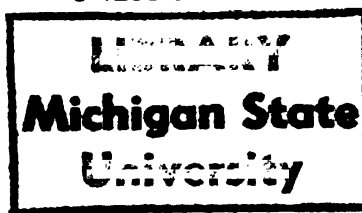




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DESIGN OF SORPTION EXPERIMENTS FOR
CONCENTRATED POLYMER SOLUTIONS ABOVE T_g

By

Linda Sue Mossner

A THESIS

Submitted to
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ABSTRACT

DESIGN OF SORPTION EXPERIMENTS FOR CONCENTRATED POLYMER SOLUTIONS ABOVE T_g

By

Linda Sue Mossner

Sorption experiments are designed for the measurement of thermodynamic equilibria and binary diffusion coefficients in polymer-solvent systems exhibiting enthalpic interactions. The effects of the Flory-Huggins and ASOG-VSP thermodynamic models on the diffusivity predictions of the Vrentas and Duda free volume theory are evaluated.

Analysis of the Vrentas and Duda free volume diffusion theory reveals that several assumptions made in the theory development place limitations on its predictive capabilities. Additivity of free volumes on mixing may not be reasonable for polymer-solvent systems with strong enthalpic interactions. Relating the free volume of a liquid to the viscosity with the WLF equation appears invalid for many organic solvents in the experimental temperature ranges of interest. The activation energy and solvent to polymer jumping unit ratio parameters appear to be best determined by fitting the free volume diffusivity equation to actual diffusivity data rather than using calculations with a physical interpretation.

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TABLE OF CONTENTS

<u>Item</u>	<u>Page</u>
LIST OF TABLES	v
LIST OF FIGURES	vi
LIST OF SYMBOLS	ix
CHAPTER 1 Introduction	1
CHAPTER 2 Literature Review	5
2.1 Free Volume Theories for Molecular Diffusion	5
2.1-1 Duda-Vrentas Free Volume Diffusion Model	6
2.1-2 Evaluation of Model Parameters	8
2.1-3 Critical Model Assumptions	12
2.1-3.1 Volume Change on Mixing	12
2.1-3.2 Free Volume and Viscosity of Liquids	16
2.2 Thermodynamic Models Applicable to Polymer Systems	20
2.3 Thermal Degradation of Poly(vinyl Acetate)	26
2.4 Previous Sorption Studies of Poly(vinyl Acetate)	26
CHAPTER 3 Microbalance Experimental Procedure	34
3.1 Microbalance Polymer Diffusion Apparatus	34
3.2 Polymer Sample Preparation	40
3.3 Operating Procedures	42
3.4 Limitations of Microbalance Apparatus	44
CHAPTER 4 Analysis of Free Volume Diffusion Theories	49
4.1 Effect of Jumping Unit Ratio on Diffusivity Predictions	49
4.2 Determination of Infinite Dilution Activity Coefficient	56

<u>Item</u>	<u>Page</u>
4.3 Effect of Thermodynamic Model on Predictions of the Free Volume Diffusion Theory	60
4.3-1 Maximum in Diffusivity Curve	60
4.3-2 Influence of Thermodynamic Parameter on Mutual Diffusion Coefficient	73
4.3-3 Linearized Free Volume Diffusion Models	74
CHAPTER 5 McBain-Bakr Sorption Balance	94
5.1 Proposed Polymer Diffusion Apparatus	94
5.2 Polymer Sample Preparation	99
5.3 Operating Procedures	100
5.4 Data Analysis	103
5.4-1 Analysis of Complete Sorption Curve	103
5.4-2 Analysis of Low Solvent Concentration Data	106
CHAPTER 6 Summary and Conclusions	108
CHAPTER 7 Recommendations	111
APPENDIX A Data Acquisition Program for Polymer Diffusion Apparatus	113
APPENDIX B Activity Data for Poly(vinyl Acetate)-Solvent Systems	118
APPENDIX C Predicted Diffusivity Data for Poly(vinyl Acetate)-Solvent Systems	124
APPENDIX D Maximum in Diffusivity versus Solvent Weight Fraction Curves	140
LIST OF REFERENCES	143

LIST OF TABLES

<u>Item</u>	<u>Page</u>
2.1 Volume Change on Mixing for Polymer-Solvent Systems	14
2.2 Previous Sorption Studies of Poly(vinyl Acetate)	31
4.1 ξ and $\tilde{V}_1^*$ Data for Methanol ξ Calculation . . .	52
4.2 Relative Error of Activity Coefficient vs. Solvent Weight Fraction Curves	61
4.3 Maxima in Diffusivity vs. Solvent Weight Fraction Curves for Poly(vinyl Acetate) Solutions	67
B.1 Experimental Activity Data for Benzene, Chloroform and Toluene in Poly(vinyl Acetate) .	118
B.2 Infinite Dilution Weight Fraction Activity Coefficients for Poly(vinyl Acetate) Solutions Determined Using Procedure 1	121
B.3 Infinite Dilution Weight Fraction Activity Coefficients for Poly(vinyl Acetate) Solutions Determined Using Procedure 2	122
B.4 Infinite Dilution Weight Fraction Activity Coefficients for Poly(vinyl Acetate) Solutions Determined Using Procedure 3	123
C.1 Chloroform-Poly(vinyl Acetate) Diffusivity Data Predictions	124
C.2 Acetone-Poly(vinyl Acetate) Diffusivity Data Predictions	127
C.3 Toluene-Poly(vinyl Acetate) Diffusivity Data Predictions	130
C.4 Methanol-Poly(vinyl Acetate) Diffusivity Data Predictions	133
C.5 Free Volume Parameters for Figures 4.7 - 4.10 and Tables C.1 - C.4	136

LIST OF FIGURES

<u>Item</u>	<u>Page</u>
3.1 Microbalance Polymer Diffusion Apparatus . . .	35
3.2 Microbalance	36
3.3 Sorption and Desorption of Chloroform by Poly(vinyl Acetate) at 70 °C	46
3.4 Sorption Experiment Using Chloroform without a Polymer Sample	47
4.1 Predicted Thermodynamic Diffusion Coefficient for Methanol-Poly(vinyl Acetate) Using $\xi = 0.45$	50
4.2 Predicted Thermodynamic Diffusion Coefficient for Methanol-Poly(vinyl Acetate) Using $\xi = 0.31$	51
4.3 Predicted Diffusivity Data for Chloroform- Poly(vinyl Acetate) with Two Sets of D_o , E_A and ξ Parameters	55
4.4 Predicted Solvent Weight Fraction Activity Coefficients for Benzene-Poly(vinyl Acetate) Solutions at 30 °C	57
4.5 Predicted Solvent Weight Fraction Activity Coefficients for Chloroform-Poly(vinyl Acetate) Solutions at 35 °C	58
4.6 Predicted Solvent Weight Fraction Activity Coefficients for Toluene-Poly(vinyl Acetate) Solutions at 40 °C	59
4.7 Comparison of Flory-Huggins and ASOG-VSP Thermodynamic Models in the Free Volume Diffusion Theory for Chloroform-Poly(vinyl Acetate) Solutions	62
4.8 Comparison of Flory-Huggins and ASOG-VSP Thermodynamic Models in the Free Volume Diffusion Theory for Acetone-Poly(vinyl Acetate) Solutions	63

<u>Item</u>	<u>Page</u>
4.9 Comparison of Flory-Huggins and ASOG-VSP Thermodynamic Models in the Free Volume Diffusion Theory for Toluene-Poly(vinyl Acetate) Solutions	64
4.10 Comparison of Flory-Huggins and ASOG-VSP Thermodynamic Models in the Free Volume Diffusion Theory for Methanol-Poly(vinyl Acetate) Solutions	65
4.11 Dependence of χ on Solvent Concentration for Poly(vinyl Acetate) Solutions at 90 °C .	69
4.12 Comparison of Flory-Huggins and ASOG-VSP Thermodynamic Models in the Free Volume Diffusion Theory for Toluene-Poly(vinyl Acetate) Solutions with $\chi = 0.5$	71
4.13 Influence of Ω_1^∞ on the Mutual Diffusion Coefficient for Chloroform-Poly(vinyl Acetate) Solutions	75
4.14 Influence of Ω_1^∞ on the Mutual Diffusion Coefficient for Acetone-Poly(vinyl Acetate) Solutions	76
4.15 Influence of Ω_1^∞ on the Mutual Diffusion Coefficient for Toluene-Poly(vinyl Acetate) Solutions	77
4.16 Influence of Ω_1^∞ on the Mutual Diffusion Coefficient for Methanol-Poly(vinyl Acetate) Solutions	78
4.17 Influence of χ on the Mutual Diffusion Coefficient for Chloroform-Poly(vinyl Acetate) Solutions	79
4.18 Influence of χ on the Mutual Diffusion Coefficient for Acetone-Poly(vinyl Acetate) Solutions	80
4.19 Influence of χ on the Mutual Diffusion Coefficient for Toluene-Poly(vinyl Acetate) Solutions	81
4.20 Influence of χ on the Mutual Diffusion Coefficient for Methanol-Poly(vinyl Acetate) Solutions	82

<u>Item</u>	<u>Page</u>
4.21 Comparison of Linearized and Complete ASOG-VSP Free Volume Diffusion Models for Chloroform-Poly(vinyl Acetate) Solutions . .	85
4.22 Comparison of Linearized and Complete ASOG-VSP Free Volume Diffusion Models for Acetone-Poly(vinyl Acetate) Solutions	86
4.23 Comparison of Linearized and Complete ASOG-VSP Free Volume Diffusion Models for Toluene-Poly(vinyl Acetate) Solutions	87
4.24 Comparison of Linearized and Complete ASOG-VSP Free Volume Diffusion Models for Methanol-Poly(vinyl Acetate) Solutions	88
4.25 Comparison of Linearized and Complete Flory-Huggins Free Volume Diffusion Models for Chloroform-Poly(vinyl Acetate) Solutions	89
4.26 Comparison of Linearized and Complete Flory-Huggins Free Volume Diffusion Models for Acetone-Poly(vinyl Acetate) Solutions . .	90
4.27 Comparison of Linearized and Complete Flory-Huggins Free Volume Diffusion Models for Toluene-Poly(vinyl Acetate) Solutions . .	91
4.28 Comparison of Linearized and Complete Flory-Huggins Free Volume Diffusion Models for Methanol-Poly(vinyl Acetate) Solutions .	92
5.1 Proposed Polymer Diffusion Apparatus	95
5.2 Sorption Chamber for Proposed Polymer Diffusion Apparatus	96

LIST OF SYMBOLS

a_1	solvent thermodynamic activity
A	constant in Arrhenius viscosity equation
A^*	constant defined by equation (15)
A_i	combined free volume coefficient of component i
B	constant in density equation (82)
c_i	concentration of component i
$(c_1^g)_2$	first WLF constant of polymer
$(c_1^g)_2$	second WLF constant of polymer
C	solvent concentration
C_o	initial solvent concentration
C_1	final solvent concentration
C_E	equilibrium solvent concentration
D	binary mutual diffusion coefficient
D_o	preexponential factor in equation (1)
D_1	self-diffusion coefficient of solvent
D_{01}	preexponential factor in equation (3)
$\bar{D}$	average variable diffusion coefficient over a solvent concentration interval
$\mathcal{D}_i$	intrinsic diffusion coefficient of component i
DP	degree of polymerization
e	base of natural logarithm
E_a	activation energy in Arrhenius viscosity-temperature equation (33)

E_A	activation energy for diffusion in free volume model
f_{Hi}^g	fractional hole free volume of component i at the glass transition temperature
G_1, G_2	constants in equation (35)
G_3, G_4	constants in equation (81)
I	integral defined in equation (72)
K_1	free volume coefficient of linearized ASOG-VSP and Flory-Huggins free volume diffusion model
K_2	thermodynamic coefficient of linearized ASOG-VSP free volume diffusion model
K_3	thermodynamic coefficient of linearized Flory-Huggins free volume diffusion model
K_{1i}, K_{2i}	free-volume parameters of component i
L	thickness of polymer film
M_i	molecular weight of component i
M_j	molecular weight of polymer jumping unit
$M(t)$	weight pickup of solvent in polymer film at time t
$M(\infty)$	weight pickup of solvent in polymer film at equilibrium
$\bar{M}_n$	number-average molecular weight
$\bar{M}_w$	weight-average molecular weight
$\bar{M}_v$	viscosity-average molecular weight
P_1	solvent vapor pressure
P_1^0	saturated vapor pressure of solvent
Q	constant in density equation (82)
r	ratio of polymer molar volume to solvent molar volume
R	gas constant
R_i	initial slope of sorption curve

R_l	solvent size term
S_i	number of size groups (carbon atoms) in component i
t	time
T	absolute temperature
T_c	critical temperature
T_r	reduced temperature
T_{br}	reduced temperature at the boiling point
T_{gi}	glass transition temperature of component i
v	mass-average velocity in x-direction
v_i	mass-average velocity of component i in x-direction
$\bar{V}_l$	solvent molar volume
V_i	partial molar volume of component i
$\hat{V}_i^o$	specific volume of pure component i
$\hat{V}_i$	partial specific volume of component i
$\hat{V}_i^*$	specific critical volume of pure component i
$\tilde{V}_i^o$	specific molar volume of pure component i
$\tilde{V}_i^*$	specific molar critical volume of pure component i
$\hat{V}_{FH}$	specific hole free volume
$\hat{V}_{FHi}^o$	specific hole free volume of pure component i
ΔV_{mix}	volume change on mixing
w_i	weight fraction of component i
x	distance
x_i	mole fraction of component i

α_i	thermal expansion coefficient of component i
α_{ci}	thermal expansion coefficient of the "non-hole" free volume of component i
γ_1	solvent mole fraction activity coefficient
γ_1^S	solvent entropic activity coefficient
γ_1^G	solvent enthalpic activity coefficient
γ_1^∞	infinite dilution solvent mole fraction activity coefficient
γ	overlap factor in free volume diffusion model
η_i	viscosity of pure component i
μ_1	chemical potential of solvent in mixture
ξ	ratio of molar critical volume of solvent jumping unit to that of polymer jumping unit
δ_i	solubility parameter of component i
ρ_i	mass density of component i
ρ_{mp}	mass density at the melting point
ρ_{bp}	mass density at the boiling point
ϕ_i	volume fraction of component i
χ	Flory-Huggins interaction parameter
Ω_1	solvent weight fraction activity coefficient
Ω_1^∞	infinite dilution solvent weight fraction activity coefficient

CHAPTER 1

Introduction

In order to analyze many of the mass transfer problems involved with polymer processing, binary mutual diffusion coefficients are needed for molten polymer-solvent systems. The molecular diffusion of monomers, initiators and low molecular weight condensation products can strongly influence the rate of a polymerization process. After the completion of a polymerization process, volatile components including solvents, monomers, condensation by-products and other impurities must be removed. These devolatilization procedures involve molecular diffusion in concentrated polymer solutions and melts at elevated temperatures. Unfortunately very little experimental diffusivity data is available for polymer-solvent systems, especially at elevated temperatures. It is difficult to measure these diffusion coefficients at the higher temperatures which are characteristic of polymer purification processes. In addition, the experimental difficulties are increased due to the strong dependence of the diffusion coefficients of polymer-solvent systems on temperature and concentration. Thus it is necessary to develop a method of extrapolating limited diffusivity data at lower temperatures to higher temperatures in order to adequately model and predict the

devolatilization process.

Vrentas, Duda and coworkers have developed a free volume diffusion model for the prediction of polymer-solvent diffusion coefficients for purely viscous diffusion. Their model has successfully described the temperature and concentration dependence of the diffusion coefficients for several polymer-solvent systems including toluene- and chloroform-poly(vinyl acetate) and ethylbenzene-polystyrene [J1,L2]. Vrentas and Duda use the Flory-Huggins thermodynamic model in their free volume diffusion theory to describe the polymer-solvent enthalpic and entropic interactions. This model can typically describe athermal polymer-solvent systems fairly well. However, there is evidence that the Flory-Huggins thermodynamic model is not adequate for systems with significant enthalpic interactions between the solvent and the polymer as evidenced by diffusion studies involving toluene-poly(methyl methacrylate) and carbon disulphide-polystyrene [L2].

Misovich and Grulke have developed a correlation for solvent activity coefficients in concentrated polymer solutions based upon the ASOG (Analytical Solution of Groups) group-contribution model with an empirical size correction used to extend the model to polymer solutions. The ASOG-VSP thermodynamic model has one adjustable parameter which is a true constant with concentration unlike the adjustable parameter in the Flory-Huggins

thermodynamic model which can vary with concentration for many polymer-solvent systems. The ASOG-VSP thermodynamic model has been shown to represent experimental activity data for a variety of polymer-solvent systems including systems with enthalpic interactions that are not well represented by the Flory-Huggins model [M3].

Several assumptions made in the development of the free volume diffusion model are discussed and analyzed. These include the neglecting of a volume change on mixing for polymer-solvent systems, the determination of solvent free volume parameters from low temperature viscosity data and the assumption of a constant Flory-Huggins interaction parameter with temperature and concentration. The procedures for determining several of the theory parameters are also discussed. Finally, the effect of the two thermodynamic models on predictions of the free volume diffusion theory are illustrated.

Careful design of polymer sorption experiments is necessary to study the effect of the thermodynamic model on predictions of the free volume diffusion theory. A polymer diffusion apparatus, consisting of a microbalance mounted inside a vacuum chamber, was set up to conduct constant pressure sorption experiments to measure polymer-solvent diffusion coefficients. Temperature, pressure and weight gain measurements are continually collected, stored and plotted with an IBM PC-XT personal computer. Several severe experimental difficulties were encountered with this

experimental apparatus and procedure.

Because of the difficulties encountered with the microbalance set-up, a new polymer diffusion apparatus has been designed along with a variety of constant pressure sorption experiments for poly(vinyl acetate)-solvent systems. The extension of helical quartz springs will be used to measure the weight gain of polymer samples due to the sorption of organic solvents at pressures above and below atmospheric and temperatures up to 100 °C above the glass transition temperature of the pure polymer. The solvents chosen for study, including chloroform, acetone, toluene and methanol, were chosen on the basis of verifying and extending existing experimental data, having experimentally reasonable vapor pressures and diffusion coefficients at the temperatures of interest and exhibiting a variety of polymer-solvent enthalpic interactions. Diffusivity predictions are made for all four systems using both the Flory-Huggins and ASOG-VSP thermodynamic models in the free volume diffusion theory.

CHAPTER 2

Literature Review

2.1 Free Volume Theory for Molecular Diffusion

Free volume theory for molecular diffusion is based on two requirements. In order for a molecule to migrate in solution, a void space of sufficient volume must appear adjacent to the molecule, and the molecule must possess enough energy to jump into this void. The probability of a jump occurring is thus the product of the probabilities of these two conditions being met. On this basis Cohen and Turnbull [C2,T3] derived an expression for self-diffusion coefficients as a function of hole free volume. Their results can be summarized as follows:

$$D_1 = D_0 \exp(-E_A/RT) \exp(-\gamma \hat{V}_1^* / \hat{V}_{FH}) \quad (1)$$

where E_A is the critical energy a molecule must obtain to overcome neighboring attractive forces, $\hat{V}_1^*$ is the critical hole free volume necessary for a molecule to jump into and γ is an overlap factor introduced because the same free volume is available to more than one molecule.

Fujita [F6,F7] utilized this expression as a starting point for a free volume description of the temperature- and concentration-dependence of the diffusion coefficient in polymer-solvent systems. Assumptions made in the

development of Fujita's model limit its applicability to polymer-solvent systems of low solvent concentration (solvent volume fractions less than 0.15) and to systems with the molecular weight of the solvent equal to the molecular weight of a jumping unit of the polymer chain. For organic solvent-polymer systems, the molecular weight of the solvent is often close to the molecular weight of the polymer jumping unit since most polymers are formed from monomers which are themselves organic solvents. Another shortcoming of this model is the requirement of diffusivity data at several conditions to evaluate the constants of the theory [V8].

Vrentas and Duda removed the restrictive assumptions from Fujita's free volume theory to develop an improved free volume diffusion model [V4,V5] with predictive capabilities for the determination of polymer-solvent diffusion coefficients for purely viscous diffusion which give good agreement with experimental data for several polymer-solvent systems. Modifications and improvements have been made in this model in a long series of papers [D5-7,J1-3,L2,V2,V3,V7,V8,V9,V11,V12].

2.1-1 Vrentas-Duda Free Volume Diffusion Model

The most recent version of the Vrentas-Duda free volume diffusion theory can be summarized as follows: The binary mutual diffusion coefficient for a polymer-solvent system is given by:

$$D = D_1 (\rho_2 \hat{V}_2 \rho_1 / RT) (\partial \mu_1 / \partial \rho_1)_{T,P} \quad (2)$$

D_1 , the self-diffusion coefficient of the solvent, represents the effect of free volume changes in the diffusion coefficient and is given by:

$$D_1 = D_{01} \exp[-(w_1 \hat{V}_1^* + w_2 \xi \hat{V}_2^*) / \hat{V}_{FH}] \quad (3)$$

where $\hat{V}_1^*$ and $\hat{V}_2^*$ are specific critical volumes of the pure solvent and pure polymer, respectively, necessary for a molecule to migrate in a liquid. The preexponential factor describing the energy needed to overcome neighboring attractive forces, D_{01} , is given by:

$$D_{01} = D_0 \exp(-E_A / RT) \quad (4)$$

The ratio of molar critical volume of solvent jumping unit to that of polymer jumping unit, ξ , is given by:

$$\xi = \hat{V}_1^* M_1 / \hat{V}_2^* M_j \quad (5)$$

The specific hole free volume of the mixture, $\hat{V}_{FH}$, is assumed to be a linear combination of the specific hole free volume of the solvent and the polymer and is given by:

$$\hat{V}_{FH} / \xi = (K_{11} / \xi) w_1 (K_{21} + T - T_{g1}) + (K_{12} / \xi) w_2 (K_{22} + T - T_{g2}) \quad (6)$$

where K_{11} , K_{12} , K_{21} and K_{22} are physical parameters of the pure solvent and pure polymer. In terms of volumetric properties of the pure polymer:

$$K_{21} = \hat{V}_2^0(T_{g2}) (\alpha_2 - (1 - f_{H2}^g) \alpha_{c2}) \quad (7)$$

$$K_{22} = f_{H2}^g / (\alpha_2 - (1 - f_{H2}^g) \alpha_{c2}) \quad (8)$$

$$f_{H2}^g = \hat{V}_{FH2}^0(T_{g2}) / \hat{V}_2^0(T_{g2}) \quad (9)$$

where α_2 and α_{c2} are the thermal expansion coefficients of the polymer and the "non-hole" free volume (interstitial free volume and occupied volume) of the polymer,

respectively. f_{H2}^g is the fractional hole free volume of the polymer at the glass transition temperature, $\hat{v}_2^0$ is the specific volume of the polymer and $\hat{v}_{FH2}^0$ is the specific hole free volume of the polymer. A detailed derivation of these equations is given by Vrentas and Duda [V4,V5]. Similar equations can be written for the pure solvent.

The second group in equation (2), the chemical potential derivative, represents the effect of thermodynamic changes in the diffusion coefficient. Vrentas, Duda and coworkers used the Flory-Huggins theory to obtain the following equation for the thermodynamic factor:

$$(\hat{v}_2^0 \hat{v}_1^0 / RT) (\partial \mu_1 / \partial \phi_1)_{T,P} = (1 - \phi_1)^2 (1 - 2\chi \phi_1) \quad (10)$$

where χ , which describes the enthalpic and entropic interactions between the solvent and polymer, is assumed to be a constant, independent of temperature and concentration for a given polymer-solvent system. ϕ_1 is the volume fraction of solvent given by:

$$\phi_1 = w_1 \hat{v}_1^0 / (w_1 \hat{v}_1^0 + w_2 \hat{v}_2^0) \quad (11)$$

where $\hat{v}_1^0$ and $\hat{v}_2^0$ are the pure component specific volumes of the solvent and polymer, respectively.

2.1-2 Evaluation of Model Parameters

The variation of D with temperature and weight fraction can be determined for a particular polymer-solvent system once the following parameters are known: D_0 , E_A , ξ ,

$$\hat{V}_1^0, \hat{V}_2^0, \hat{V}_1^*, \hat{V}_2^*, \chi, K_{11}/\zeta, K_{12}/\zeta, K_{21} - T_{g1}, K_{22} - T_{g2},$$

To evaluate these parameters, Vrentas, Duda and coworkers assume the following data to be available:

- (1) Density-temperature data for the pure polymer and pure solvent.
- (2) Viscosity-temperature data for the pure polymer and pure solvent.
- (3) At least three values of the diffusivity for the polymer-solvent system at two or more temperatures.
- (4) Thermodynamic data from which χ can be determined.

The procedures used by Vrentas, Duda and coworkers for determining the theory parameters are as follows:

- (1) $\hat{V}_1^0$ and $\hat{V}_2^0$ are obtained from appropriate density data. $\hat{V}_1^*$ and $\hat{V}_2^*$ are estimated by equating them to equilibrium liquid volumes at 0 K [V4,V8].

A method discussed by Hayward [H2] for these estimations relates the liquid volumes at 0 K to the liquid volumes at the melting point.

$$\hat{V}_1^0(0 \text{ K}) = 0.91 \hat{V}_1^0(T_{mp}) \quad (12)$$

- (2) $K_{11}/\zeta, K_{12}/\zeta, K_{21} - T_{g1}$ and $K_{22} - T_{g2}$ can be estimated from viscosity-temperature data for the pure polymer and pure solvent. The parameters K_{22} and $\zeta \hat{V}_2^*/K_{12}$ are related [V5] to the WLF constants of the polymer, $(c_1^g)_2$ and $(c_2^g)_2$ by:

$$K_{22} = (c_2^g)_2 \quad (13)$$

$$\zeta \hat{V}_2^*/K_{12} = 2.303(c_1^g)_2 (c_2^g)_2 \quad (14)$$

Values of $(c_1^g)_2$ and $(c_2^g)_2$, derived from viscosity-temperature data, have been tabulated for a large number of polymers [F1].

The viscosity of the pure solvent, η_v , can be expressed as:

$$\ln \eta_1 = \ln A^* + (\hat{\Delta} \hat{V}_1^*/K_{11})(K_{12} + T - T_{g1}) \quad (15)$$

where A^* is considered to be effectively constant. The quantities $\hat{\Delta} \hat{V}_1^*/K_{11}$ and $K_{12} - T_{g1}$ can be determined from a non-linear regression analysis of viscosity-temperature data based on equation (15). Alternatively, equation (15) can be rearranged into the following form:

$$\frac{T - T_{\text{ref}}}{\ln \frac{\eta_1(T_{\text{ref}})}{\eta_1(T)}} = \frac{T - T_{g1}}{K_{31}} + \frac{K_{21}}{K_{31}} \quad (16)$$

where $K_{31} = (\hat{\Delta} \hat{V}_1^*/K_{11})/(K_{21} + T_{\text{ref}} - T_{g1})$. By plotting the left hand side of equation (16) versus T , the parameters $K_{21} - T_{g1}$ and $\hat{\Delta} \hat{V}_1^*/K_{11}$ can be obtained from the slope and y-intercept of the plot using the following equations:

$$K_{21} - T_{g1} = (\text{y-intercept})/(\text{slope}) \quad (17)$$

$$\frac{\hat{\Delta} \hat{V}_1^*}{K_{11}} = \frac{(T_{\text{ref}} + \text{y-intercept}/\text{slope})}{\text{slope}} \quad (18)$$

These two techniques are essentially equivalent and the latter is preferred for ease of use.

- (3) χ can be determined from sorption equilibrium data for a polymer-solvent system at pressures near

atmospheric if the thermodynamics of the liquid solution are adequately characterized by the Flory-Huggins equation.

$$a_1 = P_1/P_1^0 = \phi_1 \exp(\phi_2 + \chi \phi_2^2) \quad (19)$$

- (4) D_o , E_A and ξ can be determined from equations (2), (3), (4), (6), (10) and (11) and at least three diffusivity data points using non-linear regression techniques. The data must be collected at two or more temperatures so that D_o , ξ and E_A can be determined separately. Alternatively, since ξ represents the ratio of the molar critical volume of the solvent jumping unit to that of the polymer jumping unit, this parameter can be determined from diffusivity data for another solvent in the same polymer using the relation:

$$\frac{\xi(\text{solvent 1})}{\xi(\text{solvent 2})} = \frac{\tilde{V}_1^*(0\text{ K})(\text{solvent 1})}{\tilde{V}_1^*(0\text{ K})(\text{solvent 2})} \quad (20)$$

where $\tilde{V}_1^*$ is the specific molar critical volume of the pure solvent. This relation is only valid if each solvent molecule entirely jumps in the transport process. Vrentas, et al. [V11] calculate values for the ethylbenzene-polystyrene system using diffusivity data for other solvents in polystyrene. The ξ values determined from 12 of the 15 solvents examined are within 13% of the ξ value determined directly from ethylbenzene-

polystyrene data.

