_0 , the predicted concentration dependence of diffusivity was correct to within a factor of 2 over the entire concentration range. The only restriction was that the initial data point and the concentration range of application should be above T_{11} . For data above 160-165 C, there would be no restriction at all since all solvent concentrations would be above T_{11} at those temperatures.

4.4 Temperature and Concentration Dependence

Equations (85)-(87) above were used to describe the temperature dependence of the diffusivity data. To test the predictions of these equations against the experimental data, an Arrhenius plot was made according to equation (87). Figures 3 and 4 are these plots, corresponding to the fixed size parameter ratio $y = M_2/M_1$ and the variable size parameter y given by (69). The plots are semilog plots of D_0 versus reciprocal absolute temperature, on which data points which are consistent with the Arrhenius expression



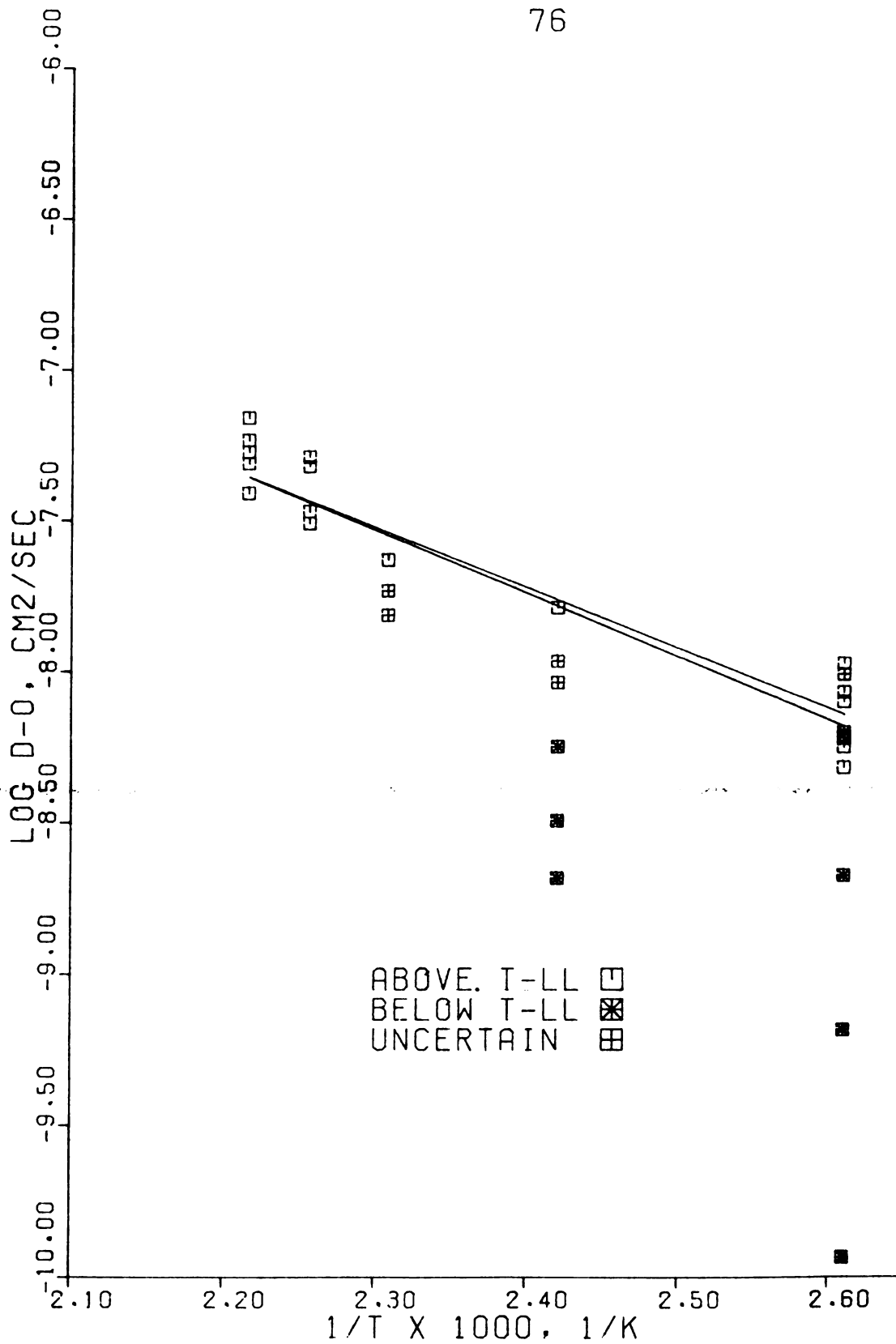


FIGURE 4. ARRHENIUS PLOT OF ASOG PREDICTIONS WITH VSP

(85) will lie on a straight line. D_0 values for experimental points above T_{11} were found as described in section 4.3, and tabulated in Table 9.

TABLE 9
 D_0 Values for Experimental Data Above T_{11}

Temperature (degrees C)	Weight Fraction Toluene	$D_0 \times 10^9$	
		ASOG	VSP
110	0.230	6.87	9.90
	0.329	6.49	10.8
	0.431	4.55	8.61
	0.498	3.90	8.07
	0.584	2.69	6.12
	0.598	2.61	6.06
	0.655	1.97	4.86
	0.658	2.29	5.74
	0.090	7.94	9.23
140	0.110	9.08	10.9
	0.130	13.2	16.3
	0.013	15.3	15.6
160	0.023	18.1	18.8
	0.058	21.2	23.4
	0.004	53.2	53.6
170	0.006	50.1	50.6
	0.018	32.3	33.4
	0.048	28.6	31.0
178	0.005	72.2	72.8
	0.014	56.6	58.0
	0.014	50.5	51.7
	0.016	47.0	48.3
	0.041	36.4	39.0

To remove some of the arbitrariness in the choice of experimental points, all the points were plotted in Figures 4 and 5. These figures showed that all of the low temperature, low concentration points below T_{11} would not fit. In particular, the three lowest concentration points (lowest D_0 values) at 110 C (highest reciprocal temperature) are far from the others at that temperature, as are the three lowest concentration points at 140 C. The

remaining low temperature points and all of the high temperature points fitted in a narrow band around the straight lines indicated, which represented a linear regression fit of the data above T_{11} . If a linear fit were attempted using the experimental points below T_{11} , the slope of the line would be much larger in absolute value, corresponding to an apparent increase in activation energy below T_{11} . This was consistent with the diffusion data of Duda and Vrentas (1968), referred to earlier as evidence for the T_{11} transition. They find an activation energy of 14.0 kcal/mol above T_{11} compared to 44.0 kcal/mol below T_{11} for n-pentane-polystyrene.

The regression procedure used in analyzing the data in Figures 3 and 4 was as follows. Linear regression was used to find the "best fit" line for the 23 data points. The results of the regression were a slope and intercept for the line, which was then plotted in the figures. This slope and intercept were identified as the activation energy E and the temperature and concentration independent diffusivity D_{00} in equations (85)-(87). These numerical results were tabulated in Table 10 for both the ASOG and VSP models. UNIFAC results were also included in Table 10, although a UNIFAC plot was not included because of its similarity to the ASOG plot in Figure 3. The "goodness of fit" correlation coefficient r^2 was also included in Table 10.

A second linear regression was then performed on the data in Figures 3 and 4, but with all uncertain experimental points eliminated. Three types of uncertain experimental points were defined. The first was all points which were not known with certainty to be below T_{11} , i.e., those points which fell into the T_{11} transition ranges given in Tables 6 and 7 rather than above the ranges given. The second type was all points at very low concentration which had D_0 values that differed appreciably from other points at the same temperature and nearby in concentration. These points were considered to be in error due to lack of precision, since in all cases only one significant digit was available for the concentration variable. The third type was points which differed from nearby concentration points in such a way as to reverse a trend of increase or decrease in D_0 values with concentration. These points were considered to be in experimental error. The points eliminated were listed in Table 11. 14 points remained and produced the second regression lines in Figures 3 and 4, as well as the numerical results in Table 12, analogous to Table 10.