2.1-3 Critical Model Assumptions

2.1-3.1 Volume Change on Mixing

Equation (6) assumes the free volumes of the pure solvent and pure polymer are additive in solution. The validity of this assumption may depend on the particular polymer-solvent system. The additivity of free volumes can be considered reasonable for systems where there are no strong interactions between the polymer and solvent leading to large volume changes in the solution process [P3]. Pezzin and Gligo [P2] have shown the volumes are additive to within 0.2% for the cyclohexanone-poly(vinyl chloride) system. Baker, et al. [B1] have shown a relatively large volume contraction for the n-pentane-polyisobutylene system and concluded that volume contraction occurs whenever two aliphatic hydrocarbons of widely different chain lengths are mixed. Vrentas and Duda [V5] show the volume change on mixing increasing with temperature for the ethylbenzene-polystyrene system. Eichenger and Flory [E1-E3] reported slight volume changes on mixing for benzene-natural rubber and benzene- and cyclohexane-polyisobutylene systems.

Höcker and Flory [F3,H4,H5] show a volume change on mixing for ethylbenzene-, methyl ethyl ketone- and cyclohexane-polystyrene systems. The volume changes on mixing for

these polymer-solvent systems are summarized in Table 2.1.

The effect volume change on mixing has on the binary mutual diffusion coefficient can be seen by starting with the equation of continuity written as:

$$\partial c_1 / \partial t + \partial / \partial x (c_1 v_1) = 0 \quad (21)$$

$$\partial c_2 / \partial t + \partial / \partial x (c_2 v_2) = 0 \quad (22)$$

for the solvent and polymer, respectively. These equations describe the rates at which solvent and polymer concentrations change at a point. The second term in each equation, representing the rate of change in the total mass flux for each component, can be divided into two terms representing the rate of change with time of the diffusive flux and the convective flux for each component. Thus

$$\partial c_1 / \partial t = - \partial / \partial x (D_1 \partial c_1 / \partial x) - \partial / \partial x (c_1 v) \quad (23)$$

$$\partial c_2 / \partial t = - \partial / \partial x (D_2 \partial c_2 / \partial x) - \partial / \partial x (c_2 v) \quad (24)$$

where v is the mass-average velocity in the x -direction and D_1 and D_2 are the intrinsic diffusion coefficients of the solvent and polymer, respectively. Intrinsic diffusion coefficients are defined such that the reference cross-section through which components 1 and 2 transfer is arbitrarily defined so that no bulk flow occurs through it. This frame of reference is necessary because systems with a volume change on mixing do not have a cross-section of constant total volume on each side by which the binary mutual diffusion coefficient is traditionally defined.

At constant temperature and pressure

Table 2.1 Volume Change on Mixing for Polymer-Solvent Systems

<u>Polymer-Solvent System</u>	<u>Temp(°C)</u>	<u>ΔV_{mix}</u>	<u>Concentration</u>	<u>Ref.</u>	<u>χ</u>
Natural rubber-benzene	25	+0.09%	0.50	[E1]	0.42-0.51
PIB-benzene	24.5	+0.35%	0.55	[E2]	0.67-1.12
PIB-cyclohexane	25	-0.14%	0.56	[E3]	0.47-0.50
PIB-n-pentane	25	-1.25%	0.50	[E4,B1]	0.48-0.63
PVC-cyclohexanone	40	-0.20%	0.13 ^a	[P2]	---
PS-methyl ethyl ketone	25	-0.09%	0.50	[F3]	0.5-1.4
PS-ethyl benzene	25	-0.30%	0.50	[H5]	0.4-0.9
PS-cyclohexane	25	-0.14%	0.50	[H4]	0.5-0.9
PS-ethylbenzene	0	-0.15%	0.50 ^b	[V5]	---
	50	-0.25%	0.50 ^b	[V5]	---
	100	-0.40%	0.50 ^b	[V5]	---
	200	-0.80%	0.50	[V5]	---

NOTE: concentrations given in polymer segment fractions except

a = polymer volume fraction

b = polymer weight fraction

PIB = poly(isobutylene)

PVC = poly(vinyl chloride)

PS = polystyrene

$$v_1 c_1 + v_2 c_2 = 1 \quad (25)$$

where v_1 and v_2 are the partial molal volumes of the solvent and polymer, respectively. Differentiating equation (25) with respect to c_1 yields:

$$(\partial c_2 / \partial c_1)_{P,T} = -v_1 / v_2 \quad (26)$$

Using equation (25) and (26) in equation (24) gives:

$$-\frac{v_1}{v_2} \left[\frac{\partial c_1}{\partial t} \right] = -\frac{\partial}{\partial x} \left[\mathcal{D}_2 \frac{v_1}{v_2} \left(\frac{\partial c_1}{\partial x} \right) \right] - c_2 \frac{\partial v}{\partial x} + \frac{v_1}{v_2} \left[\frac{\partial c_1}{\partial x} \right] v \quad (27)$$

Combining equation (27) into equation (23) using equation (25) results in the cancellation of the terms containing v and gives:

$$\frac{\partial v}{\partial x} = v_1 \frac{\partial}{\partial x} \left[\mathcal{D}_1 \frac{\partial c_1}{\partial x} \right] - v_2 \frac{\partial}{\partial x} \left[\mathcal{D}_2 \frac{v_1}{v_2} \left(\frac{\partial c_1}{\partial x} \right) \right] \quad (28)$$

Integrating Equation (28) by parts from $-\infty$ to x yields:

$$v = v_1 (\mathcal{D}_1 - \mathcal{D}_2) \frac{\partial c_1}{\partial x} + \int_{-\infty}^x \frac{c_2}{c_1} \left[\mathcal{D}_1 + \mathcal{D}_2 \frac{v_1 c_1}{v_2 c_2} \right] \left[\frac{\partial v}{\partial c_1} \right] \left[\frac{\partial c_1}{\partial x} \right]^2 dx' \quad (29)$$

It is assumed v and $(\partial c_1 / \partial x)$ equal zero at $x = -\infty$.

Substituting equation (29) into equations (23) and (24) results in the following form of the equation of continuity for the solvent and polymer, respectively:

$$\frac{\partial c_1}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial c_1}{\partial x} \right] - \frac{\partial}{\partial x} \left[c_1 \int_{-\infty}^x \frac{D}{v_2 c_1} \left[\frac{\partial v}{\partial c_1} \right] \left[\frac{\partial c_1}{\partial x} \right]^2 dx' \right] \quad (30)$$

$$\frac{\partial c_2}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial c_1}{\partial x} \right] - \frac{\partial}{\partial x} \left[c_2 \int_{-\infty}^x \frac{D}{v_2 c_1} \left[\frac{\partial v}{\partial c_1} \right] \left[\frac{\partial c_1}{\partial x} \right]^2 dx' \right] \quad (31)$$

where D , the traditional binary mutual diffusion coefficient is related to $\mathcal{D}_1$ and $\mathcal{D}_2$ by:

$$D = \mathcal{D}_1 v_2 c_2 + \mathcal{D}_2 v_1 c_1 \quad (32)$$

D defined as such only has physical significance if there is no volume change on mixing. The second terms in equations (30) and (31) vanish when there is no volume change on mixing and equations (30) and (31) reduce to the usual diffusion equations known as Fick's 2nd law of diffusion.

When there is a significant volume change on mixing for a polymer-solvent system, evaluation of the effect of the volume change on the diffusion coefficient depends on an appropriate model for $\partial V_2 / \partial c_1$. The effect the volume change has on the diffusion coefficient increases as the magnitude of the concentration gradient increases and thus the diffusion coefficients obtained from sorption experiments with large step changes in solvent concentration, such as polymer swelling experiments, are most affected.

2.1-3.2 Free Volume and Viscosity of Liquids

Vrentas, Duda and coworkers determine the free volume parameters for the polymer and solvent by fitting pure component viscosity data with the WLF equation derived by Williams, Landel and Ferry [W1]. The WLF equation relates the viscosity of a liquid to its free volume and is based on a linear variation of free volume with temperature resulting in the form of equation (15). For polymers, the WLF equation is generally accepted to be valid for temperatures in the range of T_g to $T_g + 100$ K although some deviations from this behavior have been reported [S1].

There is no generally accepted method for estimating the polymer free volume parameters at temperatures exceeding $T_g + 100$ K, but these temperatures are usually beyond the range of interest.

There is considerable question as to the applicability of free volume theory to viscous transport at temperatures significantly above the glass transition temperature. At low temperatures, the principle factor in viscous flow is the availability of free volume for a flowing molecule. At high temperatures, where there is a sufficient free volume available, the viscosity is determined primarily by the energy required for the molecule to jump from one site in a liquid to another.

A variety of viscous behavior has been observed in liquids. Garfield and Petrie [G2] have fit experimental viscosity data for dibenzyl succinate and dicyclohexyl phthalate with the WLF equation. At temperatures above $T_g + 100$ K the predicted viscosities fall below the experimental data. T_g for a liquid is defined usually as that temperature at which the viscosity of the liquid reaches 10^{13} P [B2]. The molecular relaxation time at this viscosity exceeds 15 minutes which is comparable with the time scale of a normal experiment and thus the properties of the liquid appear to be "frozen" in time.

Barlow, et al. [B2] describe another type of viscous behavior for several aromatic hydrocarbons and phthalates. The free-volume equation fits the experimental viscosity

data in two separate temperature regions with two different sets of constants, also with deviations from the predicted behavior at high temperatures. This discontinuity in the viscosity behavior in the region of an "intersection temperature" was seen in molecules with short side group attachments to the benzene ring. For example, n-butyl benzene showed this discontinuity while n-hexyl benzene did not. A proposed explanation of this behavior by Barlow, et al. is that above the "intersection temperature" the molecules flow as single units while below this temperature small molecular aggregates constitute the unit of flow. Barlow, et al. suggest an Arrhenius relationship of the form:

$$\ln \eta_1 = A + E_a/RT \quad (33)$$

to describe the temperature dependence of viscosity at temperatures sufficiently high so that the principle factor in viscous flow is the attaining of a critical activation energy. They fit an Arrhenius equation to experimental viscosity data for a variety of aromatic hydrocarbons and phthalates at temperatures in excess of approximately $T_g + 170$ K. At these temperatures the free volume exceeded 10 to 16% of the specific volume of the liquid.

Davies and Matheson [D1,D2] have categorized three types of viscous behavior observed in liquids: 1) Arrhenius dependence of viscosity on temperature over the whole liquid range; e.g. benzene, ethylene, cyclohexane, 2) Arrhenius behavior at high temperatures changing to a free

volume dependence at lower temperatures; e.g. toluene, ethylbenzene and 3) Arrhenius behavior at high temperatures changing to one region of free volume behavior at lower temperatures changing to another type of free volume behavior at still lower temperatures; e.g. dimethyl phthalate, isopropylbenzene. They conclude that the transition from one type of dependence of viscosity on temperature to another is due to a restriction of the rotation of molecules in a liquid. In the Arrhenius region, molecules are free to rotate about at least two axes during the time between translational jumps. In the higher temperature free volume region, molecules are able to rotate about only one axis while in the lower temperature free volume region, rotation occurs primarily as a result of molecular translational motion.

It is apparent that the WLF equation does not accurately describe the temperature dependence of viscosity for ordinary liquids over the entire temperature range. Barlow, et al. attempted a combination of a free volume relationship and an Arrhenius relationship to describe the entire temperature range but were unsuccessful. Often the temperature range of interest for organic solvents is better described by an Arrhenius relationship than a free volume relationship since the glass transition temperatures of organic solvents typically fall in the range of 100 to 200 K [B2,L2].

It is not clear that meaningful free volume parameters

can be obtained for use at higher temperatures using the WLF equation to describe the viscosity of most organic solvents. If alternative models such as an Arrhenius relationship are used to describe the temperature dependence of viscosity for solvents, the free volume parameters must be determined differently. It is conceivable that a relationship between the free volume and the density of a liquid can be developed to determine these parameters. However, much more study is required before such a conclusion can be justified.

2.2 Thermodynamic Models Applicable to Polymer Systems

Vrentas, Duda and coworkers use the Flory-Huggins theory to describe the thermodynamics of diffusion in molten polymers. The Flory-Huggins model for polymer solution activity coefficients in concentrated solutions [F2] relates solvent activity, a_1 , to solvent volume fraction, ϕ_1 , polymer volume fraction, ϕ_2 , and interaction parameter, χ , by the equation:

$$\ln a_1 = \ln \phi_1 + \phi_2 + \chi \phi_2^2 \quad (34)$$

The interaction parameter, χ , describes the effect of both enthalpic and entropic interactions between polymer and solvent molecules. Vrentas, et al. assume χ to be constant which is typically true for athermal systems where the enthalpy change on mixing is zero. Solubility data obtained for 13 amorphous polymer-solvent systems [V13] show χ to be constant over limited temperature and

concentration ranges. However, χ varies with solvent concentration for many systems of interest. Billmeyer [B3] shows χ to vary with concentration for the benzene- and toluene-polystyrene systems. Bonner and Prausnitz [B5] show χ to be concentration-dependent for benzene-polyisobutylene and chloroform-polystyrene systems. Nakajima, et al. [N1] show χ to be concentration-dependent for benzene- and vinyl acetate-poly(vinyl acetate) systems. Eichenger and Flory [E1-E4] show χ to be concentration-dependent for benzene-natural rubber and benzene-, cyclohexane- and n-pentane-polyisobutylene systems. Flory, Höcker and Shih [F3,H3,H4] show the concentration dependence of χ for methyl ethyl ketone, ethylbenzene and cyclohexane in polystyrene. Finally, Gäeckle, et al. [G1] show χ to vary with concentration for solutions of toluene, methyl ethyl ketone and ethylbenzene in polystyrene along with n-pentane and cyclohexane in polyisobutylene.

χ can also vary with temperature for many systems. Blanks, et al. [B4] have shown χ to be temperature-dependent for styrene- and ethylbenzene-polystyrene systems. Kokes, et al. [K6] show χ to be temperature- and concentration-dependent for several solvents in poly(vinyl acetate). Newman and Prausnitz [N3] show the temperature dependence of χ for a variety of solvents in polyethylene and polyisobutylene.

In the cases where χ varies with concentration and temperature, this variation should be included in the model

equations. At this time there is no generally accepted model for describing the concentration-dependence of χ although models of the form:

$$\chi = G_1 + G_2/C \quad (35)$$

have been proposed. A similar form has been proposed for the temperature dependence of χ on the basis of Hildebrand's solubility parameter concept [H3]:

$$\chi = 0.34 + (\bar{V}_1/RT)(\delta_2 - \delta_1)^2 \quad (36)$$

where $\bar{V}_1$ is the solvent molar volume and δ_1 and δ_2 are the solubility parameters of the solvent and polymer, respectively. This model is not generally applicable to all polymer systems and only provides a rough estimate of χ .

Misovich and coworkers [M3] have recently developed a correlation for solvent activity coefficients in concentrated polymer solutions based upon the ASOG (Analytical Solution of Groups) group-contribution model for calculation of activity coefficients in solution developed by Derr and Deal [D3] and Wilson [W2]. The ASOG model predicts activity coefficients as the sum of a configurational (entropic) contribution due to differences in molecular size and a group-interaction (enthalpic) contribution due primarily to differences in intermolecular forces:

$$\ln \gamma_1 = \ln \gamma_1^S + \ln \gamma_1^G \quad (37)$$

Misovich has shown that for chemically similar polymer-solvent systems, the enthalpic contribution to the activity

coefficient is negligible. The entropic activity is given by:

$$\ln \gamma_1^S = 1 - R_1 + \ln R_1 \quad (38)$$

where R_1 is the solvent size term given by:

$$R_1 = S_1 / (S_1 x_1 + S_2 x_2) \quad (39)$$

S_1 and S_2 are the number of size groups (number of carbon atoms in the molecule) found in solvent and polymer, respectively, and x_1 and x_2 are the mole fractions of solvent and polymer, respectively.

For polymer-solvent systems, $S_2 \gg S_1$ and the infinite dilution mole fraction activity coefficient (the value of γ_1 as x_1 goes to zero) is given by:

$$\gamma_1^\infty = e(S_1/S_2) \quad (40)$$

where e is the base of the natural logarithm.

It is convenient to express concentration in polymer solutions as weight fractions. At infinite dilution of solvent in pure polymer, the weight fraction activity coefficient is given by:

$$\Omega_1^\infty = \gamma_1^\infty (M_2/M_1) = e(S_1/S_2) (M_2/M_1) \quad (41)$$

where M_1 and M_2 are the molecular weights of solvent and polymer, respectively.

The size group concept in ASOG applied to polymer solutions assumes that the free volume of the polymer and solvent are equal or

$$S_2/S_1 = M_2/M_1 \quad (42)$$

This is generally not true, otherwise the densities of chemically similar polymer-solvent pairs would be equal.

This incorrect assumption leads to:

$$\Omega_1^\infty = e \quad (43)$$

which is in substantial disagreement with much experimental data.

The correction to the ASOG model as proposed by Misovich, referred to as ASOG-Variable Size Parameter (ASOG-VSP), assumes the free volumes of solvent and polymer are not equal. The correct value of the ratio S_2/S_1 is thus given as:

$$S_2/S_1 = (e/\Omega_1^\infty)(M_2/M_1) \quad (44)$$

considering Ω_1^∞ as a known parameter. A method for determining Ω_1^∞ will be discussed later. Combining equation (44) and the weight fraction forms of equation (38) and equation (39) results in the following expression for the weight fraction activity coefficient:

$$\Omega_1 = \frac{\exp \left[\frac{(e/\Omega_1^\infty)(1 - w_1)}{w_1 + (e/\Omega_1^\infty)(1 - w_1)} \right]}{w_1 + (e/\Omega_1^\infty)(1 - w_1)} \quad (45)$$

In deriving this result, the assumption $e/\Omega_1^\infty \gg M_1/M_2$ was made. This result is thus restricted to solvents of low molecular weight compared to polymer and to solutions where Ω_1^∞ is not very large.

The infinite dilution weight fraction activity coefficient, the only adjustable parameter in equation (45), can be determined experimentally by gas-liquid partition chromatography. Values of Ω_1^∞ so obtained are tabulated for many polymer-solvent systems for a range

of temperatures [C1,N2-4]. Ω_1^∞ can also be calculated from a Flory-Huggins interaction parameter, χ , using the relation [N4]:

$$\ln \Omega_1^\infty = \ln(\rho_2/\rho_1) + (1 - 1/r) + \chi \quad (46)$$

where r is the ratio of polymer molar volume to solvent molar volume.

Misovich [M3] has compared the calculated values of activity coefficients using the ASOG-VSP, Flory-Huggins and UNIFAC-FV thermodynamic models with experimentally observed values for 29 isothermal binary polymer-solvent systems. The ASOG-VSP model represented the experimental data better than either the Flory-Huggins or the UNIFAC-FV model.

The ASOG-VSP model gives an improved result for the concentration dependence of the chemical potential for polymer-solvent systems. The chemical potential derivative in equation (2) can be represented as:

$$\frac{\rho_2 \hat{V}_2 \rho_1}{RT} \left[\frac{\partial \mu_1}{\partial \rho_1} \right]_{T,P} = x_2 \frac{d \ln a_1}{d \ln x_1} = \left[\frac{(e/\Omega_1^\infty) w_2}{w_1 + (e/\Omega_1^\infty) w_2} \right]^2 \quad (47)$$

Since Ω_1^∞ in this correlation is a true constant at a given temperature, unlike χ , this equation can be used without revision for polymer solutions with enthalpic interactions.

Equations (2), (3) and (47) can be combined to get an expression for the binary mutual diffusion coefficient:

$$D = D_{01} \left[\frac{(e/\Omega_1^\infty) w_2}{w_1 + (e/\Omega_1^\infty) w_2} \right]^2 \exp \left[- \frac{w_1 \hat{V}_1^* + w_2 \xi \hat{V}_2^*}{V_{FH}/5} \right] \quad (48)$$

2.3 Thermal Degradation of Poly(vinyl Acetate)

Thermal depolymerization of polymers can occur at elevated temperatures. The thermal decomposition of poly(vinyl acetate) is an autocatalytic process resulting in the formation of acetic acid. The temperature range for the sorption experiments is far below temperatures of degradation for poly(vinyl acetate). Van Krevelen [V1] has reported no thermal degradation of poly(vinyl acetate) after heating in a vacuum for 30 minutes at 269 °C. Grassie [G3] has reported a 5% evolution of acetic acid from poly(vinyl acetate) after heating at 213 °C for 5 hours. The normal temperature range for the devolatilization of poly(vinyl acetate) is within $T_g \leq T \leq T_g + 100$ °C so depolymerization should not be an important factor in this process.

2.4 Previous Sorption Studies of Poly(vinyl Acetate)

Ju [J1] has studied the constant and variable pressure sorption of toluene and chloroform in poly(vinyl acetate) at temperatures slightly above T_g of the pure polymer. The diffusion coefficients calculated from both methods are in good agreement and show a strong dependence on temperature and concentration, increasing with both. The experimental data compares favorably with the diffusion coefficients predicted from the free volume diffusion theory of Vrentas and Duda.

Kishimoto [K3] has studied the sorption, desorption and permeation of methanol in poly(vinyl acetate) at a range of temperatures above and below T_g of the pure polymer. The diffusion coefficients calculated from each method agree within experimental error and show a strong dependence on temperature and concentration, increasing with both. Ju, et al. [J3] have favorably compared this methanol diffusivity data of Kishimoto with the predicted values from the free volume theory of Vrentas and Duda. Kishimoto and associates [K2] have also studied the sorption and desorption of water in poly(vinyl acetate) at a range of temperatures above and below T_g of the pure polymer. The diffusion coefficient for water was found to be less temperature dependent than for organic solvents in poly(vinyl acetate) and showed little or no concentration dependence up to solvent weight fractions of 0.025.

Kishimoto's observations on the diffusion of water in poly(vinyl acetate) agree with those of Long and Thompson [L3] who also studied the sorption and desorption of water in poly(vinyl acetate) at temperatures above and below T_g of the pure polymer. They found the diffusion coefficient to be independent of concentration up to solvent weight fractions of 0.04. Kokes and Long [K4,K5] have studied the sorption and desorption of a variety of organic solvents in poly(vinyl acetate). The diffusion of methanol, propyl chloride, allyl chloride, propylamine, isopropylamine and carbon tetrachloride was studied at 40 °C. The diffusion

of acetone, benzene and 1-propanol was studied at 30, 40 and 50 °C. All of the solvents showed a strong increase in the rate of diffusion with increasing concentration. Acetone, benzene and 1-propanol show an increase in the rate of diffusion with temperature. Kokes and Long conclude that the magnitude of the rate of diffusion into poly(vinyl acetate) is markedly influenced by the size and shape of the penetrant molecules but does not appear to depend strongly on the chemical nature of the penetrant.

Hansen [H1] has studied the sorption and desorption of methanol, chlorobenzene, ethylene glycol monomethyl ether, and cyclohexanone in poly(vinyl acetate) at 25 °C. He found the diffusion coefficients of these four organic solvents in poly(vinyl acetate) to vary exponentially with concentration at low solvent weight fractions. Hansen presents a method to "correct" diffusion coefficients which are strongly concentration dependent yet determined from experimental data using solutions to the diffusion equation which assume a constant diffusion coefficient. He also concludes that the molecular size and shape of the solvent are far more important in determining the magnitude of the diffusivity than the hydrogen- or polar-bonding tendencies of the solvent.

Finally, Meares [M2] has studied the steady-state permeation of allyl chloride in poly(vinyl acetate) at 40 °C. The diffusion coefficients determined from the permeation data disagree with those of Kokes and Long [K5]

although both sets of data extrapolate to the same diffusivity in the limit of zero solvent concentration. Meares concludes that transient and steady-state determinations of diffusion in polymers agree when there is no polymer swelling but that, at finite concentrations of the diffusing penetrant, the polymer chains do not have time to reach an equilibrium state during the transient-state experiments resulting in a higher value of the diffusion coefficient.

Vapor-liquid equilibrium data has been obtained for poly(vinyl acetate) and a variety of organic solvents. Newman and Prausnitz [N4] have determined infinite dilution weight fraction activity coefficients from gas-liquid chromatography. Fourteen organic solvents in poly(vinyl acetate) were studied at temperatures ranging from 100 to 200 °C. Kokes, et al. [K4] have determined Flory-Huggins interaction parameters from equilibrium sorption of organic vapors in thin films of poly(vinyl acetate). Seven organic solvents were studied at temperatures ranging from 30 to 50 °C. Thompson and Long [T2] have determined the variation of χ for the water-poly(vinyl acetate) system with concentration at 40 °C. Katchman and McLaren [K1] have also studied the sorption of water vapor by poly(vinyl acetate). Vrentas, et al. [V13] have tabulated constant χ values for tetrahydrofuran, toluene and chloroform in poly(vinyl acetate) and their deviations over the temperature and concentration intervals studied. Nakajima,

et al. [N1] have determined activity coefficients of benzene and vinyl acetate in poly(vinyl acetate) at 30 °C for the complete range of concentrations. Bonner and Prausnitz [B6] have measured the activity coefficient of isooctane in poly(vinyl acetate) at 100 °C using sorption and desorption techniques.

The experimental conditions of the sorption studies listed above are summarized in Table 2.2 including solvent, poly(vinyl acetate) molecular weight, solvent concentration and temperature.

Table 2.2 Previous Sorption Studies of Poly(vinyl Acetate)

<u>Solvent</u>	<u>MW(PVAc)</u>	<u>Temperature(°C)</u>
acetone	170,000 ^c	30,40,50
allyl chloride	170,000 ^c	40
	---	40
benzene	170,000 ^c	30,40,50
	560, 1660 ^d	30
	331,400 ^{a,£}	100-200
n-butyl acetate	331,400 ^{a,£}	125-200
n-butyl-alcohol	331,400 ^{a,£}	125-200
carbon tetrachloride	170,000 ^c	40
cellusolve solvent	331,400 ^{a,£}	125-200
chlorobenzene	--	25
chloroform	440,000 ^a	35,45
	331,400 ^{a,£}	100-200
cyclohexanone	--	25
	331,400 ^{a,£}	125-200
1,2-dichloroethane	331,400 ^{a,£}	100-200
ethyl acetate	331,400 ^{a,£}	125-200
ethylene glycol	--	25
monomethyl ether		
isooctane	83,400 ^{a,£}	110
isopropyl alcohol	331,400 ^{a,£}	125-200
isopropyl amine	170,000 ^c	40
methanol	350,000 ^c	40
	--	25
	99,000 ^c	15-65
methyl cellusolve	331,400 ^{a,£}	125-200
methyl ethyl ketone	331,400 ^{a,£}	125-200
methyl isobutyl ketone	331,400 ^{a,£}	125-200
1-propanol	170,000 ^c	40
propylamine	170,000 ^c	40
propylchloride	170,000 ^c	40
tetrahydrofuran	440,000 ^a	42.6
toluene	440,000 ^a	35,40,47.5
	331,400 ^{a,£}	100-200
vinyl acetate	1,660 ^d	30
	331,400 ^{a,£}	125-200
water	350,000 ^c	40
	--	25
	83,000 ^b	5-60
	170,000 ^c	22-60
	--	40

Table 2.2 (cont'd)

<u>Solvent Concentration</u>	<u>χ</u>	<u>Ω_1^∞</u>	<u>D^g</u>	<u>a^h</u>	<u>Ref.</u>
0.0-0.19 ^e	0.32-0.38	--	x	x	K4,K6
0.0-0.10 ^f	0.27	--	x	x	K4,K5
0.0-0.09 ^e	--	--	x		M2
0.0-0.15 ^e	0.26-0.36	--	x	x	K4,K5
0.0-1.00	0.24-0.55	--		x	N1
inf. dil.	--	5.56-6.19		x	N4
inf. dil.	--	6.55-7.25		x	N4
inf. dil ^f	--	5.86-7.13		x	N4
0.0-0.12 ^f	--	--	x		K5
inf. dil ^e	--	5.84-6.29		x	N4
0.0-0.28 ^f	--	--	x		H1
0.0-0.50 ^f	-0.44	--	x	x	J1
inf. dil ^e	--	1.84-2.56		x	N4
0.0-0.29 ^e	--	--	x		H1
inf. dil	--	4.58-4.75		x	N4
inf. dil	--	2.68-3.46		x	N4
inf. dil ^e	--	5.78-6.21		x	N4
0.0-0.18 ^e	--	--	x		
0.0-0.16 ^f	--	--		x	B6
inf. dil	--	6.60-8.02		x	N4
0.0-0.13 ^e	0.66	--	x	x	K4,K5
0.0-0.07 ^f	--	--	x		F4
0.0-0.11 ^e	--	--	x		H1
0.0-0.15 ^f	1.07-1.19	--	x		K3
inf. dil	--	6.20-6.46		x	N4
inf. dil	--	6.38-6.50		x	N4
inf. dil ^e	--	8.22-8.62		x	N4
0.0-0.09 ^e	1.04-1.30	--	x	x	K4,K5
0.0-0.12 ^e	0.59	--	x	x	K4,K5
0.0-0.07 ^e	0.75	--	x	x	K4,K5
0.0-0.12 ^f	0.63	--	x	x	J1
0.0-0.20 ^f	0.78	--	x	x	J1
inf. dil	--	6.40-6.78		x	N4
0.0-1.00	0.09-0.51	--		x	N1
inf. dil ^f	--	5.45-6.47		x	N4
0.0-0.05 ^f	--	--	x		F4
0.0-0.05 ^f	--	--		x	K1
0.0-0.03 ^f	--	--	x		K2
0.0-0.025 ^f	--	--	x		L3
0.0-0.070 ^f	2.0-3.0	--		x	T1

Table 2.2 cont'd)

NOTE: a = weight-average molecular weight, $\bar{M}_w$
 b = number-average molecular weight, $\bar{M}_n$
 c = viscosity-average molecular weight, $\bar{M}_v$
 d = degree of polymerization, DP
 e = volume fraction, ϕ_1
 f = weight fraction, w_1
 g = diffusivity data included
 h = activity data included

$$a, \text{E} = \bar{M}_n = 83,350$$

$$a, \text{F} = \bar{M}_n = 33,100$$

inf. dil = infinite dilution

CHAPTER 3

Experimental Procedure

3.1 Microbalance Polymer Diffusion Apparatus

A schematic diagram of the microbalance polymer diffusion apparatus used for experimentation is shown in Figure 3.1. The weight of the polymer sample is continuously monitored by a Cahn 2000 electrobalance of 1 or 2.5-gram capacity, a 0.1-gram sensitivity and an accuracy of $\pm 0.1\%$ of the output recorder range. The weighing unit may be operated under a variety of environments such as vacuum, flowing gas or atmospheric conditions.

The microbalance operates by a process of taring. Weights to be measured are counterbalanced on the opposite side of a balance beam with tare weights. If the sample gains or loses weight, the balance beam rotates so that an opaque flag on one end of the beam uncovers part of a photocell thereby causing an increase in photocell current (see Figure 3.2). The photocell current is amplified and sent to the coil of a torque motor which rebalances the beam. The coil voltage is a direct measure of the force due to the sample weight. The DC output voltage from the microbalance control unit is linear in the measured weight to within 0.025% of full scale. Variations in light

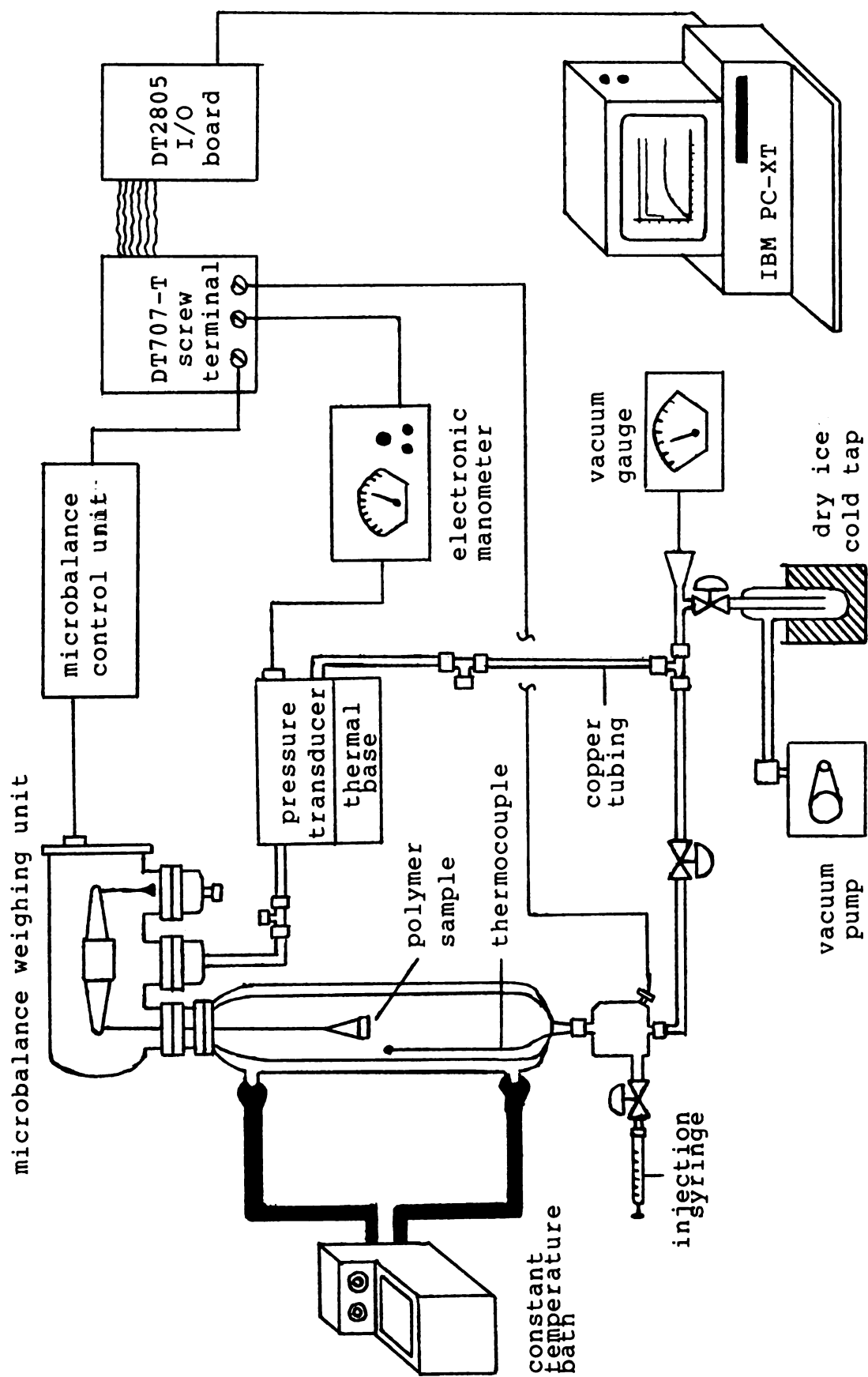


Figure 3.1 Microbalance Polymer Diffusion Apparatus

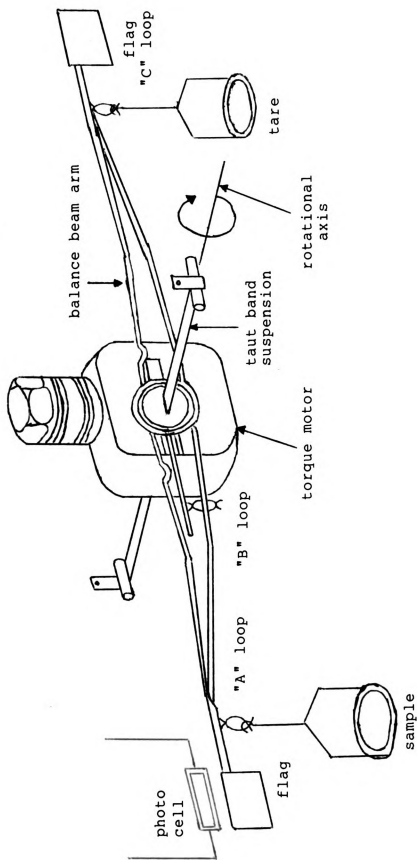


Figure 3.2 Microbalance

intensity around the microbalance which can affect the microbalance operation are minimized by an infrared light placed above the microbalance weighing unit. The infrared heat lamp also serves to maintain the temperature of the weighing unit above room temperature.

The temperature inside the weighing unit is monitored with a small thermometer placed inside the glass jar. The polymer sample temperature is maintained by circulating hot water or oil from a Haake constant temperature bath around the outside of a jacketed glass tube attached to the weighing unit. A constant temperature can be maintained to within $\pm 0.5^{\circ}\text{C}$. An iron-constantan thermocouple placed in the sorption chamber near the polymer sample is used to measure temperature. The DC output voltage of the thermocouple was calibrated using a digital multimeter.

The system pressure is measured with a Datametrix Type 570 Barocel pressure sensor capable of measuring absolute pressure from 0 to 1000 torr. The pressure sensor is mounted on a thermal base which maintains a constant ambient temperature to minimize zero shift in the transducer. A Datametrix 1173 electronic manometer is used to obtain pressure readings. The meter has a DC voltage output which is linear in pressure and was calibrated using a mercury manometer. The manometer has an accuracy of $\pm 0.05\%$ of the reading $\pm 0.01\%$ of the transducer range.

The analog DC voltage signals from the thermocouple,

electronic manometer and microbalance are monitored at specified time intervals by an IBM PC-XT Personal Computer. The detection devices are connected to the computer through a Data Translation DT707-T screw terminal with a thermocouple cold-junction compensation (CJC) circuit. When the wires from a measurement thermocouple are connected to the screw terminal, a second cold-junction thermocouple of opposite electrical polarity is formed which reduces the signal of the measurement thermocouple. This cold-junction thermocouple is referenced to the ambient temperature of the screw terminal which can vary over time. The CJC circuit provides a means to determine the temperature of the DT707-T board allowing compensation for the cold-junction thermocouple formed. Variations in the ambient temperature are minimized in an air-conditioned laboratory.

The analog voltage signals are converted to digital signals by a Data Translation DT2805 analog and digital I/O board compatible with the IBM Personal Computer. The DT2805 board has a 12-bit resolution ($\pm 0.025\%$ of the channel input range) and is capable of handling eight analog inputs with bipolar input ranges of ± 10 V, ± 1 V, ± 100 mV or ± 20 mV depending on the programmable gain setting. The Data Translation PCLAB software package designed for use with the DT2805 board is used for the analog to digital conversion. The DT2805 board and the CJC circuit were calibrated according to the procedures given

in the Data Translation DT2801 Series User Manual.

The data acquisition program written for the IBM PC-XT is shown in Appendix A. The program prompts the user for the datafile name in which the time, temperature, pressure and weight readings are to be stored, the time interval between successive readings and the number of readings to be taken for that time interval. This time interval can be changed at a preset time twice during any experimental run. The program also asks for the input millivolt ranges for the temperature, pressure and weight readings so that the data can be properly plotted on the computer screen and asks for the starting points of the three plots on the computer screen.

The input channels on the DT2805 board to be used and the proper gains for each voltage are internally set in the program. The thermocouple and microbalance have output voltages in the 0-20 mV range and employ a gain of 500. The manometer has an output voltage in the 0-1 V range and employs a gain of 10.

Initiation of the compiled program sets off an internal clock. At the specified time interval, the program calls an analog input routine from the PCLAB software package which performs a single analog to digital conversion on the specified channel. One hundred successive readings are averaged and the next channel is sampled. The data points are then plotted and printed on the computer screen along with the corresponding time.

3.2 Polymer Sample Preparation

The polymer used in this study was poly(vinyl acetate) purchased from Aldrich Chemical Company. The poly(vinyl acetate) had a weight average molecular weight of 194,800 and a number average molecular weight of 63,600 as determined by light scattering in methyl ethyl ketone and gel permeation chromatography using chloroform, respectively.

The polymer samples used for the sorption experiments are thin, annealed films of poly(vinyl acetate) with an exact surface area. The polymer films are made using a hydraulic jack and platens heated by hot water from a temperature bath. The bead form of the polymer is placed between the platens that have been covered with aluminum foil, along with metal shims which act as spacers between the pressing plates to achieve the desired film thickness. The platens are heated to 90 °C (60 °C in excess of poly(vinyl acetate)'s glass transition temperature) for a period of 30 minutes. The soft polymer is then subjected to a normal stress of approximately 24,000 psi and is allowed to anneal at the elevated temperature for a period of 8 hours. The platens are then cooled to room temperature with tap water while the polymer film is still under pressure.

The resulting polymer film is then removed from the press and small samples are cut out using a circular steel punch. The aluminum foil is removed from one side of the polymer film exposing the surface through which solvent

diffusion will occur. The foil is kept on the second side of the polymer film to support the polymer in its molten state at the experimental temperatures. The adhesion of the polymer film to the foil permits analysis of the diffusion as unidirectional into the film. Three small holes are drilled into each polymer sample to attach it to the hangdown wire of the microbalance with a thin piece of wire. The thickness of each polymer sample is measured with a micrometer accurate to ± 0.00025 cm. The sample thickness can also be checked knowing the sample weight, polymer density and sample surface area. The prepared polymer samples are stored under vacuum at room temperature until they are ready to be used.

The solvents used are reagent grade. Those chosen for the sorption studies in poly(vinyl acetate) were chloroform, acetone, toluene, methanol and water. Chloroform exhibits negative enthalpic interactions with poly(vinyl acetate) having a Ω_1^∞ value of 1.5 - 2.0 in the temperature range of 50 to 130 °C. Acetone shows little enthalpic interactions with poly(vinyl acetate) having a Ω_1^∞ value near 6 at temperatures near 50 °C. Toluene shows slightly positive enthalpic interactions with poly(vinyl acetate) having a Ω_1^∞ value of 6.5 - 9 in the temperature range of 50 to 130 °C. Methanol shows moderately strong positive enthalpic interactions with poly(vinyl acetate) having a Ω_1^∞ value of 9 - 12.5 in the same temperature range. Finally water shows very strong positive enthalpic interactions with poly(vinyl acetate) having a Ω_1^∞ value

exceeding 50. All five solvents have reasonable low boiling points so as to have fairly high vapor pressures in the 50 to 130 °C temperature range to be studied.

3.3 Operating Procedures

To begin each sorption experiment, the microbalance, infrared heat lamp, electronic manometer, pressure transducer and thermal base are turned on and allowed adequate time for warmup. A polymer sample is attached to the hangdown chain of the microbalance and adequate tare weights are added to balance the sample. The DC output voltage of the microbalance is calibrated once a week according to the procedure described in the Cahn 2000 Electrobalance Instruction Manual. The vacuum sorption chamber is then assembled, sealed and evacuated using an oil diffusion and mechanical pump. The polymer sample is degassed for a period of several hours under a vacuum of 0.5 mm Hg to desorb any water vapor picked up during assembly of the diffusion apparatus. The temperature bath is set at the desired experimental temperature and hot water (or ethylene glycol) is circulated around the outside of the glass sorption chamber. To remove the baseline drift of the microbalance and the pressure transducer and to insure thermal equilibrium of the sample, the system temperature is maintained steadily for at least one hour. A heating tape is wrapped around the solvent entry line to prevent any condensation of the solvent.

The temperature in the line is kept approximately 5 to 10 °C higher than the sorption chamber temperature. The appropriate amount of solvent to achieve the desired system pressure is loaded into the injection micro-syringe.

Just before starting each experiment, zero adjustments of the microbalance and pressure transducer are made. To start the experiment, the vapor valve is opened and the solvent is injected into the vacuum chamber. The data acquisition computer program is initiated and the weight change of the polymer sample, the vapor pressure of the solvent and the temperature of the sorption chamber are recorded automatically at the specified time interval. The pressure, temperature and weight change are continuously plotted versus time on the computer screen.

Each sorption experiment at a given temperature consists of a series of constant pressure runs, with each run having a higher pressure than the succeeding one. The system temperature cannot be changed during a particular sorption experiment because the voltage signal from the microbalance changes with temperature thus distorting the zero voltage signal. After the polymer sample reaches equilibrium with respect to a given solvent vapor pressure, the increased weight of the polymer sample due to the absorbed solvent is suppressed at the microbalance control unit to bring the relative weight back to zero. The computer program is reset and a step change in vapor pressure is introduced to initiate the succeeding run.

3.4 Limitations of the Microbalance Apparatus

The polymer diffusion apparatus shown in Figure 3.1 and discussed in section 3.1 is similar to an automatically controlled system used by Vrentas and Duda and their students and proved ineffective in measuring the sorption of organic vapors into polymer samples suspended from the microbalance. The design of the apparatus limits the solvent concentration range in the polymer that can be studied at higher temperatures. Exposure of organic solvents to the microbalance components in the weighing unit was detrimental to the operation of the microbalance. The polymer sample preparation, along with the size of the polymer sample required for use with the microbalance also posed experimental problems.

For proper operation, the microbalance weighing unit must be kept at temperatures below 50 °C. Thus the solvent pressure in the sorption chamber is limited to the solvent vapor pressure at 50 °C to prevent solvent condensation on the electronic and balance components in the electrobalance weighing unit. At high temperatures for solvents with large activity coefficients, the solvent concentration range achievable in the polymer sample is severely restricted.

Severe experimental difficulties arose while using chloroform as the solvent in the sorption chamber. Unexpected sorption curves indicated the polymer sample to be losing weight after exposure to the chloroform vapor.

Figure 3.3 illustrates this behavior. Initially the polymer sample slowly gains weight for approximately 15 minutes and then rapidly loses weight. After approximately 30 minutes of weight loss, the microbalance was knocked disrupting the weight reading and a vacuum is pulled on the sorption chamber.

Due to this unexplainable sorption behavior, the sorption experiment was repeated without a polymer sample being suspended from the microbalance. The resulting sorption and desorption curves shown in Figure 3.4 resemble the mirror image of the sorption and desorption curves expected for a polymer sample. Further investigation revealed the chloroform vapors diffusing into the glue which bonds the hangdown wires and aluminum flags to the balance beam. An unequal distribution of the glue on each side of the balance beam caused unequal amounts of chloroform to be absorbed on each side of the beam. The tare side of the balance beam gained more weight than the sample side resulting in an apparent weight loss on the sample side. An attempt to repeatedly reproduce these sorption and desorption curves and thus "subtract" them from actual sorption curves with a polymer sample proved unsuccessful. The chloroform vapors eventually absorbed into the coatings on the electrical wires in the weighing unit which damaged the microbalance.

Slight difficulties were also encountered with the polymer samples as prepared according to the procedures

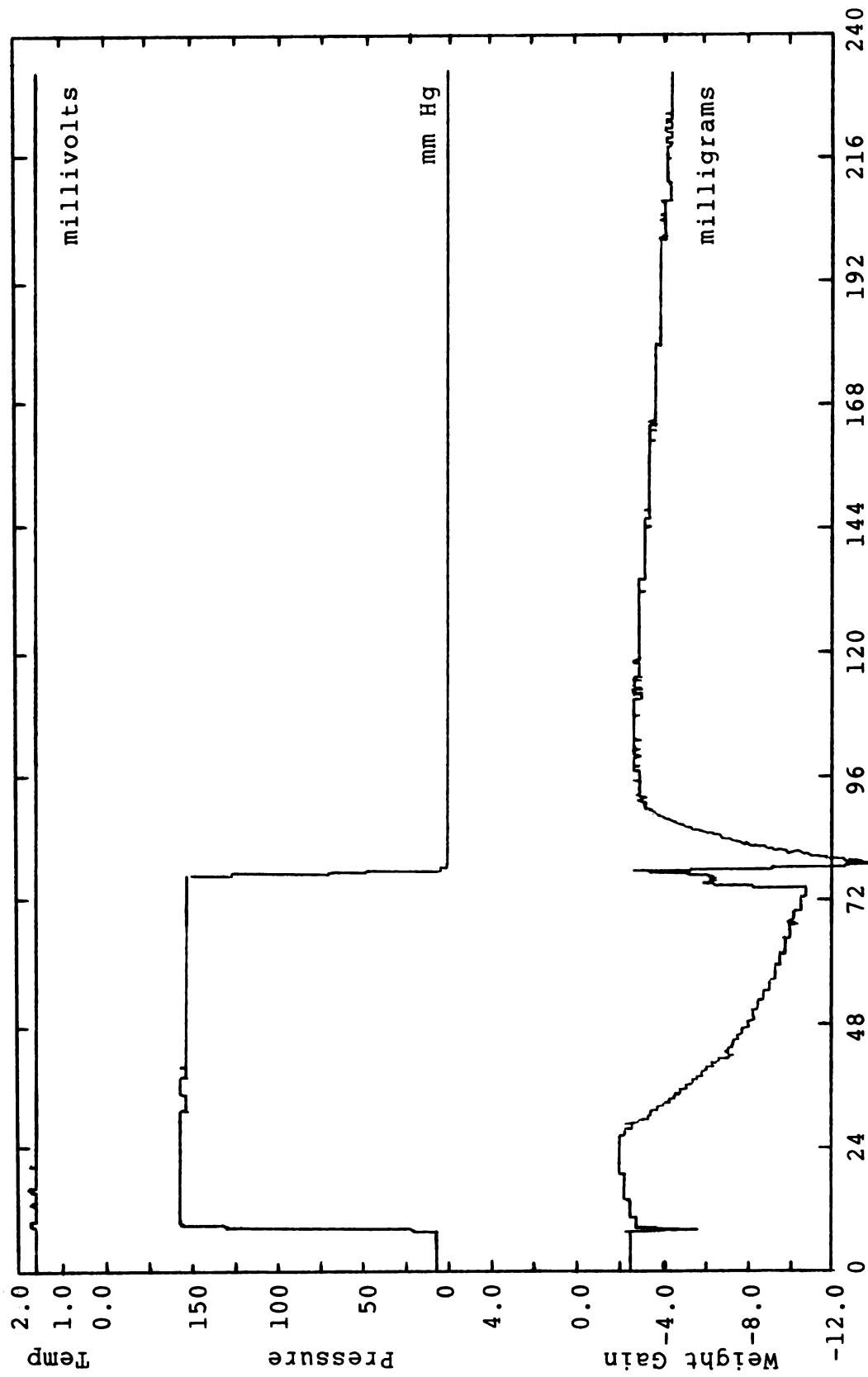


Figure 3.3 Sorption and Desorption of Chloroform by Poly(vinyl Acetate) at 70 °C.

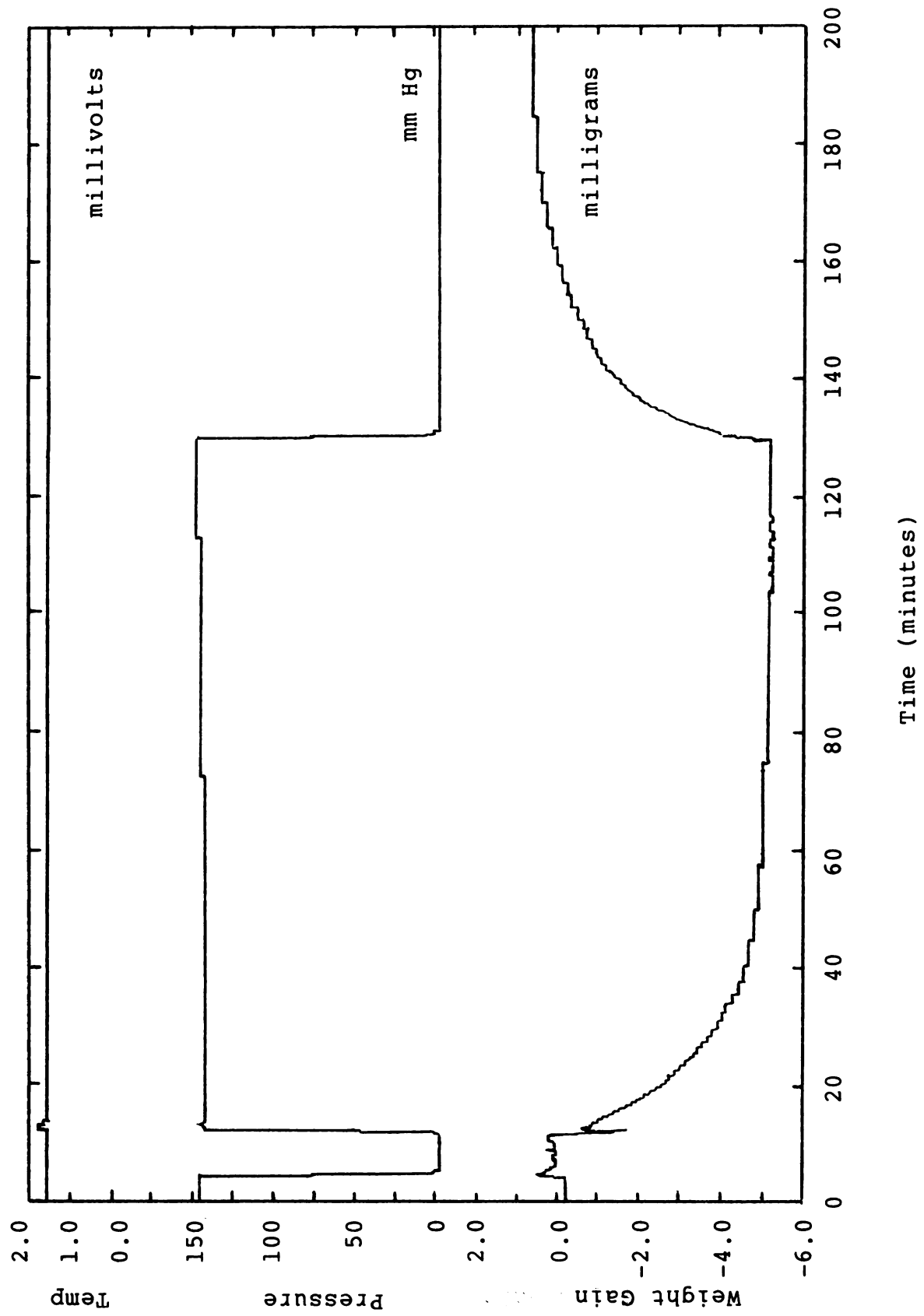


Figure 3.4 Sorption Experiment Using Chloroform without a Polymer Sample

given in Section 3.2. A flat sturdy surface for the molten polymer films was difficult to maintain with the aluminum foil backings which were not strong enough to support the weight of the polymer sample evenly. Consequently the molten polymer often flowed to the lowest side of the aluminum foil base as it hung from the microbalance.

It should be noted that the interfacing of the IBM PC-XT Personal Computer to the thermocouple, pressure transducer and microbalance for continuous data acquisition was extremely helpful in troubleshooting the polymer diffusion apparatus and analyzing results. The function of the system designed as shown in Figure 3.1 is severely limited by the exposure of the solvent to the microbalance components. Isolating the microbalance weighing unit from the sorption chamber, possibly with a nitrogen purge stream, can eliminate this problem. However, it is uncertain what the solvent concentration at the polymer surface will be using this technique. Additional difficulties are encountered with the small polymer samples required for use with the microbalance. At high temperatures, thick polymer samples are necessary for the solvent diffusion to occur over a time period long enough to collect data for a sorption curve.

On the basis of these difficulties, a new experimental system to measure the diffusion of solvents in polymer films at high temperatures and high or low pressures is proposed in Chapter 5.

CHAPTER 4

Analysis of Free Volume Diffusion Theories

The diffusivity predictions of the free volume theory of Vrentas and Duda can be greatly affected by the methods used to determine several of the theory parameters including ξ , D_0 and E_A . Also, the choice of the thermodynamic model used in conjunction with the free volume theory influences the model predictions. The Flory-Huggins thermodynamic model uses a constant value of χ which actually varies with temperature and concentration in most polymer-solvent systems. The ASOG-VSP thermodynamic model uses a constant value of Ω_1^∞ which varies with temperature but is independent of concentration. The value of Ω_1^∞ can be determined by a variety of experimental and calculational procedures. The effects of these factors are analyzed in the subsequent discussion.