TABLE 10
Linear Regression of Arrhenius Plots
for 23 Experimental Points

	ASOG	UNIFAC	VSP
E (kcal/mol)	13.2	12.5	9.6
D_{00} (cm ² /sec)	1.15×10^{-1}	5.42×10^{-2}	3.52×10^{-4}
r^2	0.907	0.902	0.860

TABLE 11
Uncertain Experimental Points

Temperature (degrees C)	Weight Fraction Toluene	Reason
110	0.230	Eliminated
	0.655	Possibly below T_{ll}
140	0.090	Experimental Error
	0.110	Possibly below T_{ll}
160	0.013	Possibly below T_{ll}
	0.023	Possibly below T_{ll}
170	0.004	Possibly below T_{ll}
	0.006	Lack of Precision
178	0.005	Lack of Precision

TABLE 12
Linear Regression of Arrhenius Plots
for 14 Experimental Points

	ASOG	UNIFAC	VSP
E (kcal/mol)	12.8	12.1	9.1
D_{00} (cm ² /sec)	6.91×10^{-2}	3.25×10^{-2}	2.20×10^{-4}
r^2	0.950	0.950	0.947

The values of r^2 close to 1 indicated a good fit of the straight lines in the Arrhenius plots. These values increased even more when the uncertain experimental points were eliminated. This provided evidence that the functional form given in equations (85) and (86) was correct in modeling the temperature dependence of diffusivity. Duda, et al (1983) reports 5.2 kcal/mol for the activation energy for diffusion in polystyrene-toluene, and 6.15×10^{-2} for D_0 .

The Arrhenius plots in Figures 3 and 4 contained both temperature dependence and concentration dependence

information. The concentration dependence could be seen by looking at the vertical spread of the D_0 values at any given temperature. This represented the amount of concentration dependence in the D_0 term, which was assumed to be concentration-independent. As such, the spread indicated the amount of uncertainty in the concentration dependence predicted by the model at that given temperature. Tables 13 and 14 summarized the uncertainty in concentration dependence seen in the ASOG, UNIFAC, and VSP models. The values given were the ratio of the largest to the smallest D_0 value at the given temperature. Since the number of data points and concentration range covered at different temperatures varied widely, comparisons of model performance between different temperatures were invalid. Comparisons between different models were valid, and showed that the VSP model had less uncertainty in concentration dependence at most temperatures. The difference was most striking at 110 C, where ASOG and UNIFAC performed relatively poorly. Since only one experimental point remained at 140 and 160 C after elimination of uncertain points, these temperatures were not included in Table 14.

TABLE 13
Ratio of Extreme D_0 Values
for 23 Experimental Points

Temperature (degrees C)	ASOG	Model UNIFAC	VSP
110	3.49	3.15	2.22
140	1.66	1.69	1.77
160	1.39	1.41	1.50
170	1.86	1.83	1.73
178	1.98	1.97	1.87

TABLE 14
Ratio of Extreme D_0 Values
for 14 Experimental Points

Temperature (degrees C)	ASOG	Model UNIFAC	VSP
110	2.83	2.61	1.88
170	1.13	1.12	1.08
178	1.55	1.55	1.49

If both temperature and concentration dependence information are known from experiment, the models could be used in a correlative rather than predictive sense. Activation energy E , and concentration and temperature independent diffusivity D_{00} resulting from a regression analysis could be used in equation (86), with concentration dependence coming from (34), to predict diffusivities as functions of temperature and concentration. This was done for the 14 point regression results. Table 15 contained the predicted D_0 values from equation (85), and Figures 5 and 6 contain plots over the range of the experimental data.