4.1 Effect of Jumping Unit Ratio on Diffusivity Predictions

Vrentas and Duda propose two methods of determining the value of the jumping unit ratio, ξ , as described in Section 2.1-2. The latter method involving equation (20) can result in significant errors in the estimation of diffusion coefficients. Figures 4.1 and 4.2 show the

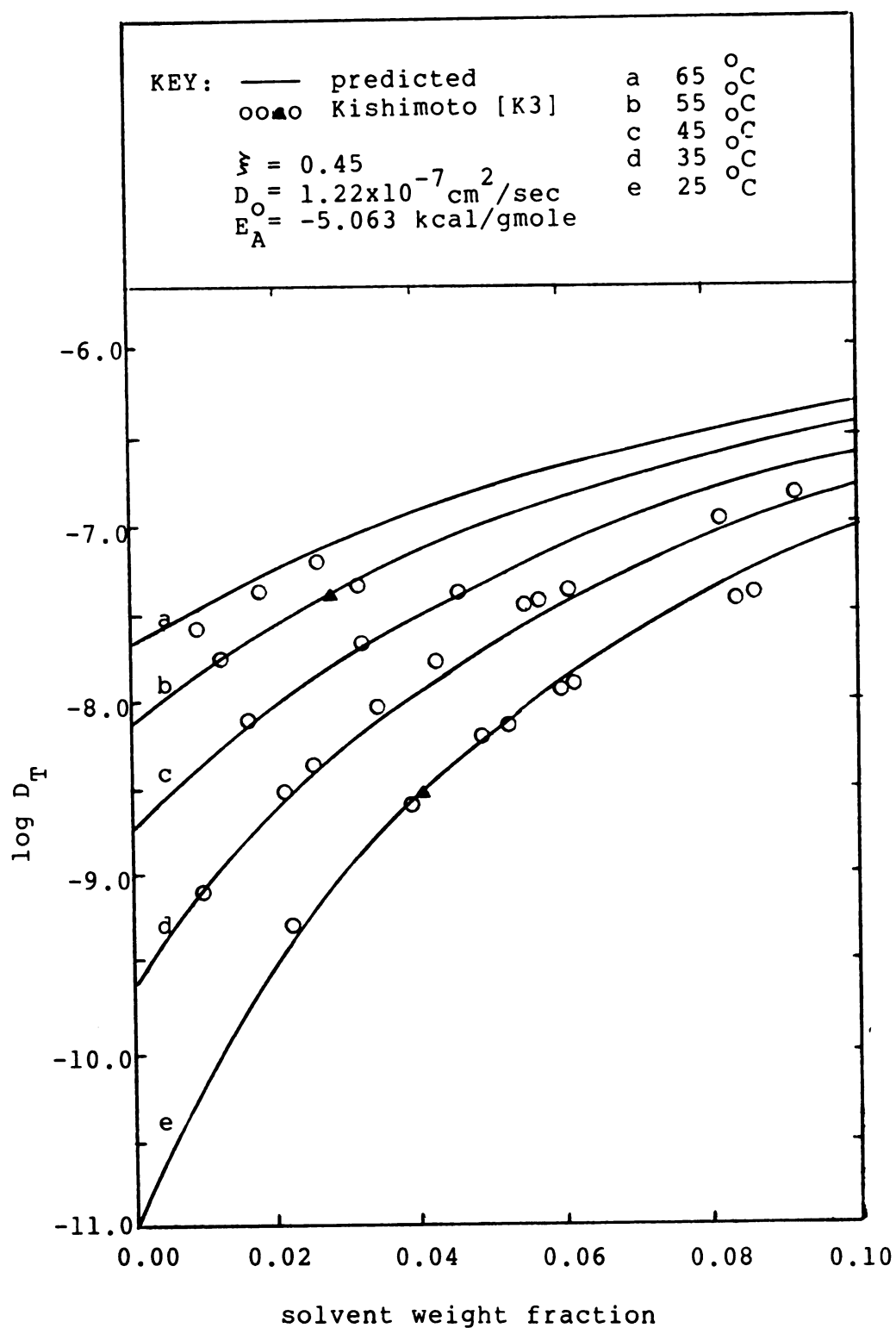


Figure 4.1 Predicted Thermodynamic Diffusion Coefficient for Methanol-Poly(vinyl Acetate) Using $\xi = 0.45$

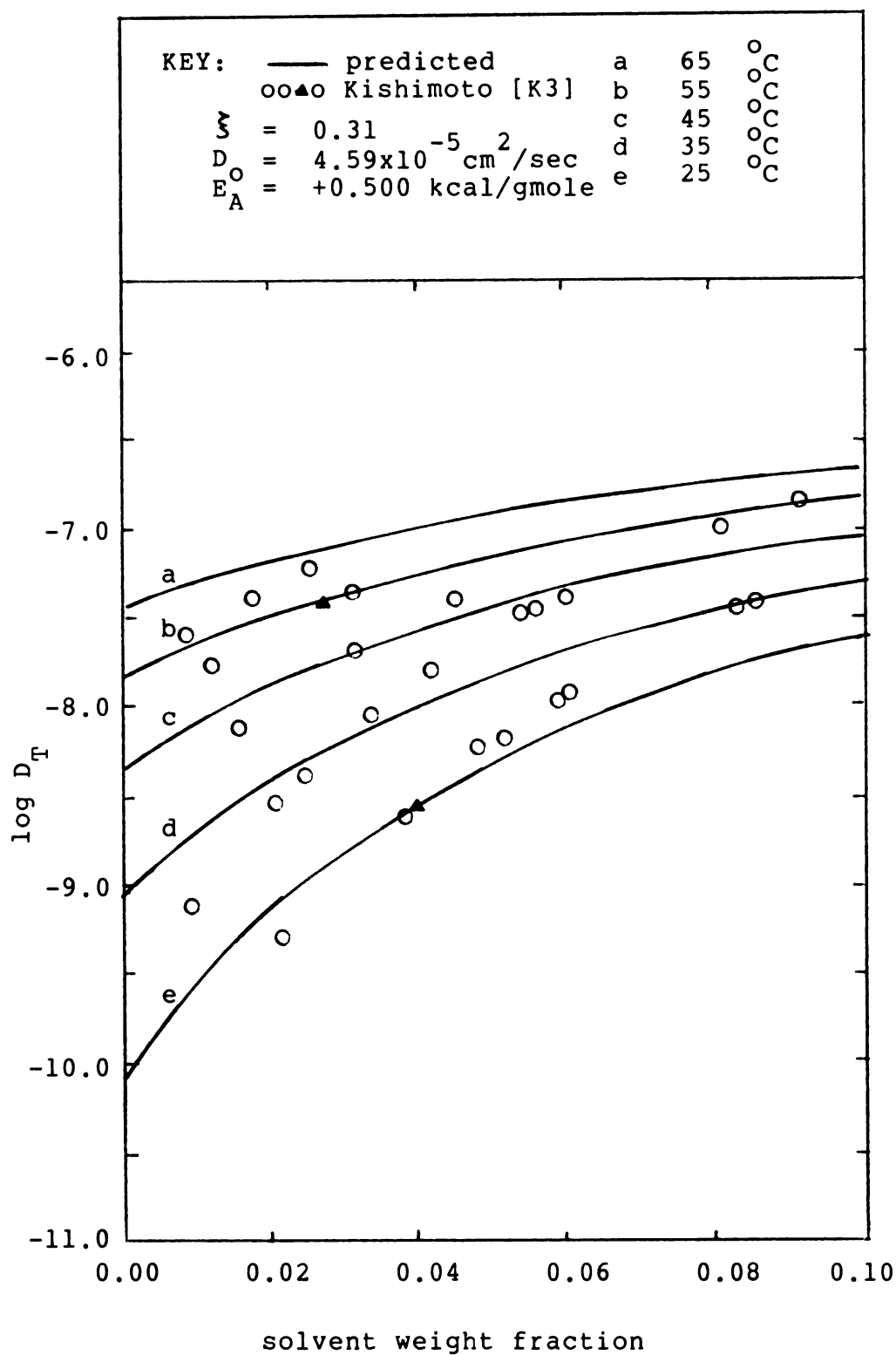


Figure 4.2 Predicted Thermodynamic Diffusion Coefficient for Methanol-Poly(vinyl Acetate) Using $\xi = 0.31$

differences in the estimated thermodynamic diffusion coefficients of methanol in poly(vinyl acetate) with two different values of ξ . The ξ value of 0.45 in Figure 4.1 was used by Ju, et al. [J3] in testing the predictive capabilities of the free volume theory of Vrentas and Duda. This ξ value was determined by Ju by solving equations (2), (3), (4), (6), (10) and (11) using three diffusivity data points at two different temperatures. The ξ value of 0.31 used in Figure 4.2 was calculated using equation (20) and diffusivity data of toluene and chloroform in poly(vinyl acetate). Both of these systems have been successfully described using the free volume theory of Vrentas and Duda [J1]. The entire molecule for all three solvents, toluene, chloroform and methanol, is expected to jump in the transport process. The ξ and $\tilde{V}_1^*$ data used for the methanol ξ calculation are summarized in Table 4.1.

Table 4.1 ξ and $\tilde{V}_1^*$ Data for Methanol ξ Calculation [J1]

<u>solvent</u>	<u>ξ</u>	<u>$\tilde{V}_1^*$ (cm³/gmole)</u>
toluene	0.86	84.4
chloroform	0.64	60.9
methanol	--	30.8

methanol $\xi = 0.31$ using toluene data and equation (20)

methanol $\xi = 0.32$ using chloroform data and equation (20)

Ju, et al. [J2] also report a linear variation of $\xi \hat{V}_2^*/K_{12}$ with the molar volume of a solvent jumping unit at 0 K for several polymers including poly(vinyl acetate).

$$\xi \hat{V}_2^*/K_{12} = (17.2 \text{ kgmole/cm}^3) \tilde{V}_1^0(0 \text{ K}) \quad (49)$$

Equation (49) is the result of a least-squares fit to $\hat{V}_2^*/K_{12}$ versus $\tilde{V}_1^0(0 \text{ K})$ data determined from actual diffusivity-temperature data for 12 solvents in poly(vinyl acetate). Using equation (47) and a $\hat{V}_2^*/K_{12}$ value for poly(vinyl acetate) of $5.94 \times 10^{-4} \text{ K}^{-1}$ as reported by Ju [J1], a ξ value of 0.31 is obtained.

The values of D_0 and E_A in each figure were calculated using the actual diffusivity data points from Kishimoto's diffusivity curve marked by solid triangles along with equations (2), (3), (4), (6), (10) and (11) for each value of ξ . For $\xi = 0.45$ the calculated D_0 and E_A values of $1.22 \times 10^{-7} \text{ cm}^2/\text{sec}$ and $-5.063 \text{ kcal/gmole}$, respectively, are different from those reported by Ju, et al. [J2] of $1.99 \times 10^{-7} \text{ cm}^2/\text{sec}$ and $+4.800 \text{ kcal/gmole}$, respectively. However, the reported E_A value of $+4.800 \text{ kcal/gmole}$ appears to be incorrectly stated and should be $-4.800 \text{ kcal/gmole}$ in order to generate the predicted diffusivity curve shown by Ju. For $\xi = 0.31$ the calculated D_0 and E_A values are $4.59 \times 10^{-5} \text{ cm}^2/\text{sec}$ and $+0.500 \text{ kcal/gmole}$, respectively.

The curves in Figure 4.1 are a good match to actual diffusivity curves presented by Kishimoto [K3]. The predicted diffusivity values in Figure 4.2 using a ξ value of 0.31 differ from those in Figure 4.1 using a ξ value of 0.45 by up to a factor of 10.

The above analysis seems to indicate that the ξ , D_0 and E_A parameters have less of a physical significance

than proposed by the theory, or an alternative method of determining these parameters is needed. They appear to be best determined by fitting a curve to as much actual diffusivity data as possible, however unique values of these parameters are not necessary for a particular polymer-solvent system. Figure 4.3 shows the diffusivity curves for two different sets of these parameters used by Ju [J1,J3] in modeling the chloroform-poly(vinyl acetate) system at 35 and 45 °C. The ξ , D_0 and E_A values in the first set of parameters are 0.65, 3.90 cm²/sec and 6.850 kcal/gmole, respectively. The second set of parameters are 0.65, 27.7 cm²/sec and 8.070 kcal/gmole, respectively. The curves are essentially identical at these temperatures. The distinction between the two curves will become more noticeable at higher temperatures due to the 20% difference in the activation energies.

In summary, it appears that the determination of the value of the jumping unit ratio is critical to the performance of the free volume theory in predicting binary mutual diffusion coefficients for polymer-solvent systems. The ξ value is best determined in conjunction with D_0 and E_A using as much actual diffusivity data as possible rather than being determined independent of D_0 and E_A . Predicting ξ for a particular polymer-solvent system using ξ data for other solvents in that polymer can result in significant errors in the diffusivity predictions. However, fitting diffusivity data

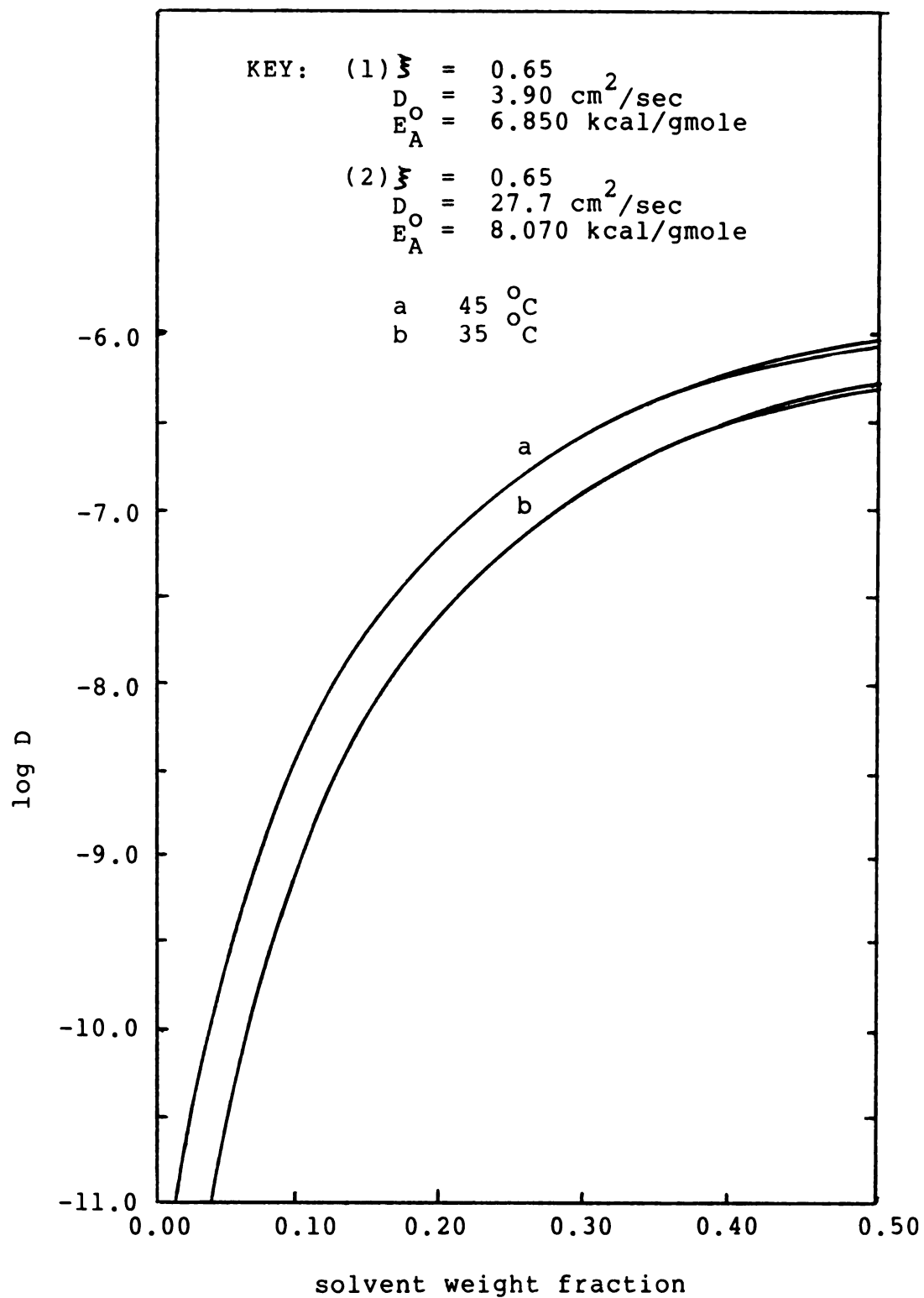


Figure 4.3 Predicted Diffusivity Data for Chloroform-Poly(vinyl Acetate) with Two Sets of ξ , D_0 and E_A Parameters

raises questions as to the actual physical significance of these parameters especially when different unique sets of parameters can result in the same predictions.

4.2 Determination of Infinite Dilution Solvent Weight Fraction Activity Coefficient

The infinite dilution weight fraction activity coefficient, Ω_1^∞ , can be determined experimentally from gas-liquid partition chromatography or calculated from a Flory-Huggins interaction parameter as discussed in Section 2.2. When either of these two methods are not available, Ω_1^∞ can be obtained from a single physical measurement of equilibrium solubility of a trace of solvent in pure polymer using equation (45) and an iterative calculation procedure as described in Appendix B. The accuracy of this method can be very questionable however, since only one experimental data point is used and slight errors in measured activity coefficients, especially at higher weight fractions, can lead to significant deviations in Ω_1^∞ . This fact is illustrated in Figures 4.4 - 4.6 by the wide variation in curves a and b for Ω_1^∞ values determined from two different vapor-liquid equilibrium data points marked by solid triangles for three solvents, toluene, benzene and chloroform, in poly(vinyl acetate). The choice of the vapor-liquid equilibrium data point to use in the Ω_1^∞ calculation is critical if only one data point is used as indicated by the relative error for each curve in Figures

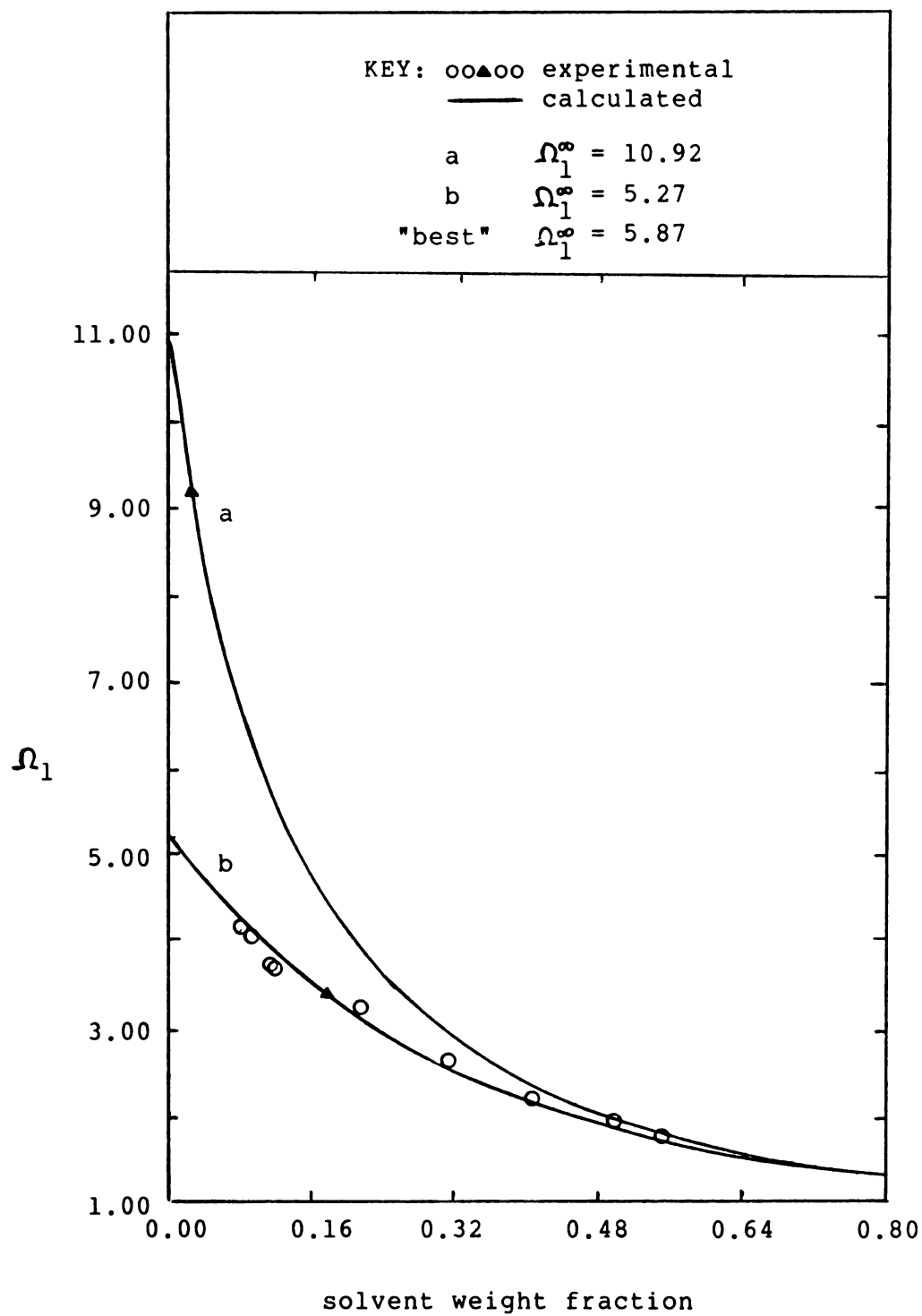


Figure 4.4 Predicted Solvent Weight Fraction Activity Coefficients for Benzene-Poly(vinyl Acetate) Solutions at 30°C

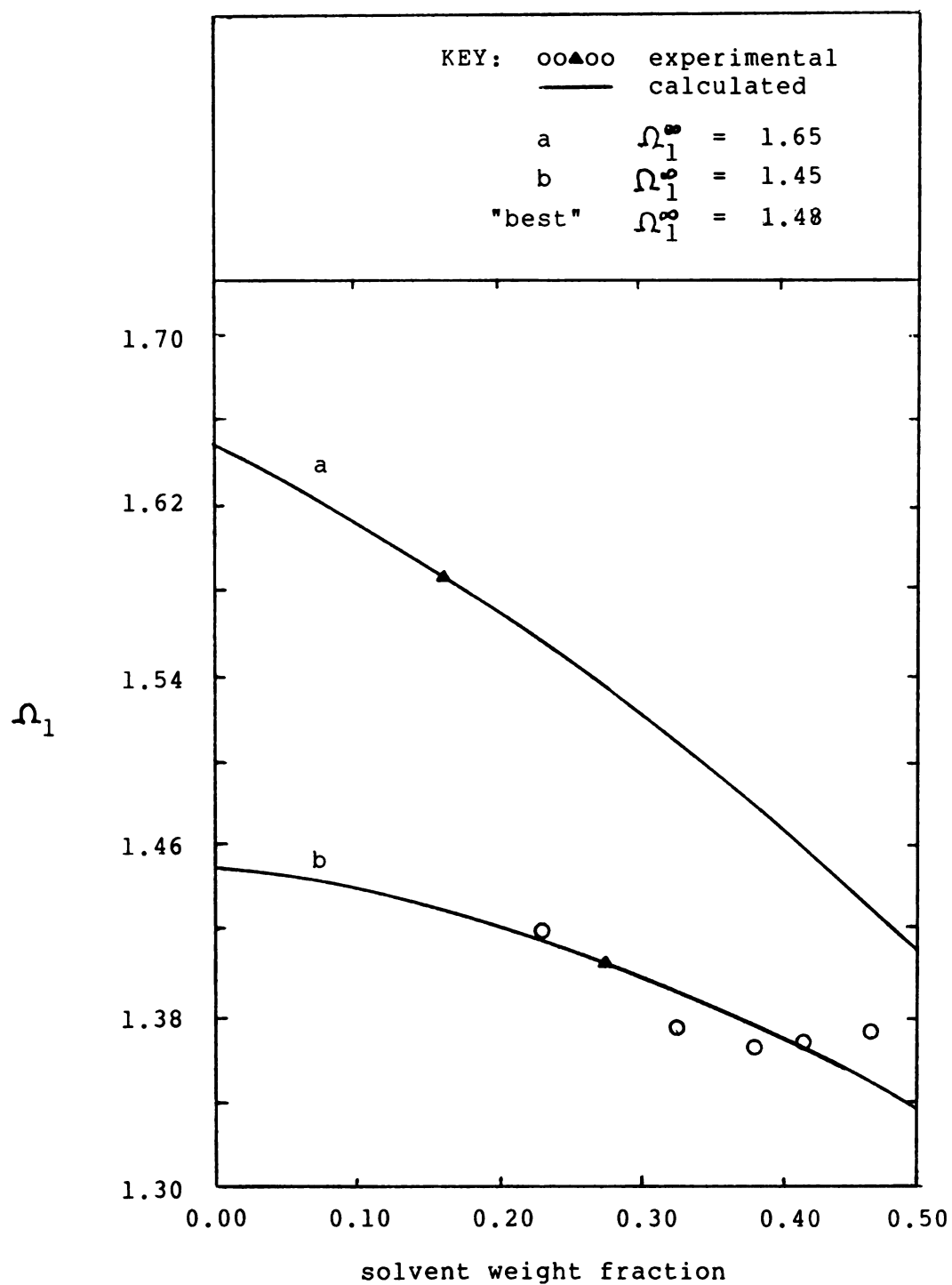


Figure 4.5 Predicted Solvent Weight Fraction Activity Coefficients for Chloroform-Poly(vinyl Acetate) Solutions at 35 °C

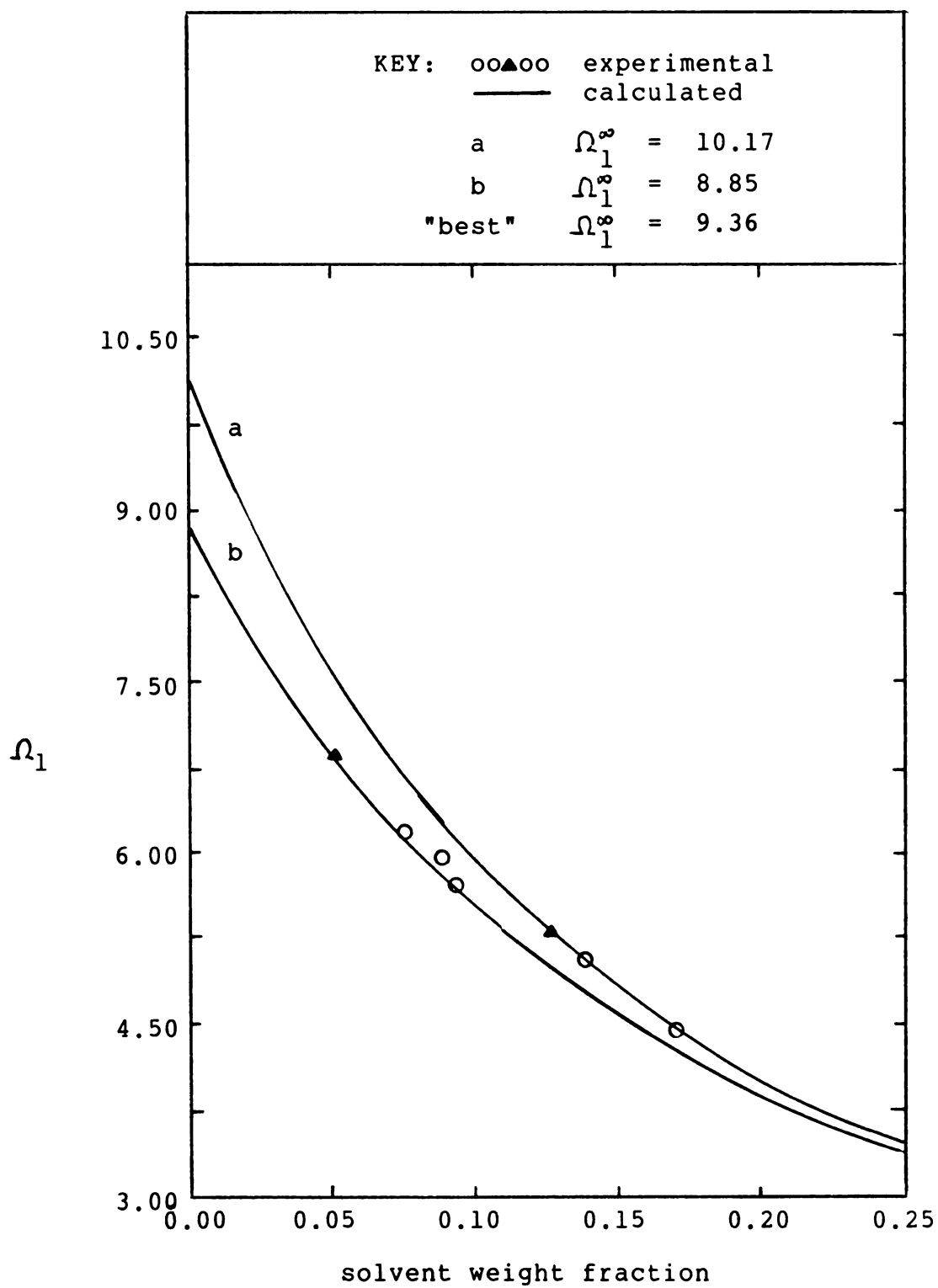


Figure 4.6 Predicted Solvent Weight Fraction Activity Coefficients for Toluene-Poly(vinyl Acetate) Solutions at 40 °C

4.4 - 4.6 shown in Table 4.2. The benzene- and chloroform-poly(vinyl acetate) data appear to have an outlying data point at the lowest solvent weight fraction. It is not clear if these data points are truly in error or if the ASOG-VSP thermodynamic model does not adequately describe these two systems for the concentration ranges shown.