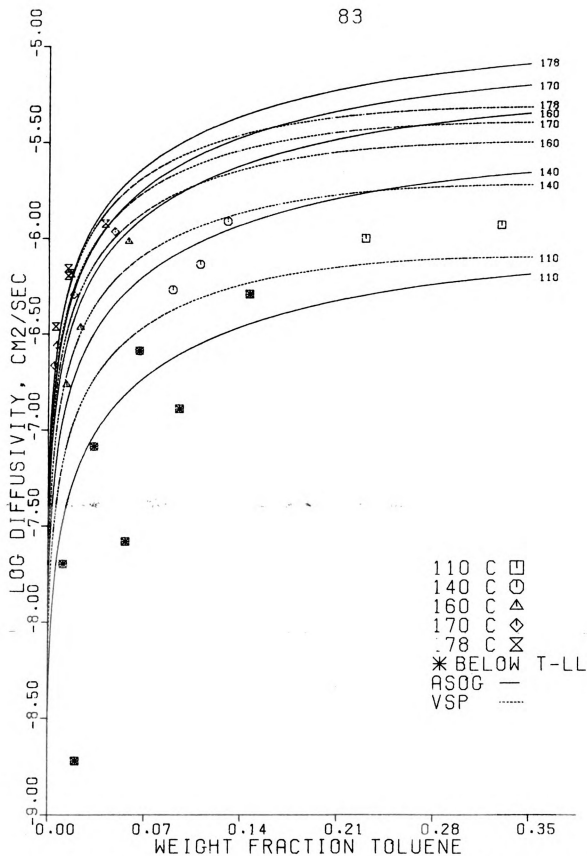


FIGURE 5. ASOG CORRELATION OF DIFFUSIVITY DATA

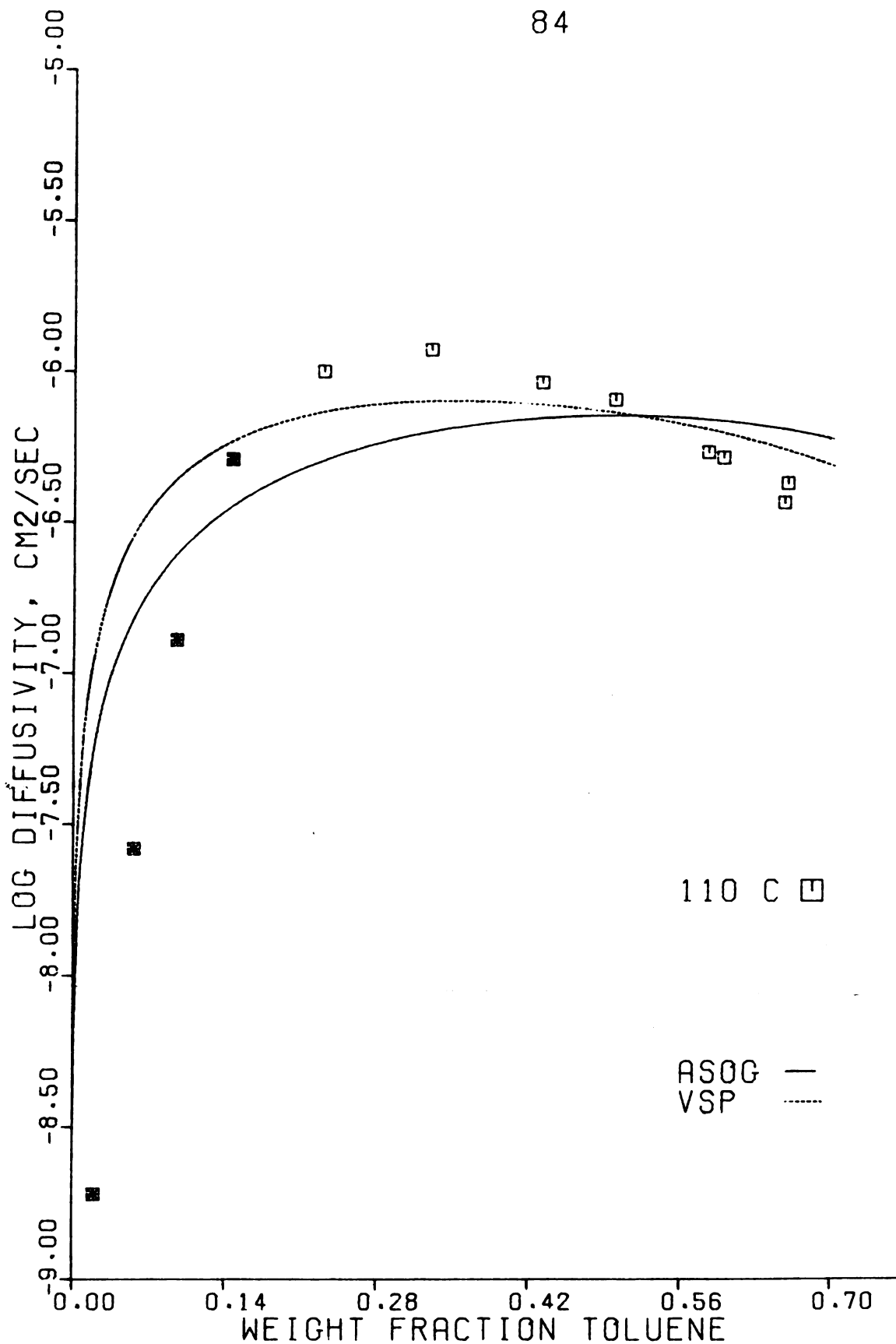


FIGURE 6. ASOG CORRELATION OF DIFFUSIVITY DATA AT HIGH SOLVENT CONCENTRATIONS

TABLE 15
Predicted D_0 Values from 14 Point
Regression Results

Temperature (degrees C)	ASOG	$D_0 \times 10^9$ UNIFAC	VSP
110	3.50	4.00	7.26
140	11.9	12.7	17.3
160	24.3	25.1	28.9
170	34.0	34.5	36.7
178	44.0	44.0	44.1

The conclusion of this section was that diffusivity in the system toluene-polystyrene could be described as a function of temperature and concentration by equation (86), which combined an Arrhenius expression for the temperature dependence with a thermodynamic model of chemical potential for the concentration dependence. This equation held above the T_{11} transition, i.e., at temperatures above 160-165 C for the entire concentration range studied, and at lower temperatures for high solvent concentrations, above a certain critical concentration. The VSP thermodynamic model gave best results. It considered the parameter γ was given by (69) or (79) rather than being assumed equal to the ratio of molecular weights. Predictions of VSP were certain to within a factor of two in the worst case (110 C), while predictions of ASOG and UNIFAC were certain to within a factor of 3 to 4 in the worst case.

4.5 Concentration Bias of D_0

Results of the previous section indicated that the models were accurate in prediction to within a factor of 2 to 4 for the experimental data used. Tables 13 and 14 gave detailed information regarding this uncertainty. We have not yet studied the cause of this uncertainty. It was apparent that the variation in D_0 with concentration was not random in most cases, but followed a systematic bias. This could be easily shown by studying a plot of D_0 not as a function of temperature, as was done in the Arrhenius plots, but rather as a function of concentration at a fixed temperature. The experimental results are plotted in such a manner in Figure 7. Several conclusions resulted from this figure. First, D_0 did not vary randomly with concentration. It changed monotonically with changes in concentration, at a given temperature. Second, the direction of this change was monotonically decreasing for nearly all the 110, 170, and 178 C data, regardless of the model used in calculating D_0 , and was increasing for the 140 and 160 C data. However, when uncertain data points are removed, no conclusion can be drawn for the 140 and 160 C data. Explanation of this concentration bias was beyond the scope of this thesis.