The accuracy of a Ω_1^∞ value based on the ASOG-VSP model can be maximized by fitting the best curve based on equation (45) to as many vapor-liquid equilibrium data points as possible. This technique will minimize the inaccuracies due to outlying method of determining Ω_1^∞ . The Ω_1^∞ value of the best fit to the experimental data for each solvent is given in Table 4.2. The experimental activity data used in Figures 4.4 - 4.6 are given in Table B.1 in Appendix B. Bonner [B7] has compiled a list of polymers for which concentrated solution vapor-liquid equilibrium data are available in the literature. Tables B.2 - B.4 in Appendix B list values of Ω_1^∞ determined using several different procedures for a variety of poly(vinyl acetate)-solvent systems at various temperatures.

4.3 Effect of the Thermodynamic Model on Predictions of the Free Volume Diffusion Theory

4.3.1 Maximum in Diffusivity Curve

For a number of polymer-solvent systems, there is a maximum in the diffusivity as a function of solvent

Table 4.2 Relative Error of Activity Coefficient vs.
Solvent Weight Fraction Curves

<u>Solvent</u>	<u>curve</u>	Ω_1^∞	<u>relative error</u>	<u>absolute error</u>	<u>Temp (°C)</u>
benzene	a	5.27	-4.8%	+7.1%	30
	b	10.92	+27.7%	+27.7%	
	"best"	5.87	-0.01%	+8.9%	
chloroform	a	1.45	-1.5%	+2.1%	35
	b	1.65	+6.7%	+6.7%	
	"best"	1.48	-0.17%	+2.5%	
toluene	a	8.85	-2.9%	+2.9%	40
	b	10.17	+4.3%	+4.4%	
	"best"	9.36	+0.01%	+2.5%	

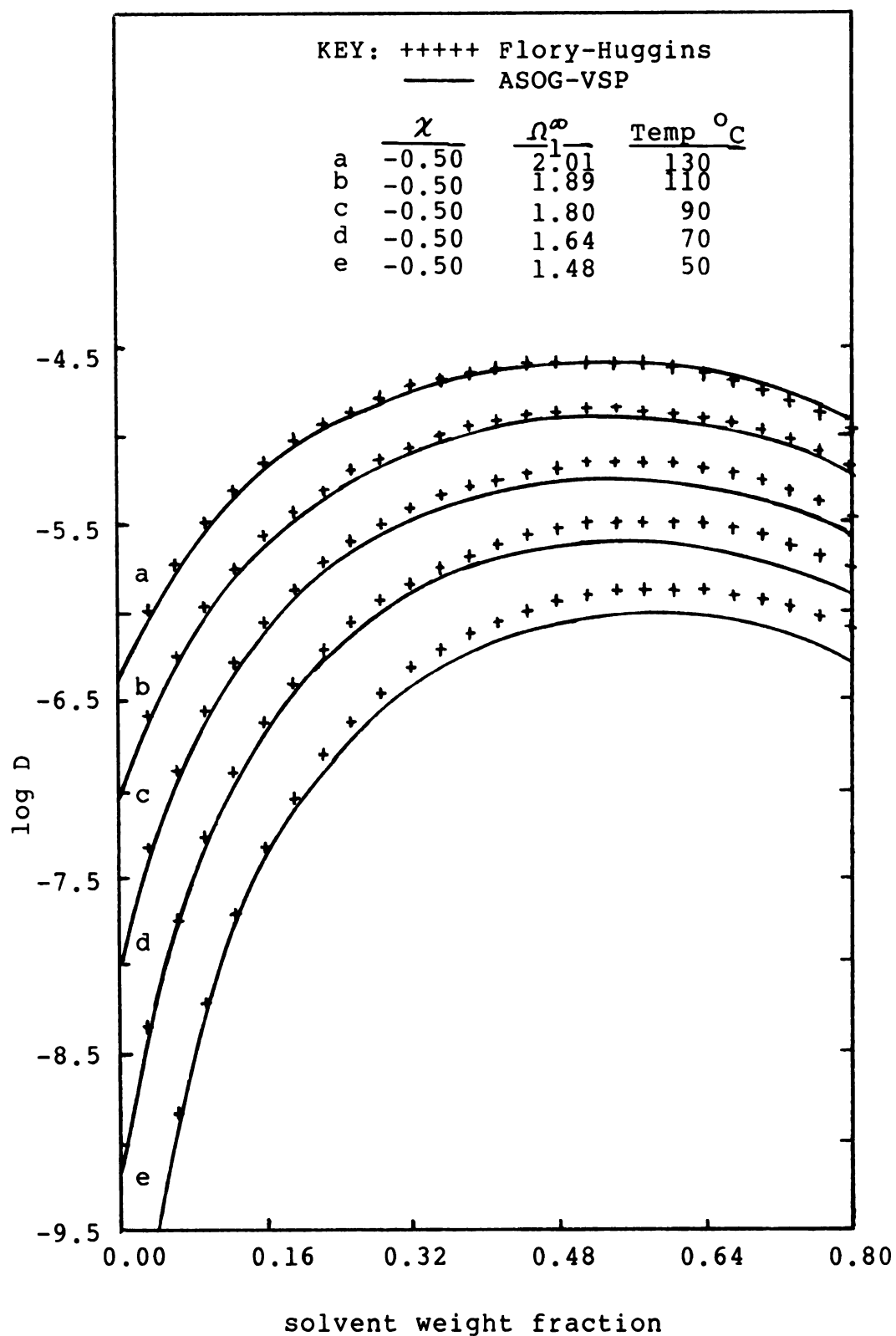


Figure 4.7 Comparison of Flory-Huggins and ASOG-VSP Thermodynamic Models in the Free Volume Diffusion Theory for Chloroform-Poly(vinyl Acetate) Solutions

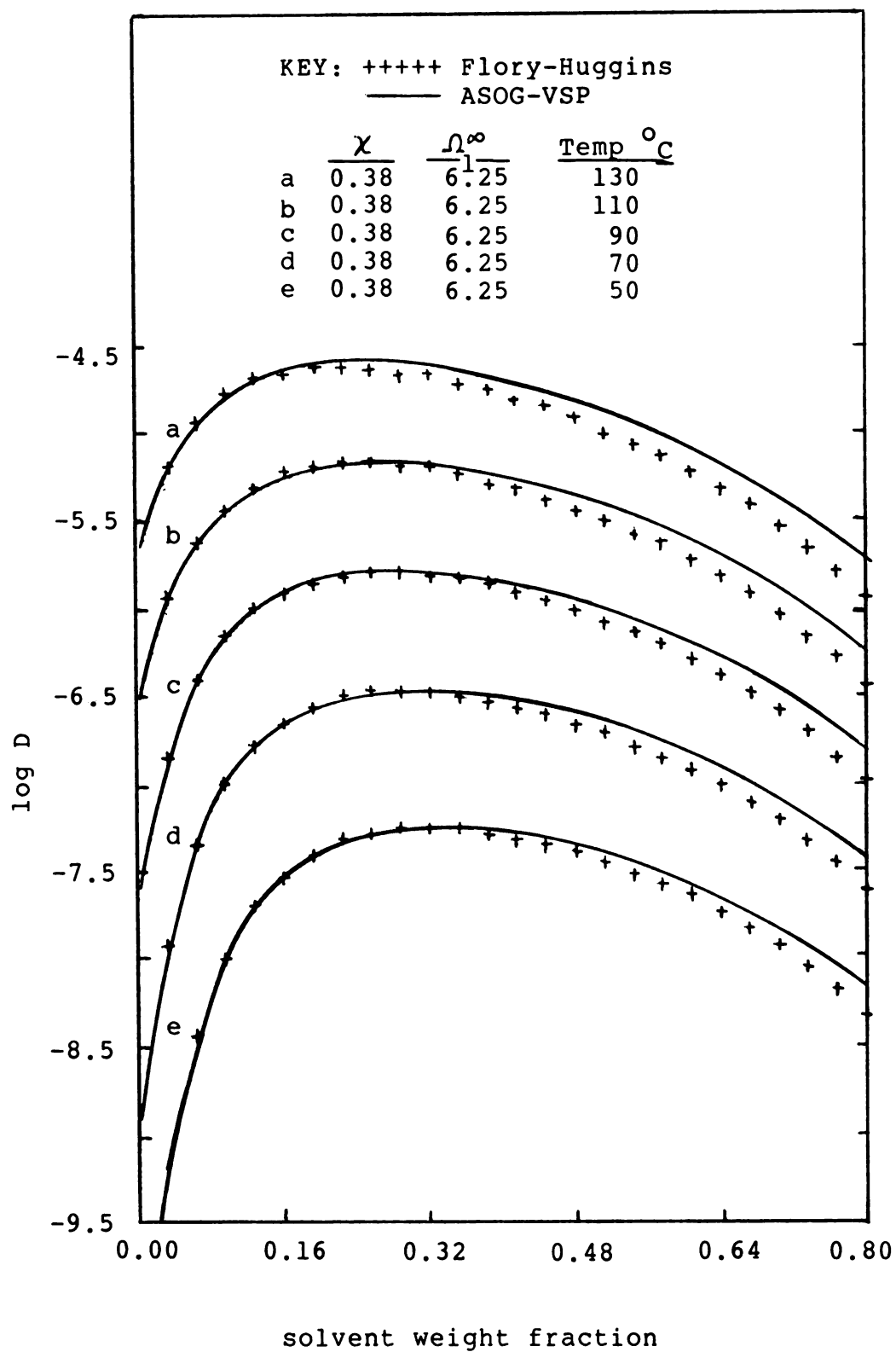


Figure 4.8 Comparison of Flory-Huggins and ASOG-VSP Thermodynamic Models in the Free Volume Diffusion Theory for Acetone-Poly(vinyl Acetate) Solutions

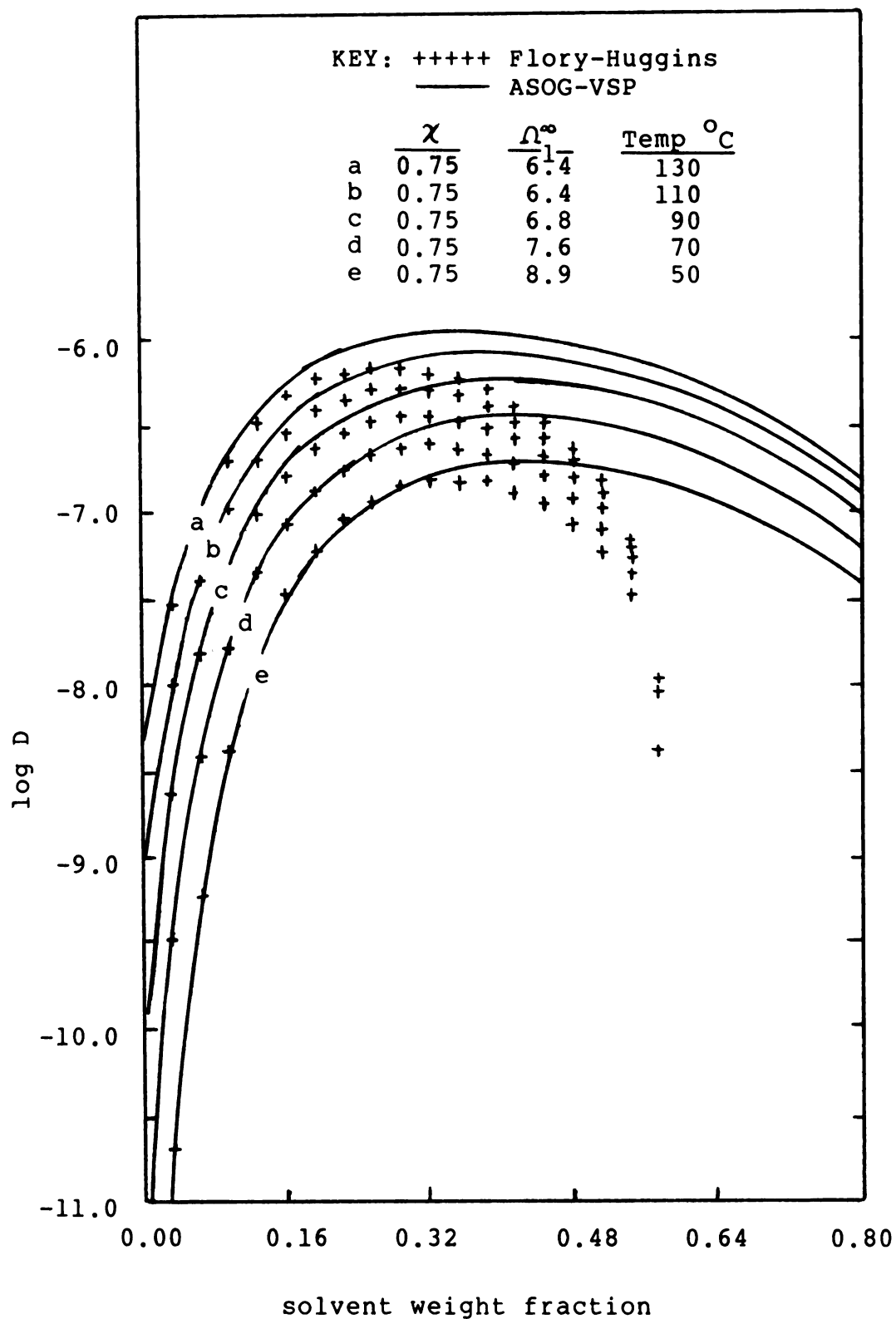


Figure 4.9 Comparison of Flory-Huggins and ASOG-VSP Thermodynamic Models in the Free Volume Diffusion Theory for Toluene-Poly(vinyl Acetate) Solutions

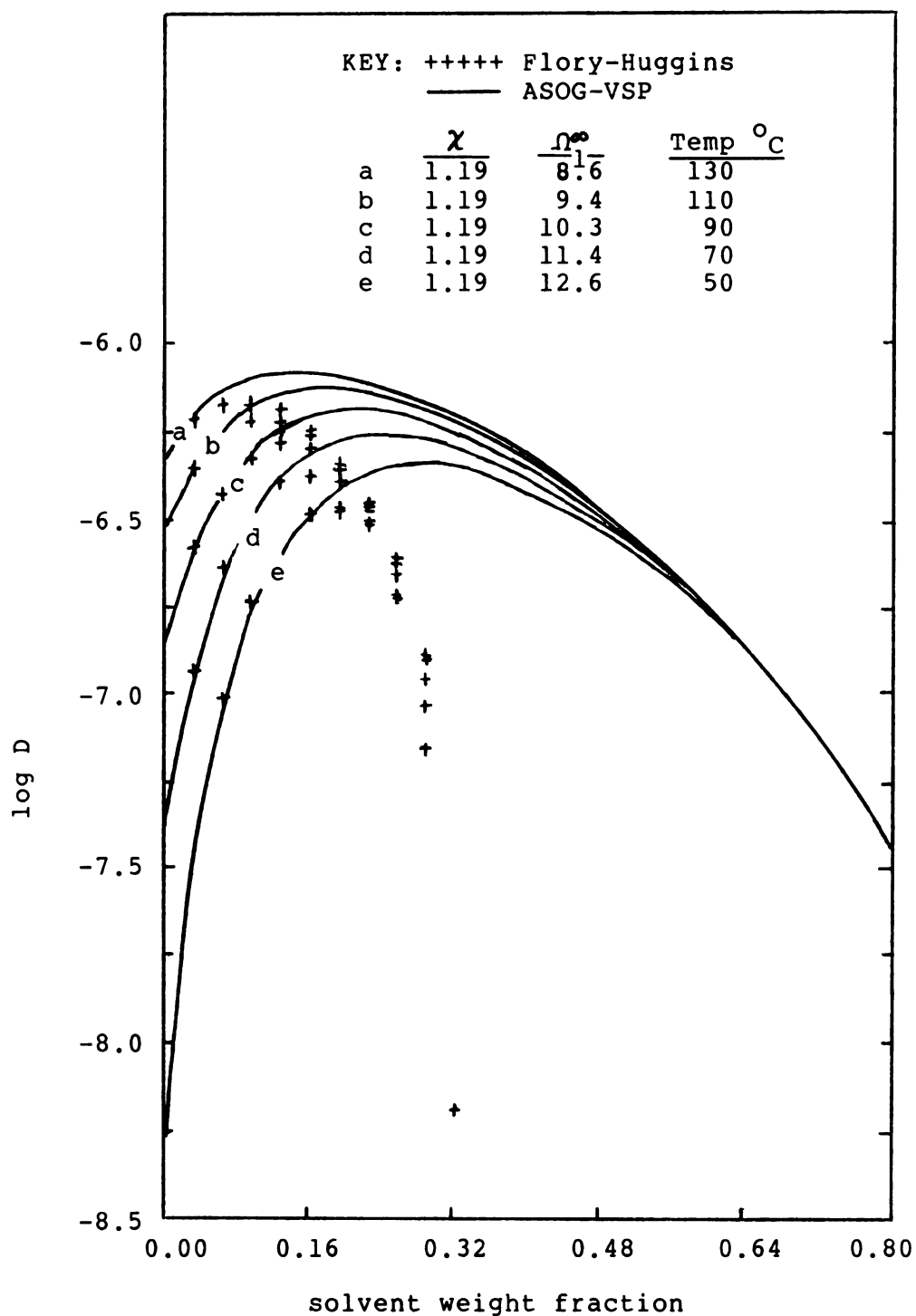


Figure 4.10 Comparison of Flory-Huggins and ASOG-VSP Thermodynamic Models in the Free Volume Diffusion Theory for Methanol-Poly(vinyl Acetate) Solutions

weight fraction. The solvent weight fraction at the maximum is affected by the choice of thermodynamic model and the value of its fitting parameters. The predicted diffusivities of chloroform, acetone, toluene and methanol in poly(vinyl acetate) using the Flory-Huggins and ASOG-VSP thermodynamic models are shown in Figures 4.7 - 4.10 and given in Tables C.1 - C.4 in Appendix C. The diffusion coefficients are calculated for a range of temperatures from 50 to 130 °C using the parameters for the free volume theory given in Table C.5 in Appendix C. The solvent weight fraction at the maximum diffusivity for each solvent and temperature is given in Table 4.3. These maximum diffusivity values were determined by finding the zero in the first derivative of the diffusivity curve as illustrated in Appendix D.

The curves based on the two thermodynamic models are similar in shape for the chloroform- and acetone-poly(vinyl acetate) systems and slightly different in magnitude at high solvent weight fractions. The diffusivity curves for the toluene- and methanol-poly(vinyl acetate) systems show distinct differences at higher solvent concentrations in both the magnitude and the shape of the curve. At this point two generalizations can be made. The deviations between the diffusivity curves predicted using both the Flory-Huggins and ASOG-VSP thermodynamic models increase as the value of χ or Ω_1^∞ increases or as the enthalpic interactions between the polymer and the solvent increase.

Table 4.3 Maxima in Diffusivity vs. Solvent Weight Fraction Curves for Poly(vinyl Acetate) Solutions

<u>Solvent</u>	<u>Temperature ($^{\circ}\text{C}$)</u>	<u>$w_{1,\text{max}}$ (ASOG-VSP)</u>	<u>$w_{1,\text{max}}$ (F-H)</u>
Chloroform	50	0.611	0.603
	70	0.578	0.579
	90	0.546	0.556
	110	0.519	0.533
	130	0.491	0.511
Acetone	50	0.327	0.319
	70	0.301	0.293
	90	0.270	0.267
	110	0.255	0.244
	130	0.234	0.222
Toluene	50	0.424	0.346
	70	0.406	0.325
	90	0.389	0.306
	110	0.372	0.288
	130	0.351	0.270
Methanol	50	0.280	0.186
	70	0.240	0.161
	90	0.206	0.136
	110	0.174	0.110
	130	0.147	0.085

Also, free volume effects on diffusion dominate at temperatures near T_g and thus as the solvent concentration is increased and T_g is lowered, distinctions between the two free volume theories become evident.

By combining the Flory-Huggins and ASOG-VSP thermodynamic models, Misovich, et al. [M3] have developed an expression for the Flory-Huggins interaction parameter in terms of the solvent weight fraction, the infinite dilution solvent weight fraction activity coefficient and the ratio of polymer density to solvent density.

$$\chi = \left[\frac{\rho_2 w_1}{\rho_1 w_2} + 1 \right]^2 \left[\frac{(e/\Omega_1^\infty) w_2}{w_1 + (e/\Omega_1^\infty) w_2} \right] - \left[\frac{\rho_2 w_1}{\rho_1 w_2} + 1 \right] + \left[\frac{\rho_2 w_1}{\rho_1 w_2} + 1 \right] \ln \left[\frac{w_1 + (\rho_1/\rho_2) w_2}{w_1 + (e/\Omega_1^\infty) w_2} \right] \quad (50)$$

Equation (50) gives a functional form for the dependence of χ on solvent weight fraction at constant temperatures as predicted by the ASOG-VSP thermodynamic model. Figure 4.11 shows the predicted dependence of χ on solvent weight fraction for chloroform, acetone, toluene and methanol in poly(vinyl acetate) at 90 °C. These curves can be used to explain the behavior of the predicted diffusivity curves in Figures 4.7 - 4.10 for the four solvents in poly(vinyl acetate). The values of χ for chloroform and acetone in poly(vinyl acetate) remain fairly constant over the concentration range, decreasing slightly with increasing solvent concentration. This behavior is characteristic of athermal polymer-solvent systems which typically have Ω_1^∞

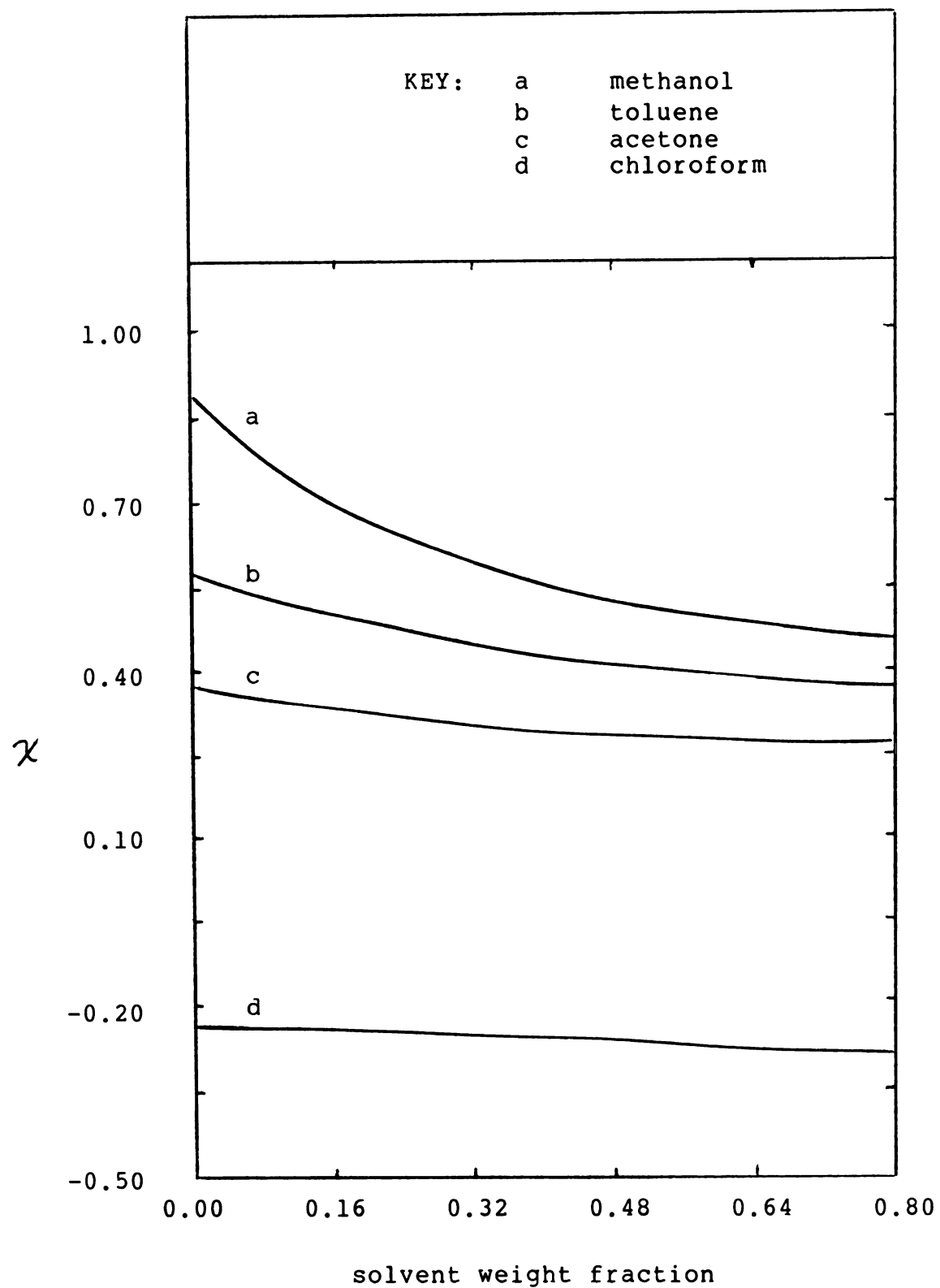


Figure 4.11 Dependence of χ on Solvent Concentration for Poly(vinyl Acetate) Solutions at 90 °C

values in the range 4-6.

The values of χ for toluene in poly(vinyl acetate) show a more marked decrease with increasing solvent concentration and greater differences between the predicted diffusivities of the two thermodynamic models are expected. However, much more extreme differences are seen in Figure 4.9. The χ value of 0.75 obtained from data of Ju [J1] used in Figure 4.9 is much higher than the average χ value near 0.50 predicted from the ASOG-VSP thermodynamic model in Figure 4.11. The χ values calculated in Figure 4.11 are obtained using experimental infinite dilution activity coefficient data at 90 °C while the χ value from Ju is obtained from low temperature (30 - 50 °C) activity data. Thus it appears that χ is not constant with temperature over these temperature ranges. If an average χ value of 0.5 is used to predict the Flory-Huggins free volume diffusion coefficients, the two theories predict much more similar results as shown in Figure 4.12.

The χ values for methanol in poly(vinyl acetate), a system with moderately strong positive enthalpic interactions, decrease rather sharply with increasing solvent concentration. Thus the predicted diffusivities for the two thermodynamic models vary significantly.

It should be noted that the Ω_1^∞ values used in Figure 4.7 - 4.10 are determined in a variety of ways. For chloroform and toluene the Ω_1^∞ values are interpolated

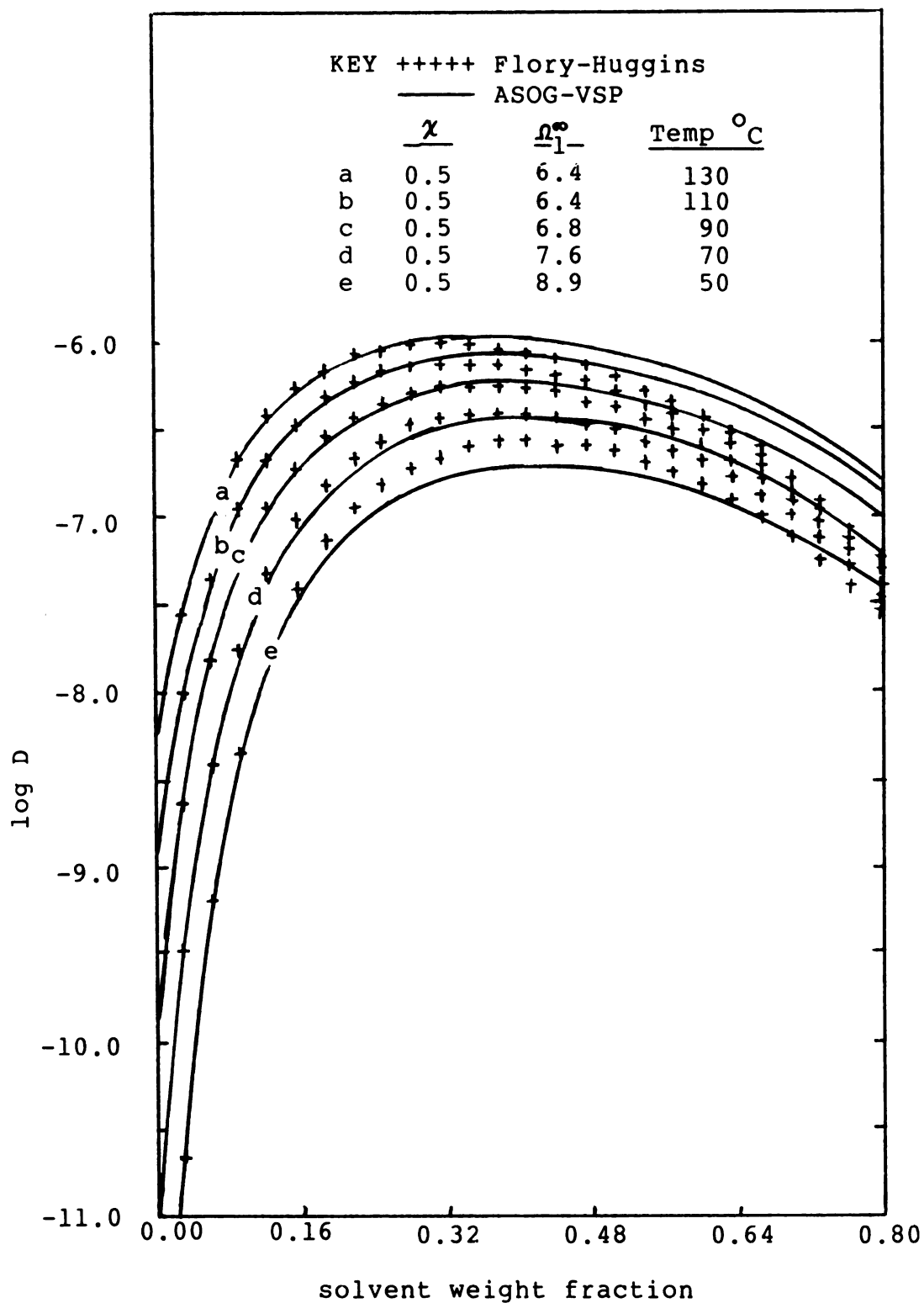


Figure 4.12 Comparison of Flory-Huggins and ASOG-VSP Thermodynamic Models in the Free Volume Diffusion Theory for Toluene-Poly(vinyl Acetate) Solutions with $\chi = 0.5$

from actual infinite dilution activity data at high and low temperatures. For acetone a constant Ω_1^∞ value is used determined from a reported χ value at 50 °C. The temperature variation of Ω_1^∞ for acetone in poly(vinyl acetate) is not known. The Ω_1^∞ data for methanol is estimated from the temperature dependence of propanol-poly(vinyl acetate) data having similar enthalpic interactions. These Ω_1^∞ determinations are discussed in more detail in Appendix C.

The diffusivity curves in Figures 4.9 and 4.10 based on the Flory-Huggins thermodynamic model for the toluene- and methanol-poly(vinyl acetate) systems show negative diffusivity values above a certain solvent weight fraction. Analysis of equation (7), the chemical potential derivative based on the Flory-Huggins thermodynamic model, reveals that the derivative and thus the diffusion coefficient becomes negative at solvent volume fractions exceeding $(1/2\chi)$. This can be seen by setting the derivative equal to zero and solving for ϕ_1 . For values of the interaction parameter greater than 0.50 or for polymer-solvent systems with positive enthalpic interactions, the Flory-Huggins thermodynamic model with a constant value of χ predicts negative diffusivities above a certain solvent weight fraction. For the toluene-poly(vinyl acetate) system where $\chi = 0.75$ and $\rho_2/\rho_1 = 1.42$ and the methanol-poly(vinyl acetate) system where $\chi = 1.19$ and $\rho_2/\rho_1 = 1.57$, the predicted diffusion coefficients become negative at solvent

weight fractions of 0.58 and 0.32, respectively. Thus the Flory-Huggins thermodynamic model with a constant value of χ over the entire concentration range can result in major errors in predicting the binary diffusion coefficient with the prediction of negative diffusivities.

Vrentas and Duda [V5] have stated that their free volume diffusion theory is not valid at low polymer concentrations where the domains of polymer molecules do not overlap. However, for polymer molecular weights of ordinary interest, the free volume theory can be used over at least 80% of the solvent weight fraction range and should predict positive diffusivities over that range. It is clear the the Flory-Huggins thermodynamic model with a constant value of χ cannot adequately describe the thermodynamics of polymer-solvent systems having significant enthalpic interactions. The ASOG-VSP thermodynamic model can describe the thermodynamics of these systems much better and easier than using the Flory-Huggins theory with a concentration-dependent χ .

4.3-2 Influence of the Thermodynamic Parameter on Predicted Diffusion Coefficients

The sensitivity of the diffusivity curves to the values of Ω_1^∞ and χ , the thermodynamic parameters, is shown in Figures 4.13 - 4.20 for four solvents in poly-(vinyl acetate) at 50 and 130 °C. The chloroform-poly(vinyl acetate) system exhibits negative enthalpic

interactions having a Ω_1^∞ value of 1.5 - 2.0 and a χ value near -0.5. The acetone-poly(vinyl acetate) system approaches athermal conditions having an estimated Ω_1^∞ value of 6.25 and a χ value of 0.38. The toluene-poly(vinyl acetate) system exhibits slightly positive enthalpic interactions having a Ω_1^∞ value of 6.4 - 8.9 and a χ value of 0.75. The methanol-poly(vinyl acetate) system exhibits moderately strong positive enthalpic interactions having a Ω_1^∞ value of 8.6 - 12.6 and a χ value of 1.19. The value of Ω_1^∞ influences the magnitude of the diffusion coefficient at higher solvent weight fractions as seen in Figures 4.13 - 4.16. The value of χ influences the predicted diffusion coefficients similarly for chloroform- and acetone-poly(vinyl acetate) systems as seen in Figures 4.17 and 4.18. The effect of χ on the toluene- and methanol-poly(vinyl acetate) systems which exhibit enthalpic interactions is much more extreme as seen in Figures 4.19 and 4.20. The upper and lower bounds on Ω_1^∞ and χ to illustrate the sensitivity of the diffusion coefficient to these parameters were chosen to be $\pm 20\%$.

4.3-3 Linearized Free Volume Diffusion Models

Another distinction between the two thermodynamic models for polymer-solvent systems can be illustrated by observing the diffusivity at low solvent weight fractions where it can be approximated by a linear

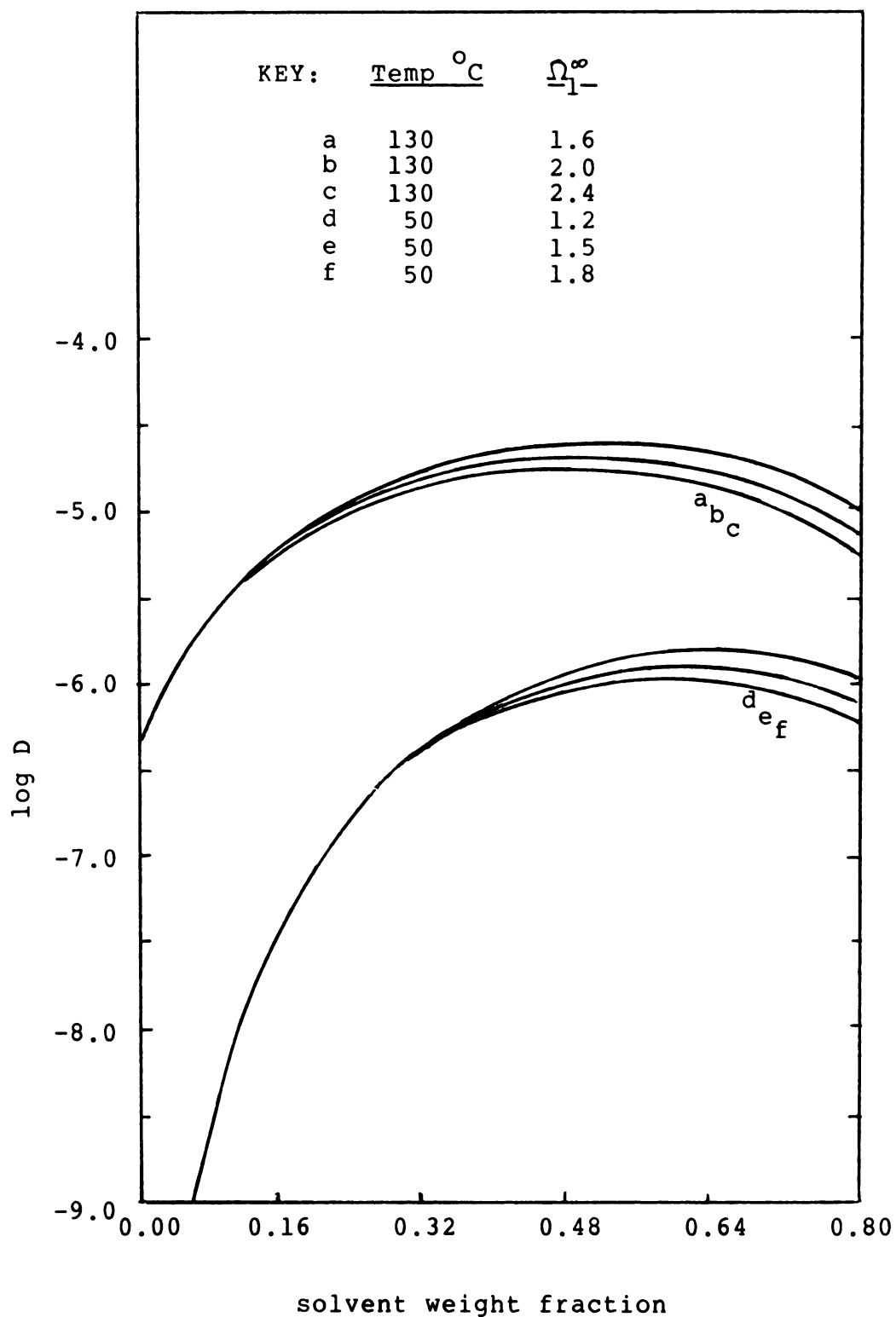


Figure 4.13 Influence of Ω_1^∞ on the Mutual Diffusion Coefficient for Chloroform-Poly(vinyl Acetate) Solutions

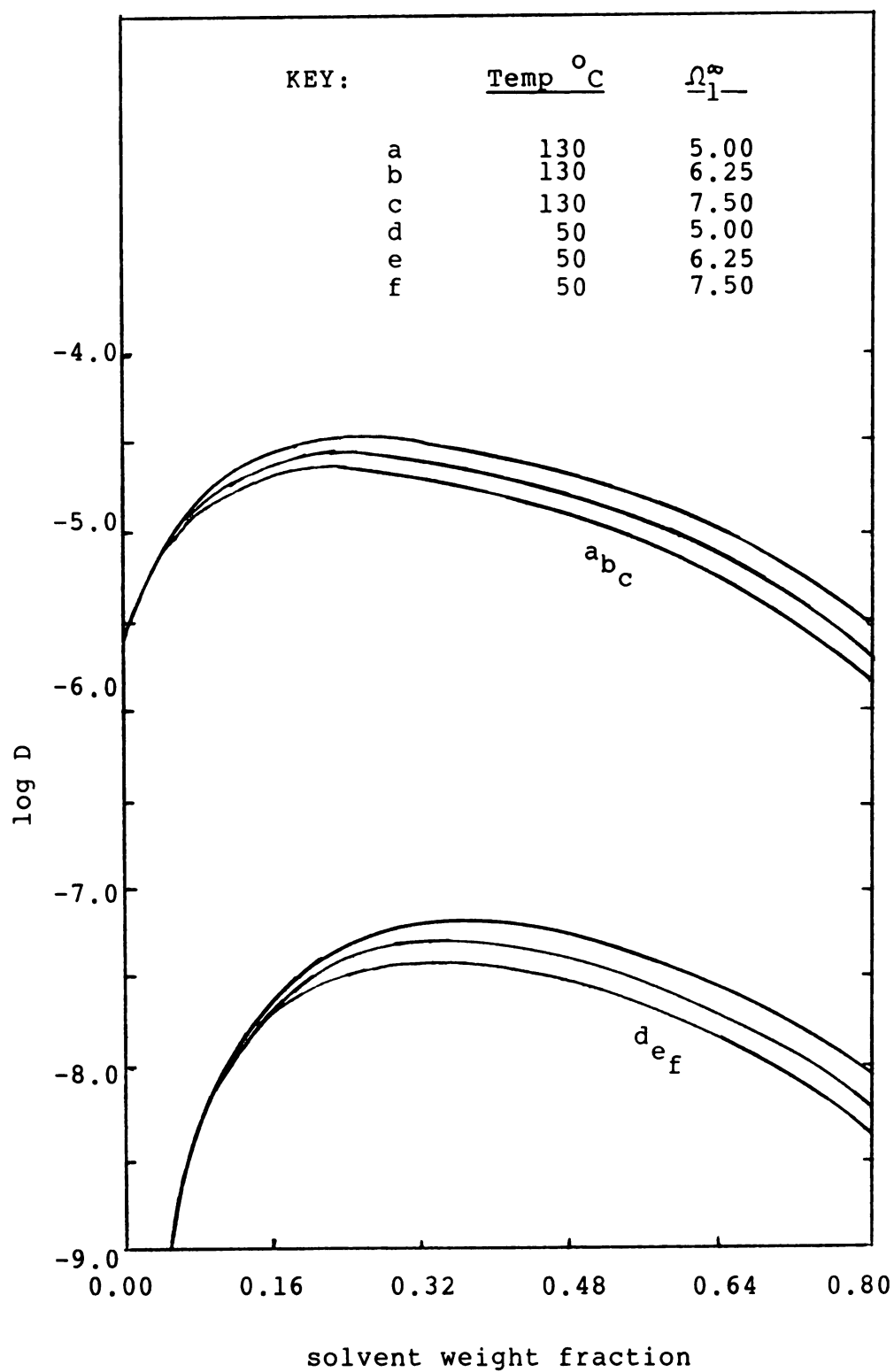


Figure 4.14 Influence of Ω_1^∞ on the Mutual Diffusion Coefficient for Acetone-Poly(vinyl Acetate) Solutions

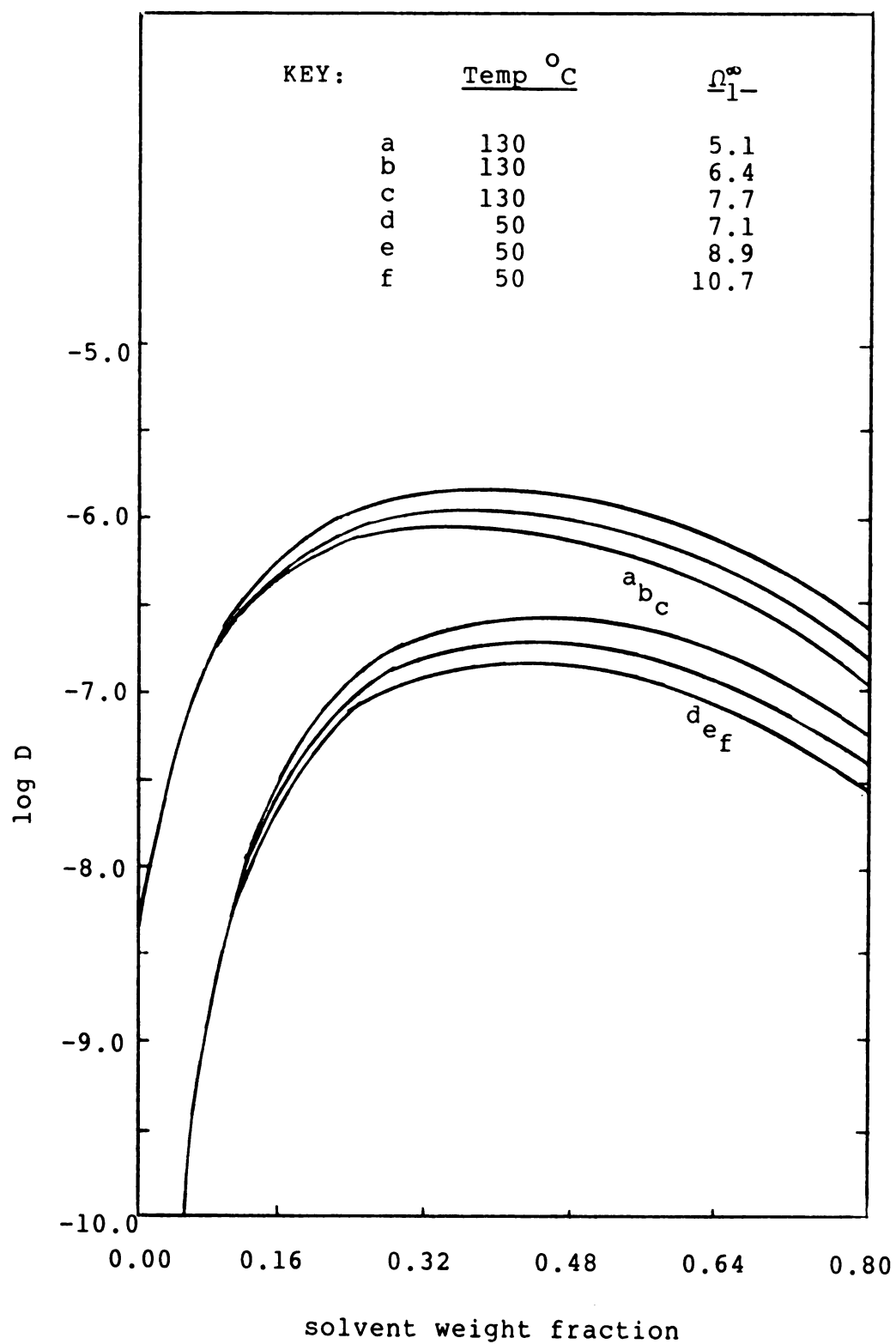


Figure 4.15 Influence of Ω_1^∞ on the Mutual Diffusion Coefficient for Toluene-Poly(vinyl Acetate) Solutions

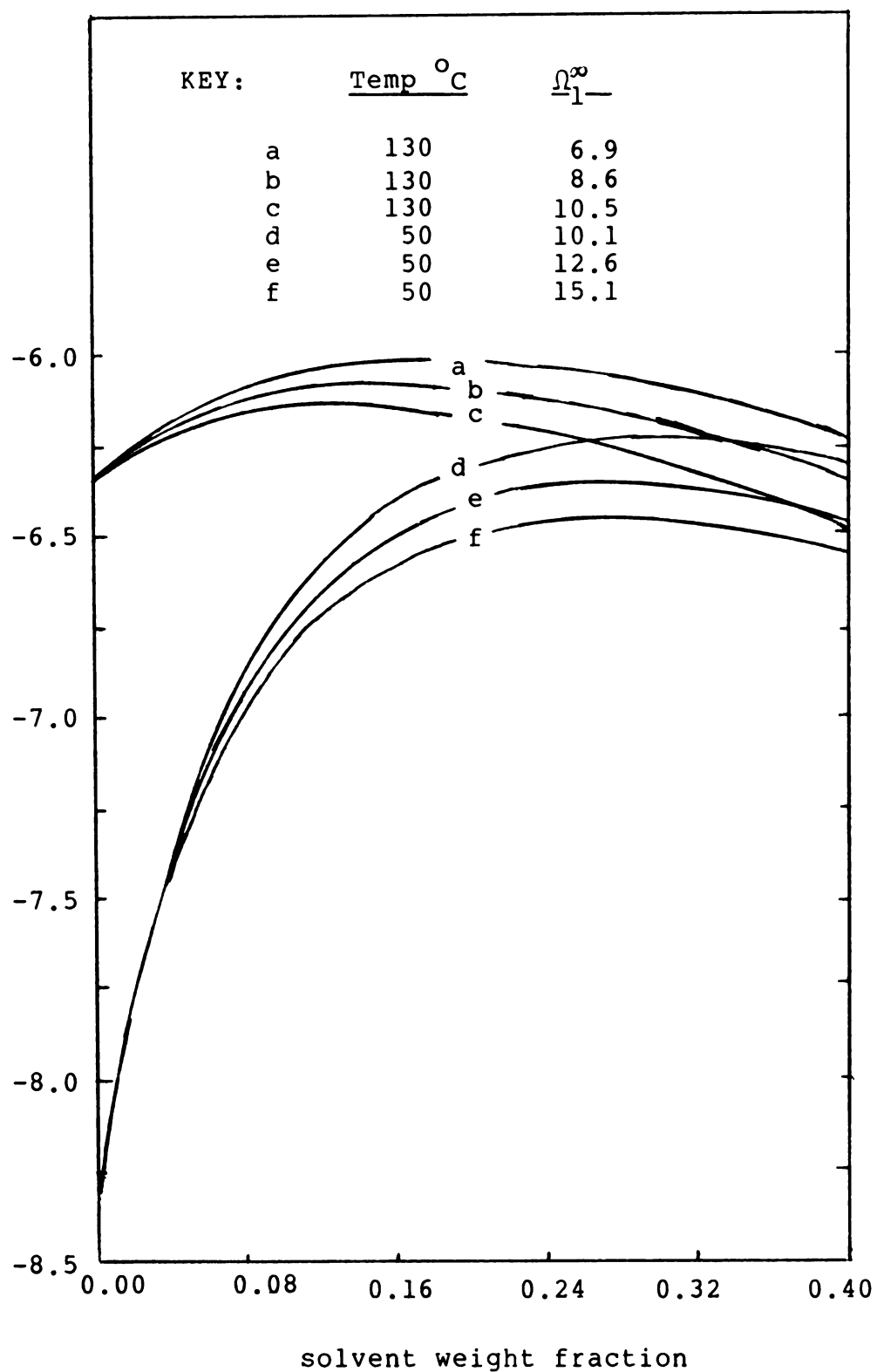


Figure 4.16 Influence of Ω_1^∞ on the Mutual Diffusion Coefficient for Methanol-Poly(vinyl Acetate) Solutions

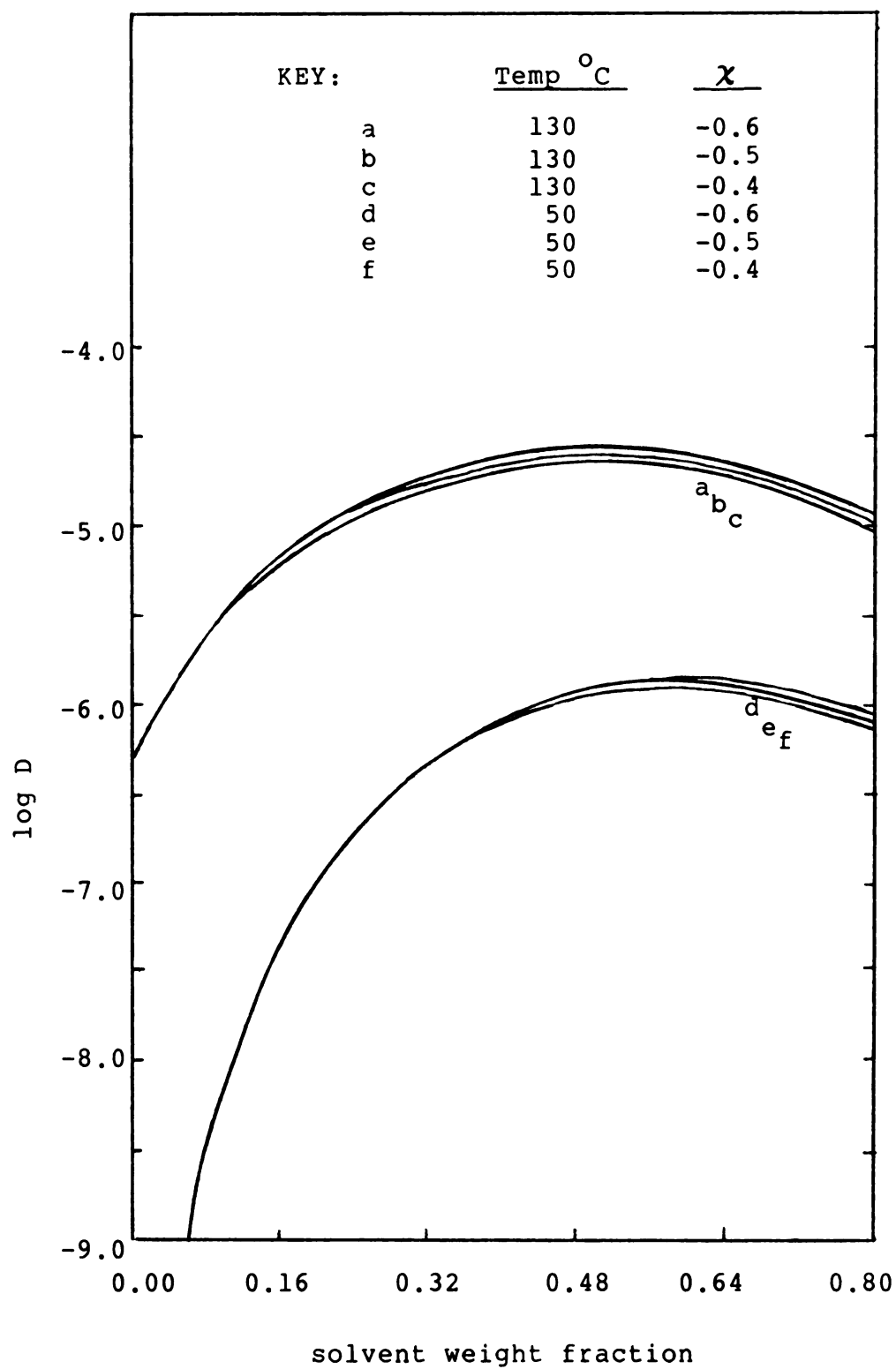


Figure 4.17 Influence of χ on the Mutual Diffusion Coefficient for Chloroform-Poly(vinyl Acetate) Solutions

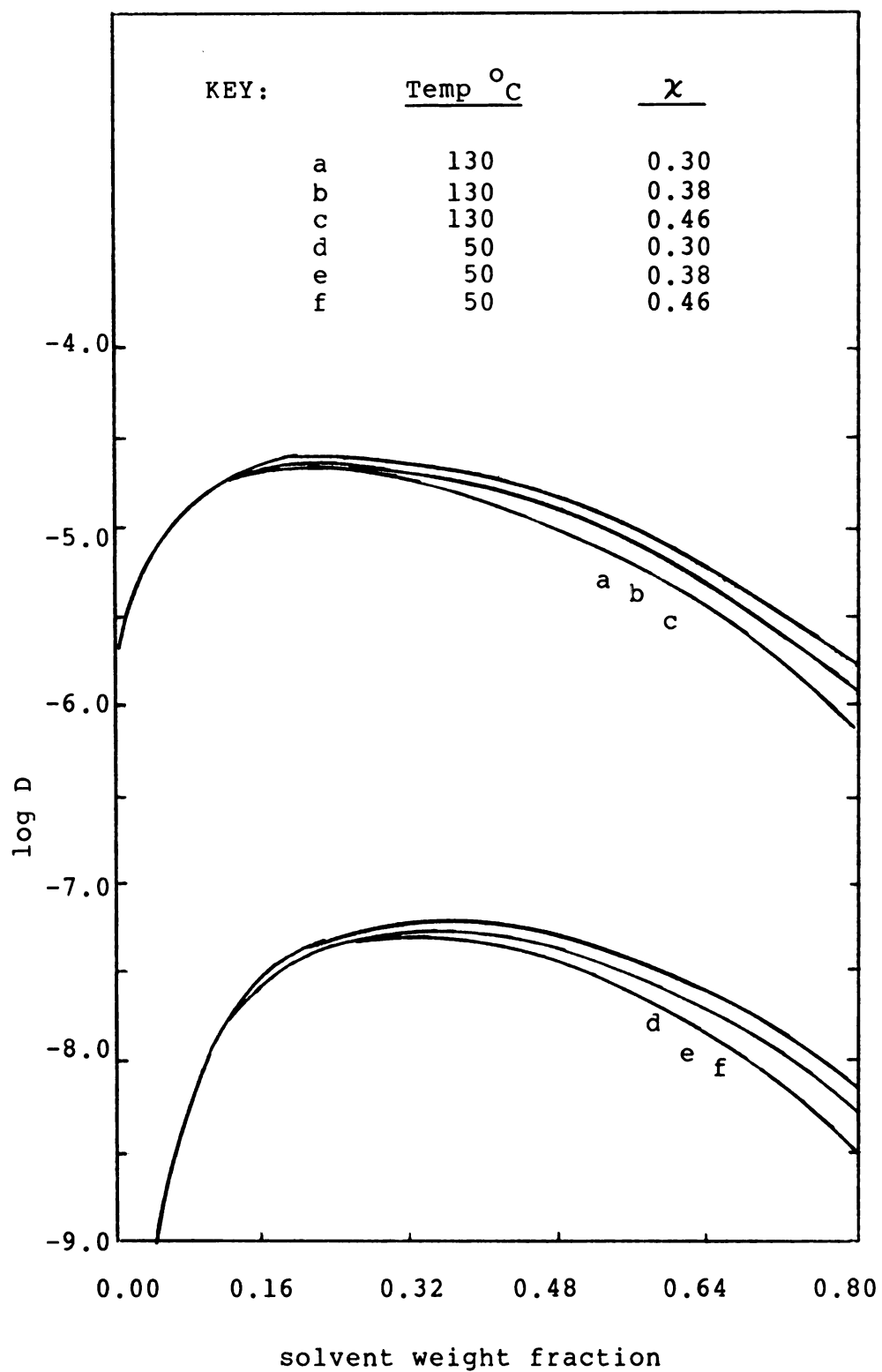


Figure 4.18 Influence of χ on the Mutual Diffusion Coefficient for Acetone-Poly(vinyl Acetate) Solutions