FIGURE 7. ASOG CONCENTRATION BIAS

CHAPTER 5

Conclusions and Recommendations

In view of the experimental and theoretical results given above from the thermodynamic models of ASOG and UNIFAC, and the body of literature summarized here, the following conclusions can be made:

1) The effect of the T_{11} transition from "fixed fluid" to "true liquid" was observable in experimental diffusion data. The value of T_{11} observed in this work, about 160-165 C, was consistent with the observations of other investigators who observe a similar phenomenon, both in diffusion experiments and in a wide range of other experiments not involving viscous flow.

2) The observed values of activation energy for diffusion above T_{11} in this study, in the range from 9 to 13 kcal/mol, were consistent with the observations of other

investigators, both qualitatively and quantitatively.

3) The observed behavior of low temperature data, below T_{11} of pure polystyrene, with the predictions of the thermodynamic models was explicable in terms of the plasticizing effect of the solvent toluene in high concentrations. At low concentrations of toluene, the polymer was not plasticized to a sufficient degree to decrease T_{11} below the experimental temperature. At high concentrations, T_{11} was lowered below the experimental temperature, so that the data fell within the "true liquid" range and agreed with the thermodynamic model for diffusivity. The toluene concentration required for agreement of the diffusivity data with predictions of the model increased as the experimental temperature was lowered, in agreement with equations describing T_{11} in plasticizer-polymer systems.

4) All diffusivity data within the "true liquid" range is consistent with equation (46) using constant parameters D_{00} and E . The particular temperature and concentration do not matter so long as T_{11} at that concentration is below the experimental temperature.

5) The correctness of the thermodynamic models above T_{11} is consistent with the molecular interpretation of T_{11} as the point above which entire molecules are free to move in a

true equilibrium liquid state.

6) The ASOG and UNIFAC models performed equally well in modeling the concentration dependence of diffusivity. However, the ASOG model with variable size parameter (VSP) showed better performance than either ASOG or UNIFAC. This was especially true in modeling infinite dilution equilibrium data, but was evident also in modeling the diffusivity data.

7) The temperature dependence of diffusivity was given accurately by an Arrhenius activation energy model, once the concentration dependence was accounted for by the thermodynamic models. However, a small concentration bias was still apparent in the zero-concentration diffusivity D_0 depending upon which original data point was used in correlating D_0 . The order of magnitude of the spread in D_0 values seemed dependent upon the spread in concentration of experimental data points at a particular temperature.

8) The thermodynamic models used here effectively described the variation of diffusivity with concentration above T_{11} . This indicates that the total effect of free volume changes and variations in solution molar density, ignored in equation (18), were small compared to the thermodynamic effects above T_{11} .

Recommendations for additional study into these topics include:

- 1) Application of the ASOG model to polar polymer-solvent systems, using the variable size parameter approach which was successful in modeling the nonpolar polystyrene-toluene system here. Such polar systems are poorly modeled by conventional (Flory-Huggins) thermodynamic models.
- 2) Application of the variable size parameter concept to the UNIFAC model.
- 3) Derivation of closed form solutions for the necessary derivative used in diffusivity modeling based upon the UNIFAC model without residual (enthalpic) interactions.
- 4) Possible derivation of closed form solutions for the necessary derivative used in diffusivity modeling based upon enthalpic interaction terms in the ASOG and UNIFAC models.
- 5) Application of the model presented here to other experimental data for nonpolar systems, e.g. polystyrene-benzene or polystyrene-ethylbenzene, to further corroborate these results.
- 6) Gathering of experimental data over a larger temperature and concentration range to further corroborate these

results. (This is difficult or impossible with current microbalance apparatus, according to Duda, et al (1973,1979).)

7) Investigation of the concentration bias in the model which was described but not explained here. Effects of free volume changes and variations in solution molar density could be studied. If the bias is the result of these effects, perhaps such effects could be modeled more simply than with conventional free volume models.

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