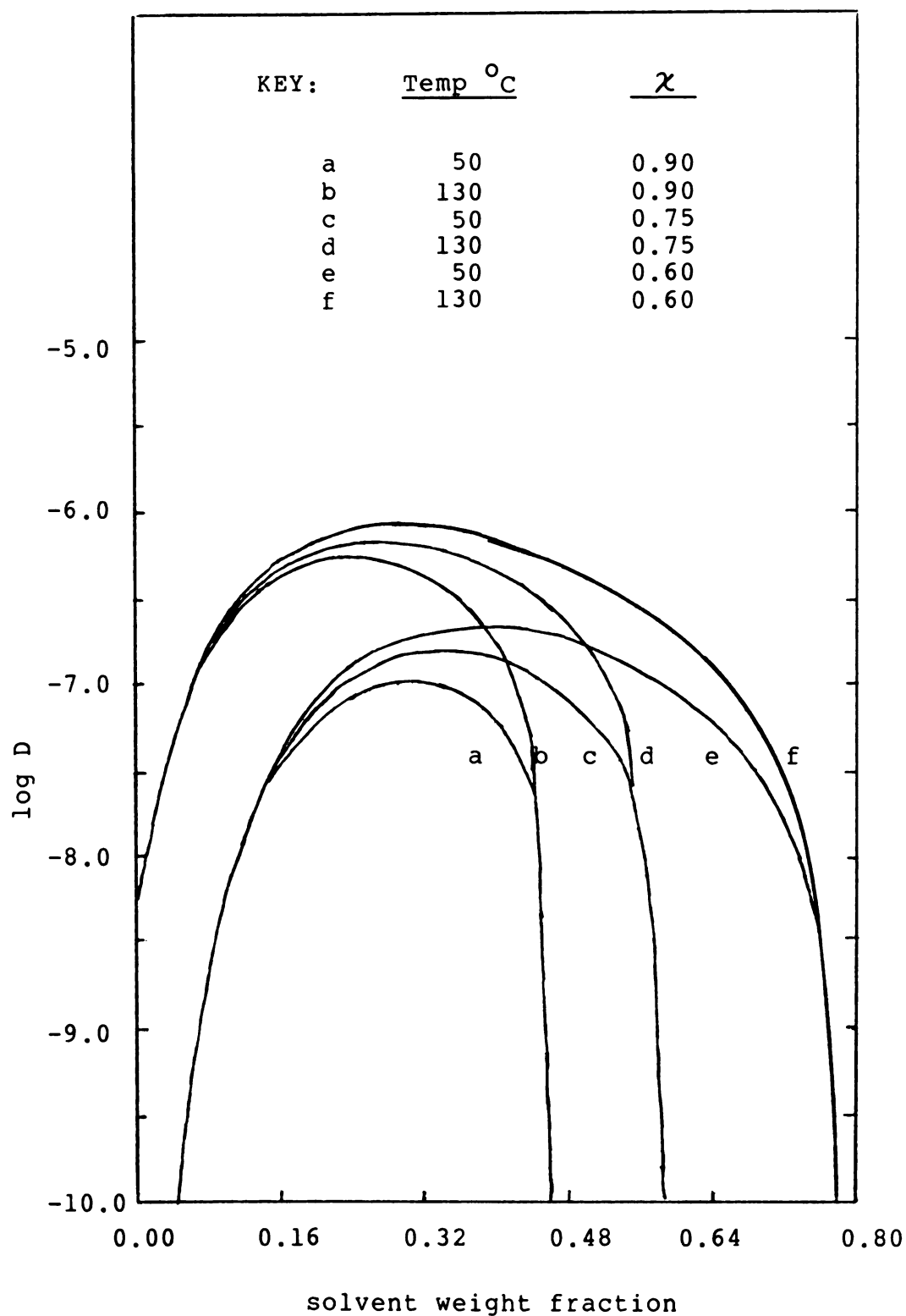


Figure 4.19 Influence of χ on the Mutual Diffusion Coefficient for Toluene-Poly(vinyl Acetate) Solutions

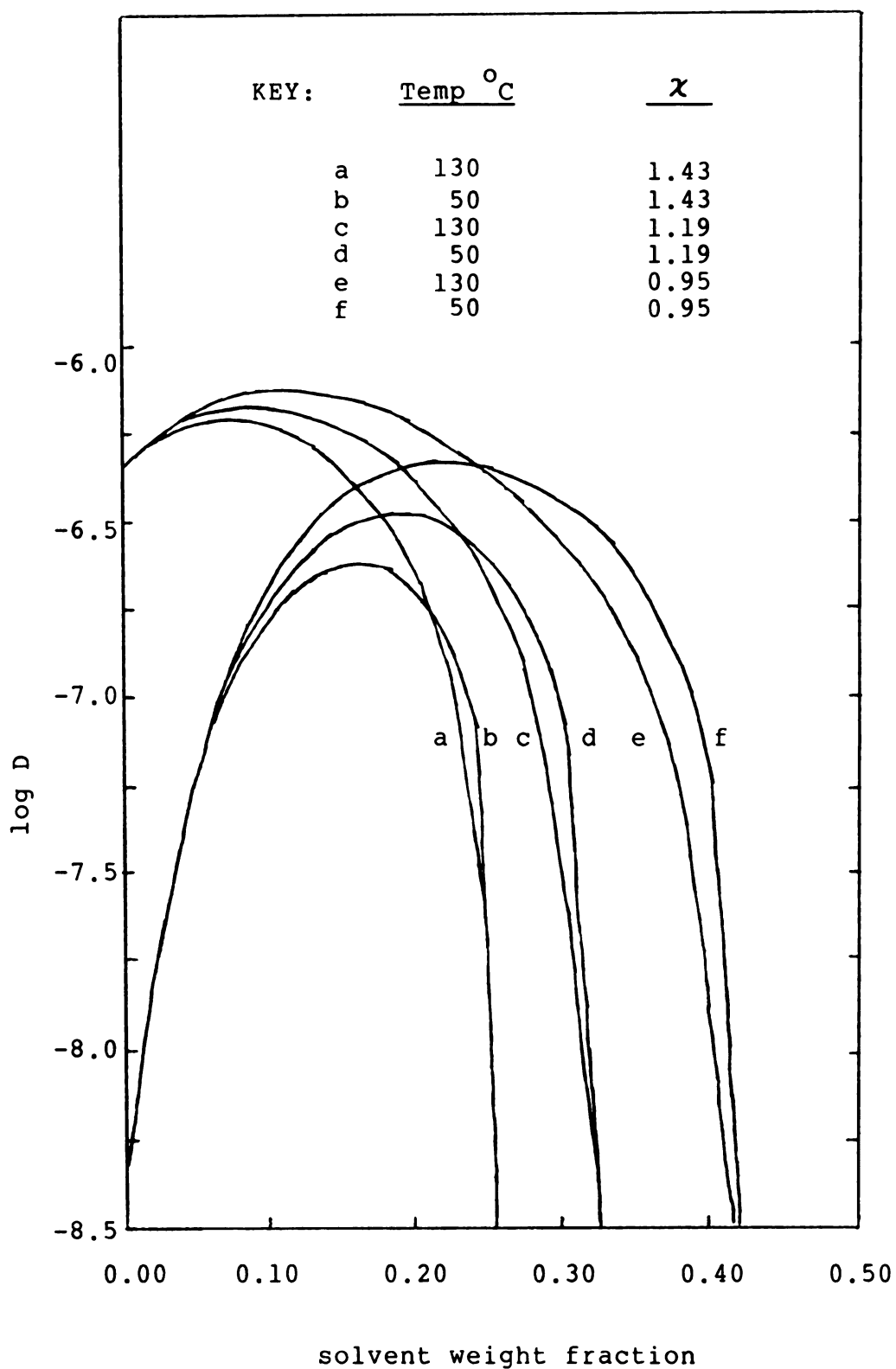


Figure 4.20 Influence of χ on the Mutual Diffusion Coefficient for Methanol-Poly(vinyl Acetate) Solutions

function of concentration. Polymer devolatilization often takes place at solvent concentrations less than 5 weight percent. A simple linear equation to describe the diffusion coefficient as a function of concentration would simplify devolatilizer design equations. The mutual diffusion coefficient equations (2) and (48) can be linearized about the point $w_1 = 0$, the pure polymer limit. The linearized model is:

$$D(w_1) = D\Big|_{w_1=0} + (\partial D / \partial w_1)_{T, w_1=0} (w_1 - 0) \quad (51)$$

For the ASOG-VSP free volume diffusion model this approach leads to a model for diffusivity at low solvent weight fractions of:

$$D(w_1) = D(0)[1 + (K_1 - K_2)w_1] \quad (52)$$

$$K_1 = (A_1 \hat{V}_2^* - A_2 \hat{V}_1^*) / A_2^2 \quad (53)$$

$$K_2 = 2 / (e / \Omega_1^\infty) \quad (54)$$

$$D(0) = D_o \exp[-(E_A / RT + \hat{V}_2^* / A_2)] \quad (55)$$

$$A_1 = (K_{11} / \xi)(K_{21} - T - T_{g1}) \quad (56)$$

$$A_2 = (K_{12} / \xi)(K_{22} - T - T_{g2}) \quad (57)$$

The term, K_1 , is the free volume factor and the term, K_2 , is the thermodynamic factor. The free volume factor decreases as the temperature increases. At temperatures well above the glass transition temperature, the thermodynamic coefficient can be of the same order of magnitude as the free volume coefficient. Thus the effect of this thermodynamic model on predictions of the free volume diffusion theory can be evaluated at higher

temperatures.

The linearized model is only applicable at low solvent concentrations. The solvent range over which the ASOG-VSP linearized model is valid varies with solvent and temperature as shown in Figures 4.21 - 4.24 for chloroform, acetone, toluene and methanol in poly(vinyl acetate). As the temperature increases, the solvent range over which the linearized model is valid widens. Thus this model may be used in many applications at higher temperatures to predict the mutual diffusion coefficient for polymer-solvent systems with the same accuracy as the complete model for low solvent concentrations.

When the Flory-Huggins free volume diffusion model is linearized about the pure polymer limit, the result is:

$$D(w_1) = D(0)[1 + (K_1 - K_3)w_1] \quad (58)$$

where

$$K_3 = 2(\hat{V}_1^0/\hat{V}_2^0)(1 + \chi) \quad (59)$$

The term K_3 is the thermodynamic factor for the Flory-Huggins thermodynamic model. Again, the linearized model is only applicable at low solvent concentrations. The solvent range over which this linearized model is valid varies with solvent and temperature and is essentially the same range over which the ASOG-VSP linearized model is valid for chloroform, acetone, toluene and methanol in poly(vinyl acetate) as shown in Figures 4.25 - 4.28.

Although both thermodynamic models produce linearized models with essentially the same solvent concentration range of applicability, the ASOG-VSP

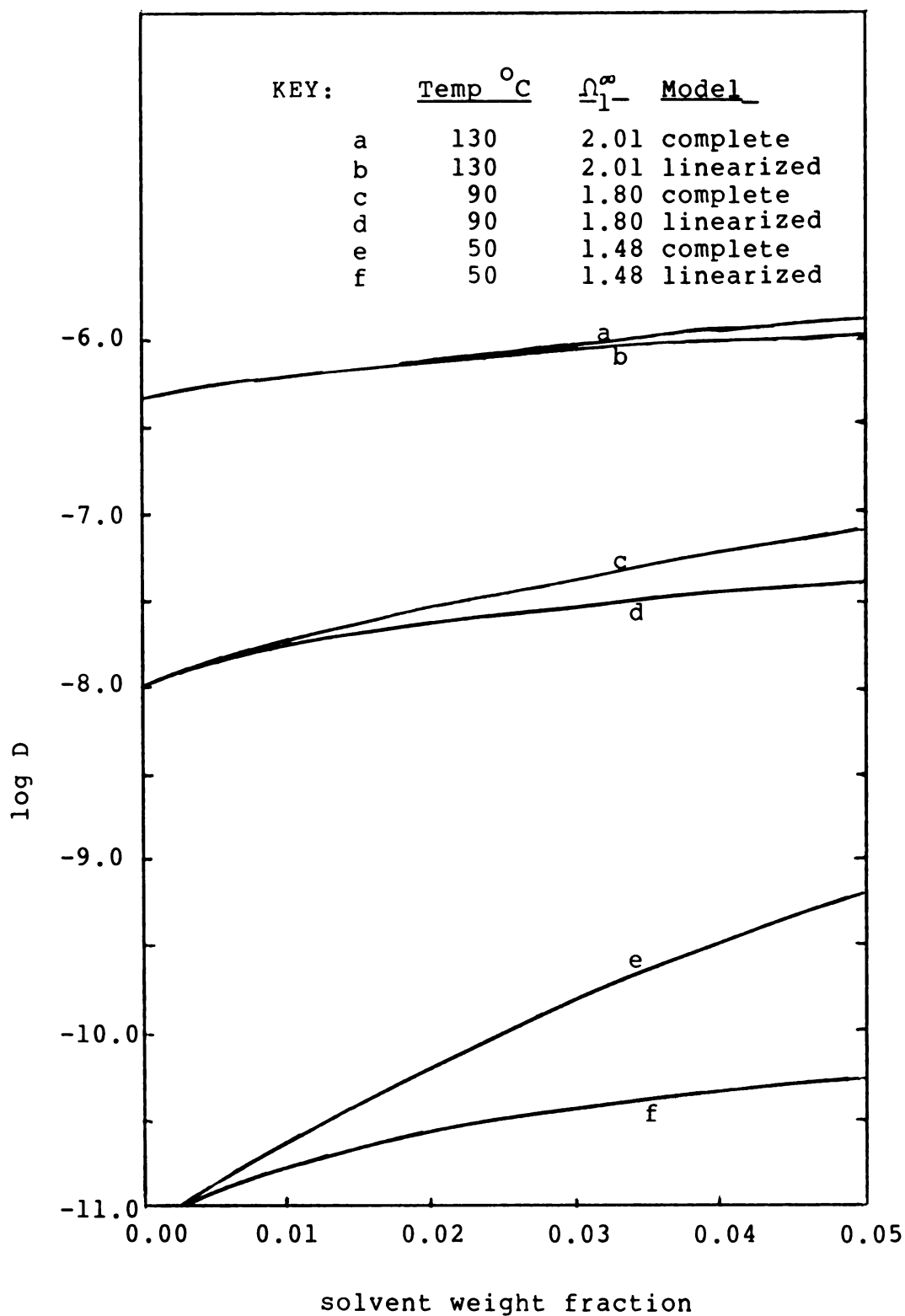


Figure 4.21 Comparison of Linearized and Complete ASOG-VSP Free Volume Diffusion Models for Chloroform-Poly(vinyl Acetate) Solutions

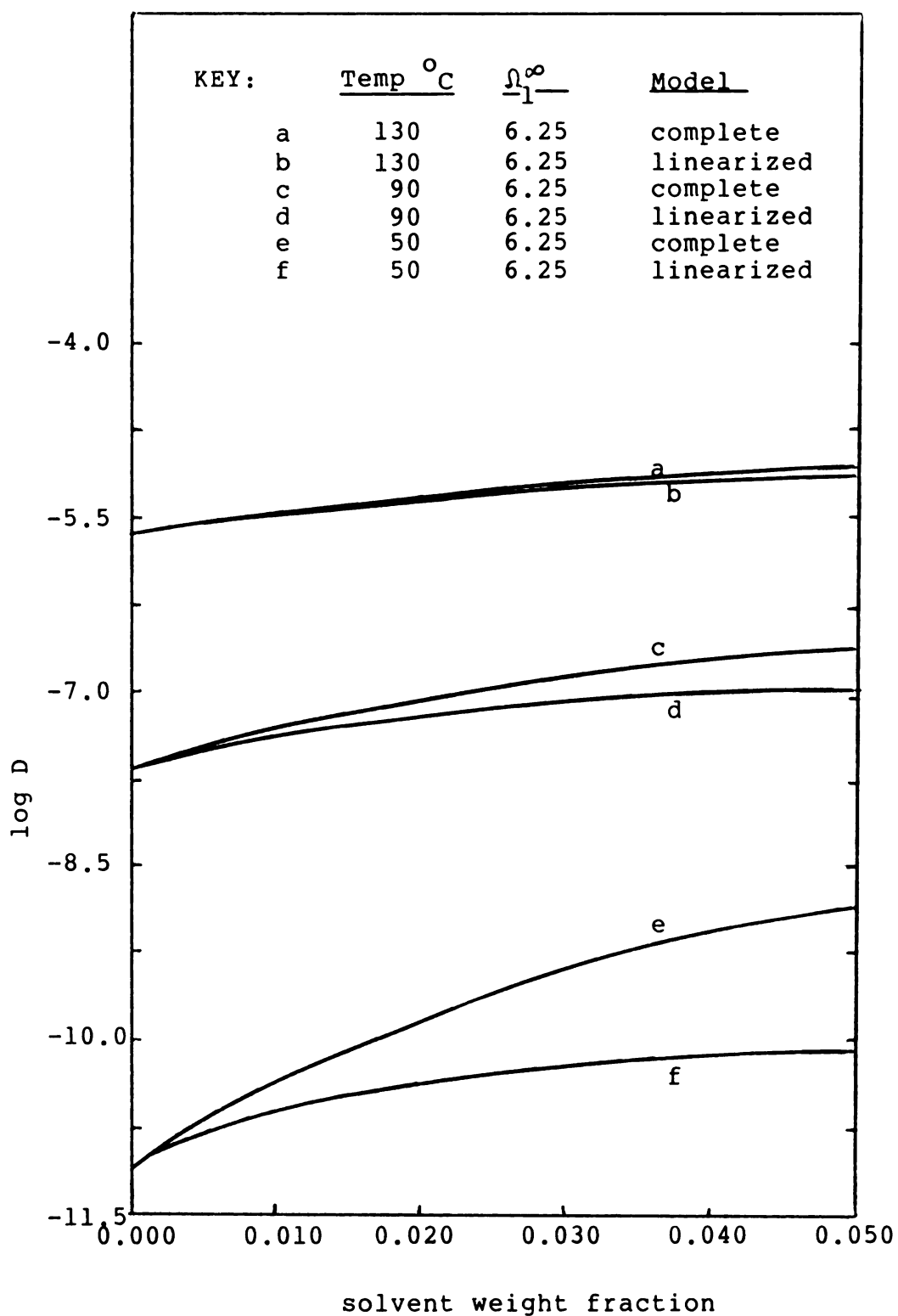


Figure 4.22 Comparison of Linearized and Complete ASOG-VSP Free Volume Diffusion Models for Acetone-Poly(vinyl Acetate) Solutions.

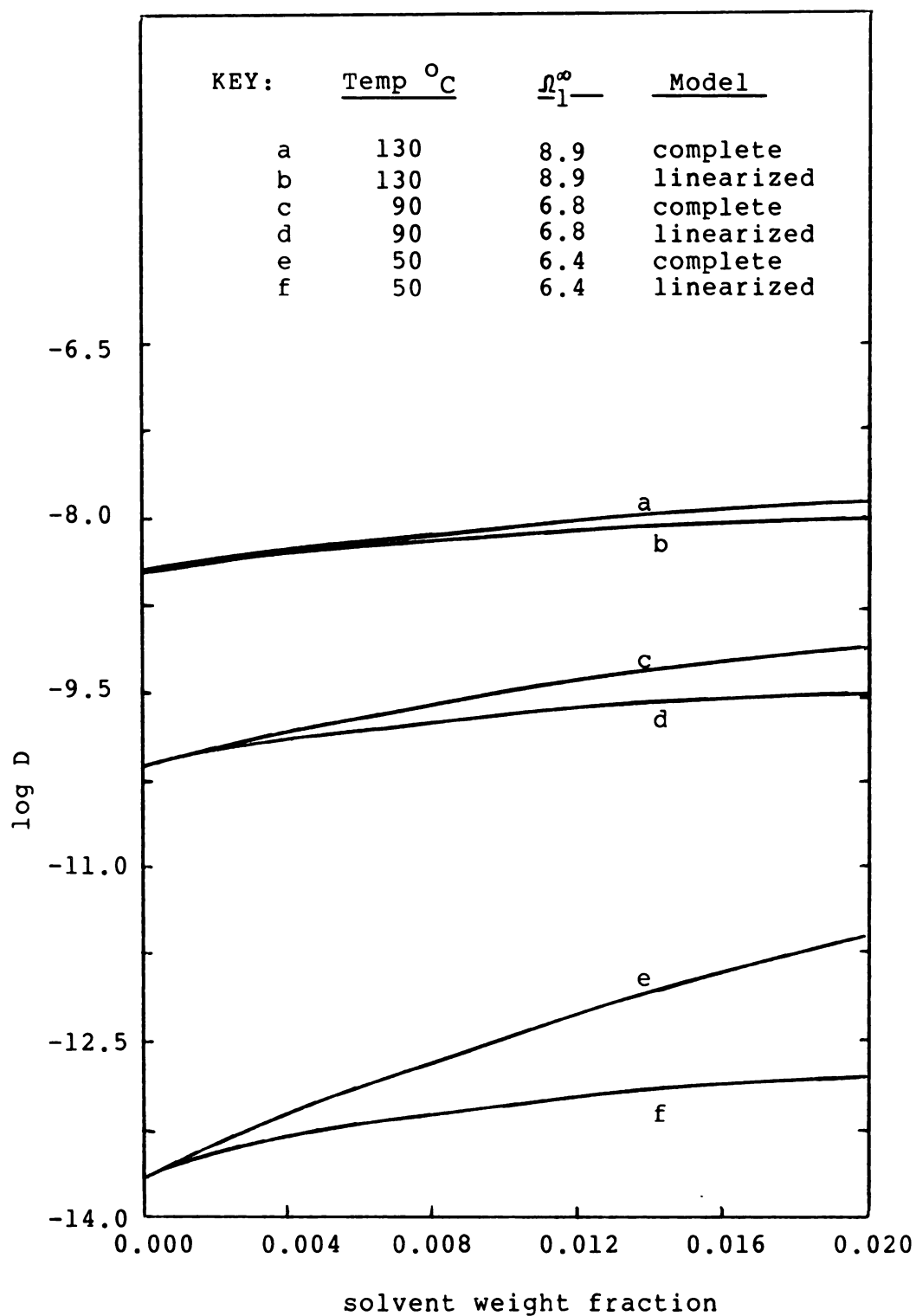


Figure 4.23 Comparison of Linearized and Complete ASOG-VSP Free Volume Diffusion Models for Toluene-Poly(vinyl Acetate) Solutions

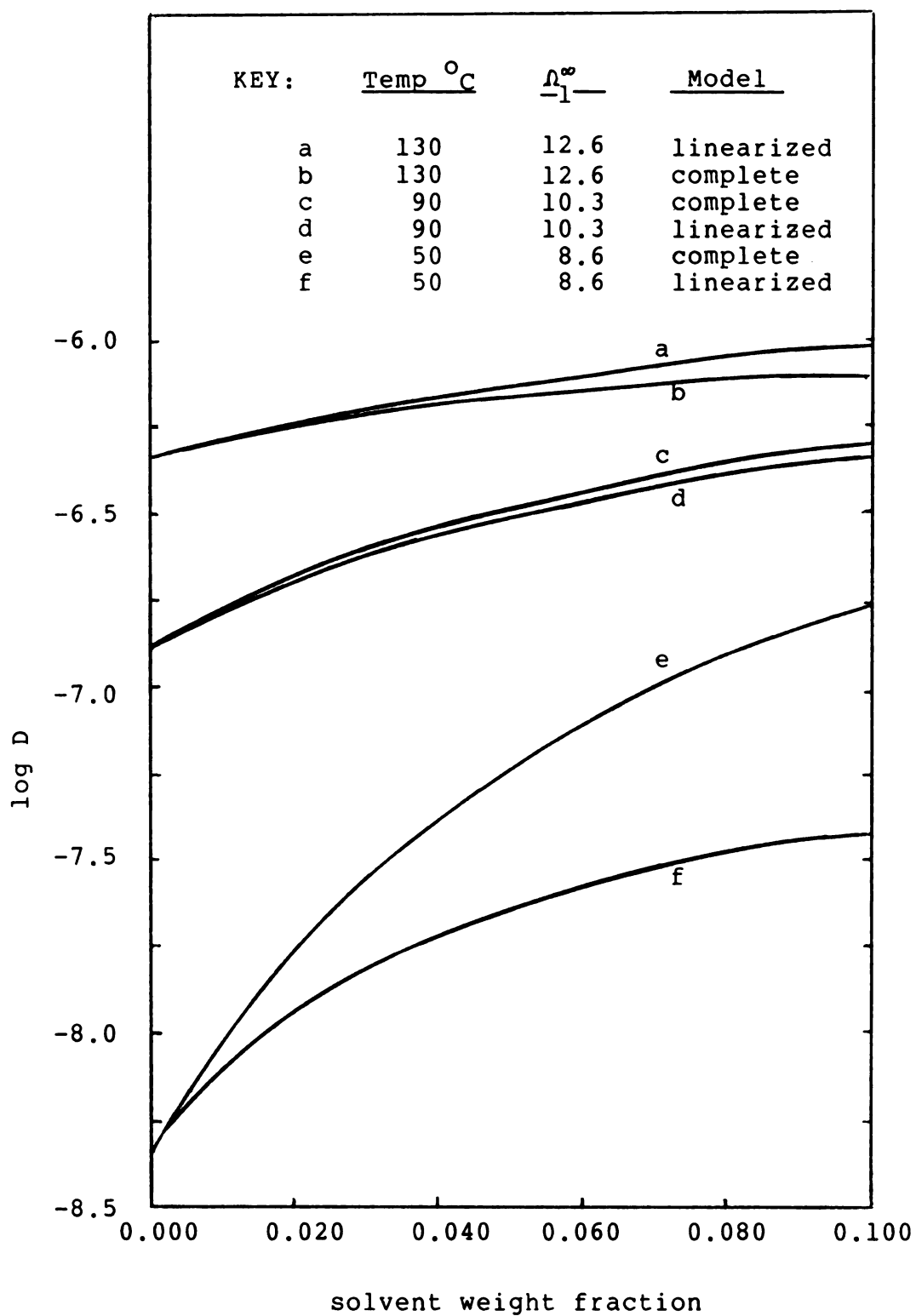


Figure 4.24 Comparison of Linearized and Complete ASOG-VSP Free Volume Diffusion Models for Methanol-Poly(vinyl Acetate) Solutions

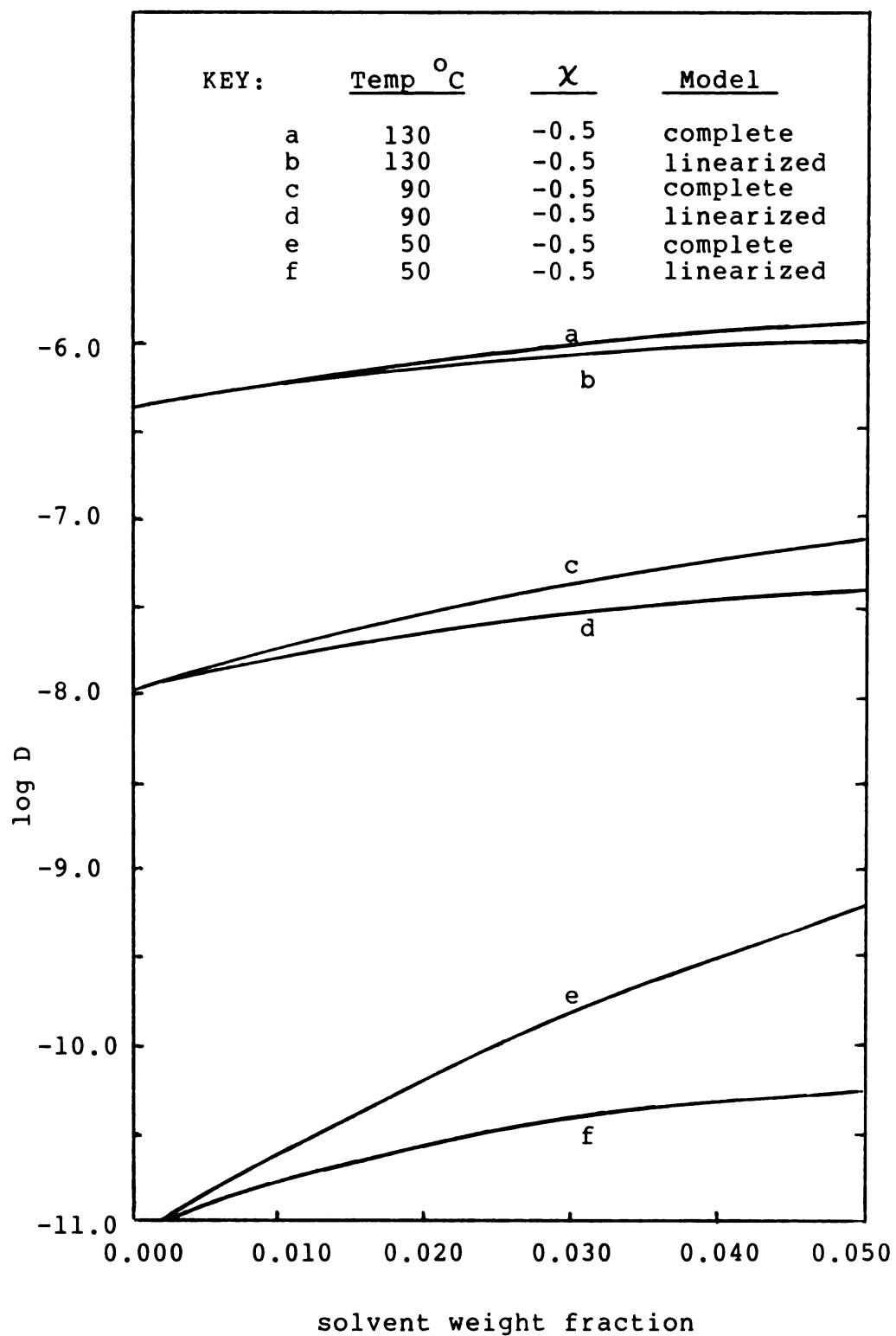


Figure 4.25 Comparison of Linearized and Complete Flory-Huggins Free Volume Diffusion Models for Chloroform-Poly(vinyl Acetate) Solutions

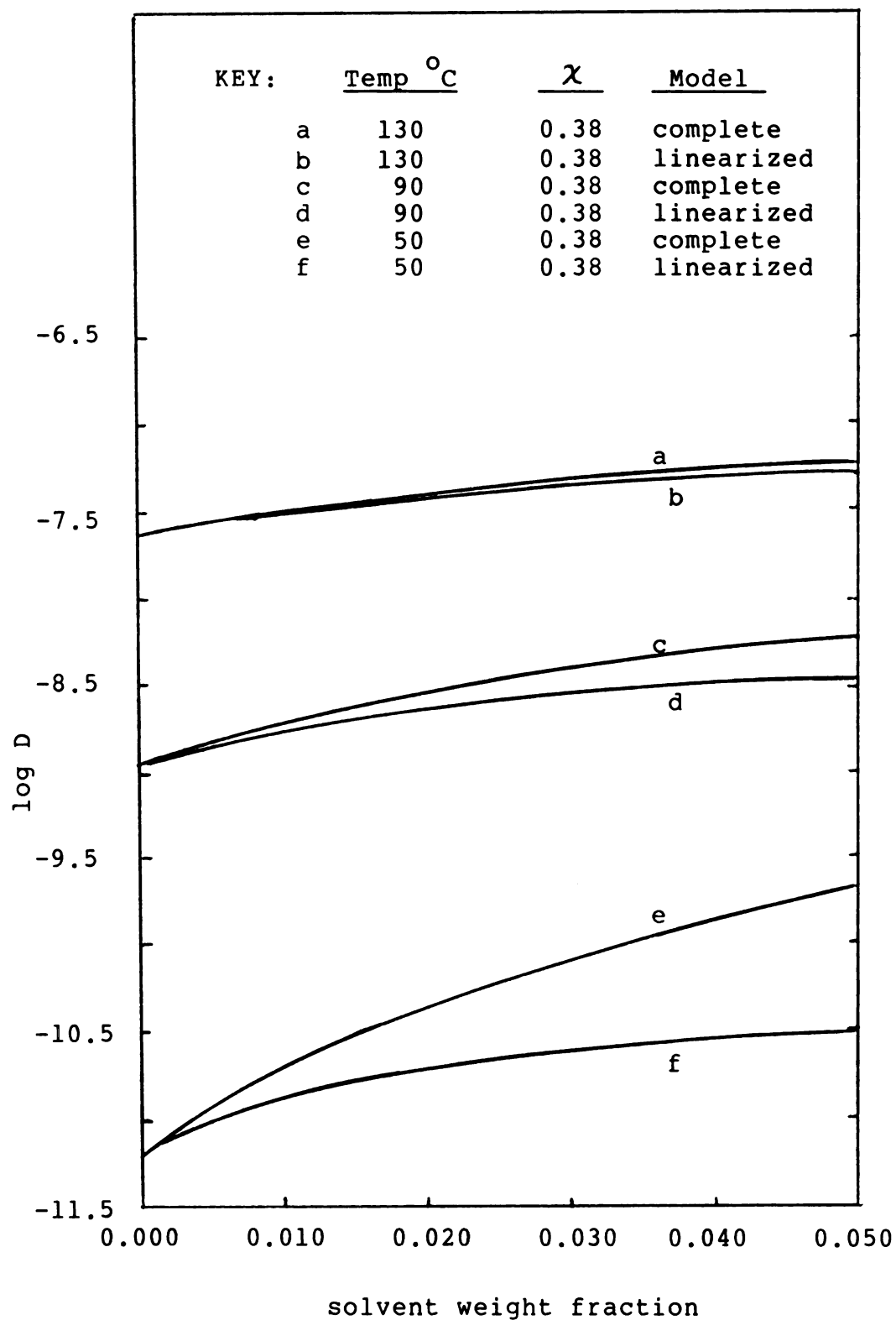


Figure 4.26 Comparison of Linearized and Complete Flory-Huggins Free Volume Diffusion Models for Acetone-Poly(vinyl Acetate) Solutions

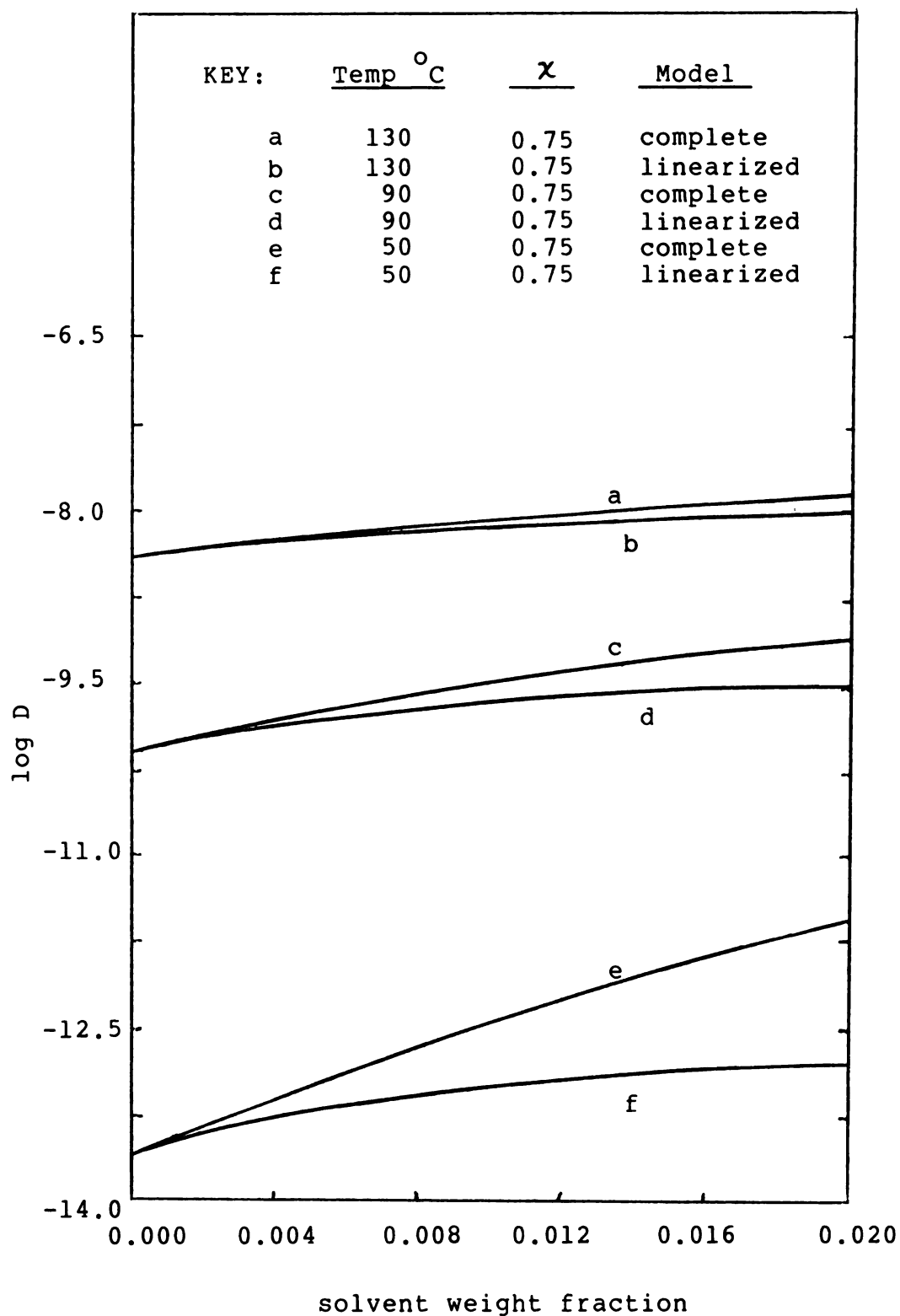


Figure 4.27 Comparison of Linearized and Complete Flory-Huggins Free Volume Diffusion Models for Toluene-Poly(vinyl Acetate) Solutions

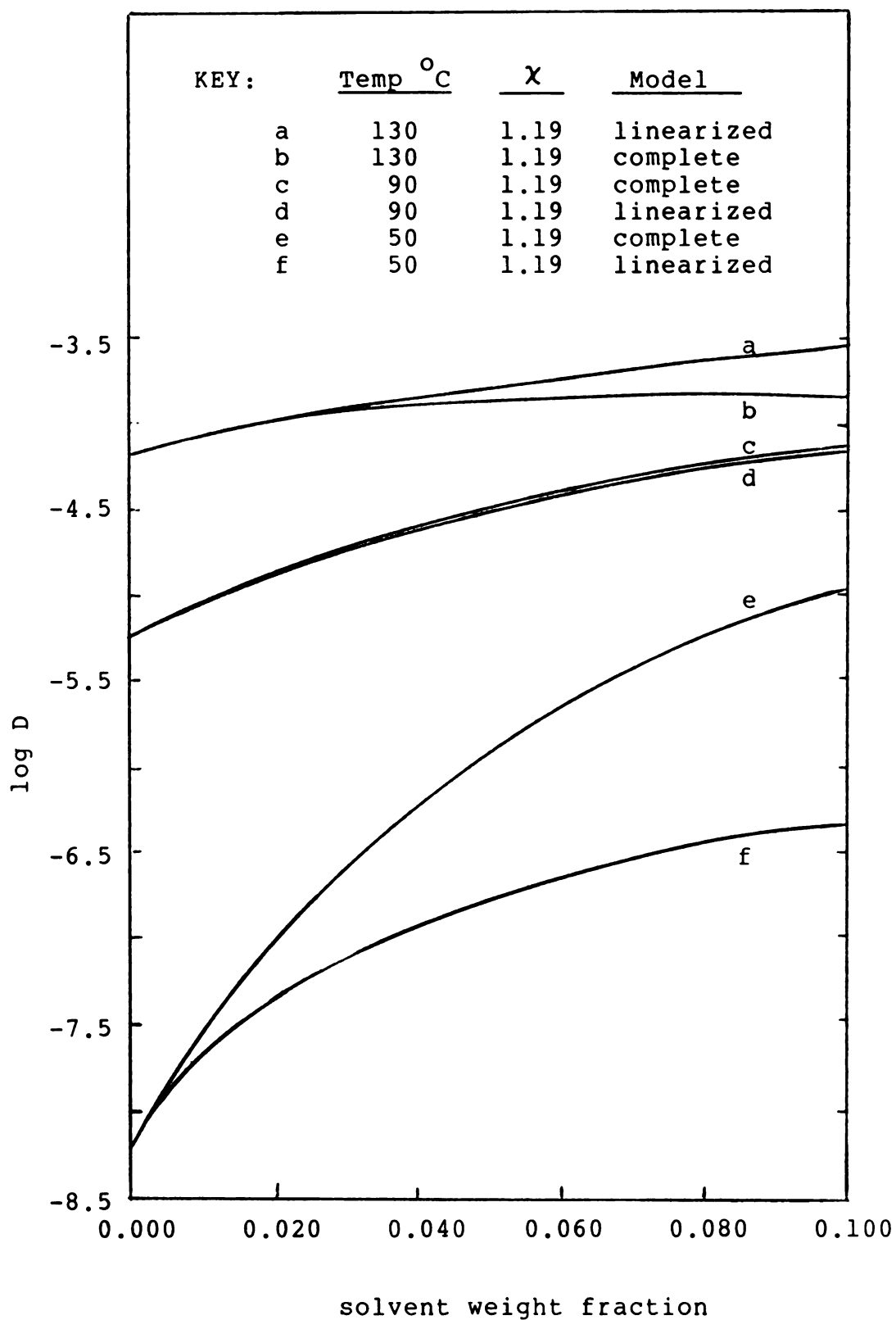


Figure 4.28 Comparison of Linearized and Complete Flory-Huggins Free Volume Diffusion Models for Methanol-Poly(vinyl Acetate) Solutions

thermodynamic model can be applied to a greater number of polymer-solvent systems with widely varying enthalpic interactions. The ASOG-VSP theory has only one adjustable parameter which is independent of concentration and varies only with temperature. It is important that a model of this temperature dependence of Ω_1^∞ for polymer-solvent systems to be developed in order to extend the predictive capabilities of the ASOG-VSP free volume diffusion theory.

CHAPTER 5

McBain-Bakr Sorption Balance

5.1 Proposed Polymer Diffusion Apparatus

The use of variations of the McBain-Bakr sorption balance [M1] for studying the rate of diffusion of solvent vapors into polymer films is well documented [B6,C3,D4,F3,F4,N1,P1,P5]. The experimental technique consists of suspending a thin polymer sample from a helical quartz spring, exposing the sample to an atmosphere of solvent vapor and determining the weight gain of the polymer sample due to sorption of the solvent by measuring the extension of the spring with time. The sorption data can be used to calculate the binary mutual diffusion coefficient for the polymer-solvent system.

The proposed polymer diffusion apparatus is shown in Figure 5.1. The details of the sorption chamber are illustrated in Figure 5.2. The basis of the design of the sorption chamber is to minimize the number of process connections around the chamber which could lead to potential leakage problems while maintaining the intended function of the chamber. The function of the sorption chamber is to maintain a vacuum as well as a pressurized atmosphere at a constant temperature for an extended period

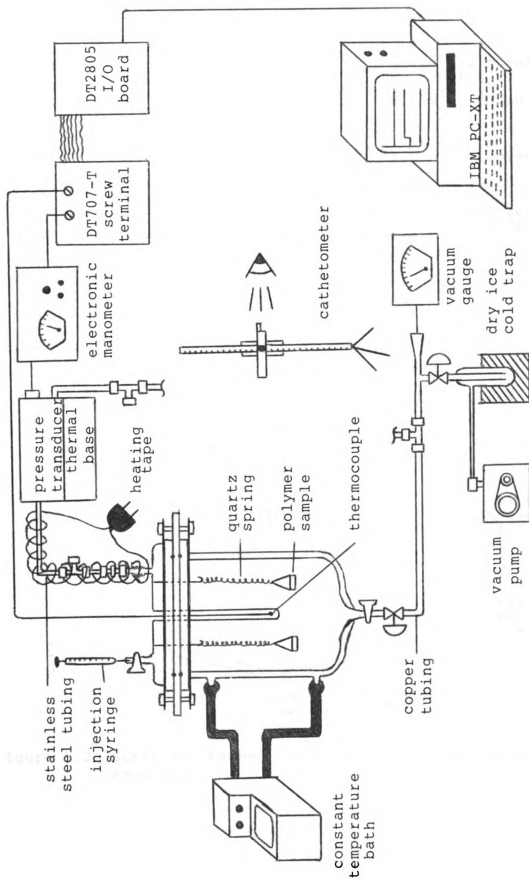


Figure 5.1 Proposed Polymer Diffusion Apparatus

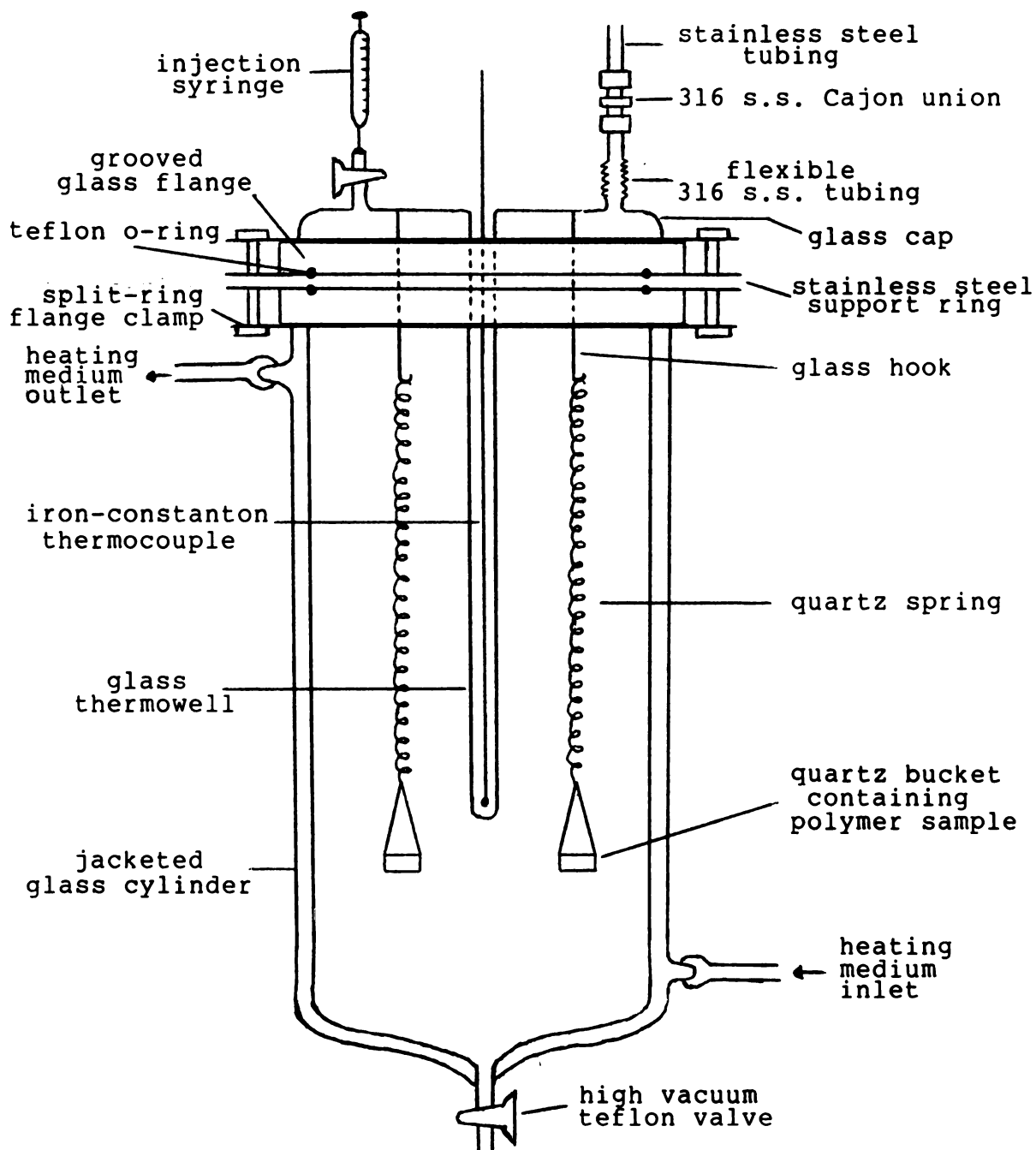


Figure 5.2 Sorption Chamber for Proposed Polymer Diffusion Apparatus

of time. The chamber consists of a flanged glass cap with two process connections clamped to a flanged jacketed glass cylinder with one process connection. The flanged pieces are grooved for o-rings and sealed together around a stainless steel support ring using teflon o-rings which will not absorb organic solvents as a typical neoprene o-ring will. The glass cylinder has an inner diameter of 4 inches and a length of 3 feet. The flanged pieces are clamped together with a split-ring flange clamp around the stainless steel ring which supports the entire chamber. This type of support will allow disassembly of the apparatus by lowering the bottom of the chamber which minimizes contact with the quartz springs which are very fragile and easily broken.

A constant temperature is maintained in the sorption chamber by circulating hot water (or ethylene glycol for temperatures above 100 °C) from a Haake constant temperature bath through the glass jacket. The temperature is measured using an iron-constantan thermocouple which is inserted into a glass thermowell extending from the glass cap halfway down into the sorption chamber.

The quartz buckets containing the polymer samples are suspended from helical quartz springs which are attached to glass hooks extending from the glass cap.

The solvent is injected into the sorption chamber with a micro-syringe through a septum inserted into a glass tube extending above the glass cap. A high vacuum

teflon valve closes off the septum from the sorption chamber in order to maintain a vacuum or pressurized atmosphere inside the chamber. The chamber is evacuated through a glass tube extending out the bottom which is also sealed using a high vacuum teflon valve. The teflon valves which are inert and impermeable to organic solvents are used instead of glass valves requiring vacuum grease which can absorb the organic solvents.

The pressure of the sorption chamber is measured through a second connection in the glass cap. Stainless steel tubing is connected by stainless steel Cajon fittings to a flexible stainless steel glass-ended tube which is attached to the glass cap. This flexible tubing minimizes the stress on the glass connection and allows for a metal-to-metal connection which can seal tightly. Stainless steel fittings are used instead of brass Cajon fittings because of the high temperatures to be encountered. The connection between the sorption chamber and the pressure transducer must be maintained at or above the temperature of the chamber to prevent condensation of the solvent vapors. A heating tape will be wrapped around the stainless steel tubing, the solvent entry tube and the glass cap to prevent heat losses through the top of the glass cylinder and maintain a constant temperature throughout the system. A variac controls the voltage sent to the heating tape which controls the temperature.

The volume of the sorption chamber is large enough

(approximately 7.5 liters) so that the pressure of the solvent vapor will not change appreciably as sorption in the sample takes place. The sorption chamber has enough space for two quartz springs so dual sorption experiments can be performed simultaneously. The quartz springs can be designed for a variety of extension constants.

The temperature and pressure in the sorption chamber are continually monitored at specified time intervals using an IBM PC-XT Personal Computer as described in Section 3.1. The weight change of the polymer sample is determined by measuring the extension of the quartz spring with time using a cathetometer. The extension of the quartz springs is linear with increasing weight and can be calibrated by noting the extension of the spring with a series of increasing weights attached to it.

5.2 Polymer Sample Preparation

The polymer films used for the sorption experiments are made using a hydraulic jack and platens heated by hot water from a temperature bath as described in Section 3.2 without the aluminum foil on each side of the film. Small samples are cut out from the polymer film using a circular steel punch. These samples are placed in circular quartz buckets of the same diameter which are suspended from the quartz springs in the sorption chamber. The quartz buckets are light so as not to add undue weight to the quartz springs. They also maintain a flat level surface for the

molten polymer samples above the glass transition temperature. The thickness of each polymer sample is measured with a micrometer accurate to ± 0.00025 cm. The sample thickness can also be checked knowing the sample weight, polymer density and sample surface area. The prepared polymer samples are stored under vacuum at room temperature until they are ready to be used.

To prepare polymer samples of thicknesses greater than 0.15 cm, multiple layers of thinner polymer samples will be used. The thin layers will be roll-pressed on top of each other to remove trapped air between the samples. The "stack" of thin polymer films will then be inserted back into the platens, and reheated under pressure. This technique will minimize the air bubbles which are retained in the polymer film when a thick sample is pressed initially.

5.3 Operating Procedures

To begin each sorption experiment, the electronic manometer, pressure transducer and thermal base are turned on and allowed adequate time for warmup. The quartz buckets containing polymer samples are attached to the quartz springs. The vacuum sorption chamber is then assembled and sealed by clamping the flanged pieces together and closing the high vacuum teflon valves. The temperature bath is set at the desired experimental temperature and hot water (or ethylene glycol) is

circulated in the glass jacket. The chamber is evacuated using the oil diffusion vacuum pump. The polymer sample is degassed for a period of several hours at the experimental temperature under a vacuum of 0.5 mm Hg to desorb any water vapor picked up during assembly of the apparatus when the polymer sample is exposed to the atmosphere. The heating tape wrapped around the solvent tube, glass cap and pressure transmission line is turned on and the temperature is kept approximately 5 °C higher than the experimental temperature in the sorption chamber. The appropriate amount of solvent to achieve the desired system pressure is loaded into the micro-syringe. The initial extension of the quartz spring after the polymer sample is completely degassed is observed using the cathetometer. The extension of the spring can be measured by noting the position of a stationary point on each end of the spring.

Just before starting each sorption experiment, zero adjustments of the electronic manometer are made. To start the experiment the vapor admission valve is opened and the solvent is injected simultaneously with the initiation of the data acquisition program. The temperature and pressure readings will be automatically recorded at specified time intervals, and the data will be plotted versus time on the computer screen.

Three types of experiments will be performed with the polymer diffusion apparatus to study solvent diffusion in poly(vinyl acetate): 1) rapid sorption and desorption

experiments to determine solvent weight fraction activity coefficients for a range of temperatures, 2) series of sorption experiments in small concentration steps to determine the concentration dependence of the diffusion coefficient and 3) sorption followed by desorption experiments to look for hysteresis in the sorption curve.

Solvent activity coefficients can be quickly determined using very thin polymer samples where the solvent vapor and polymer sample rapidly reach equilibrium. In this case only the initial and final extensions of the quartz springs need to be observed.

A series of sorption experiments in small concentration steps can be carried out as described in Section 3.3. Depending on the total time for the sample to reach equilibrium, the extension of the quartz spring is observed at certain time intervals. The time interval will vary in order to collect an adequate number of data points. Tables C.1 - C.4 in Appendix C list recommended polymer sample thicknesses and the approximate half-times for each solvent in poly(vinyl acetate) at a certain temperature and solvent weight fraction.

For the sorption-desorption series of experiments, the sorption chamber is quickly evacuated after the polymer has reached equilibrium. The extension of the quartz spring is then observed as the polymer sample desorbs the solvent vapor.

5.4 Data Analysis

5.4-1 Analysis of Complete Sorption Curve

The following assumptions can be made in modeling the sorption process:

- (1) Diffusion occurs in one dimension.
- (2) The temperature change associated with the sorption process is negligible.
- (3) The surface of the polymer film is always in equilibrium with the current vapor pressure of the solvent.
- (4) Pressure has a negligible effect on the density of the polymer phase.
- (5) No chemical reactions occur.
- (6) Diffusivity is independent of concentration.
- (7) There is no volume change on mixing.

The first assumption is valid since the thickness of the polymer sample is small compared to the area dimension. Crank [C5] has analyzed the temperature changes accompanying the sorption of vapors by a solid due to the heat of condensation given up at the surface. A temperature change of less than 0.25°C indicates the second assumption is valid. The assumption of constant diffusivity is generally not true. However the sorption experiment can be designed so that the solvent concentration changes only slightly during the experiment, and the resulting diffusion coefficient will be some

average value over that concentration interval. Vrentas, et al. [V6] have analyzed the step-change sorption problem and concluded that the average diffusion coefficient obtained represents the actual diffusivity at a concentration which lies at 0.7 of the weight fraction concentration interval when the diffusion coefficient increases exponentially with solvent concentration. The error associated with this process was shown to be less than 5 percent.

The general equation describing this one-dimensional diffusion is:

$$\partial C / \partial t = D (\partial^2 C / \partial x^2) \quad (60)$$

The associated initial and boundary conditions are:

$$C(x, 0) = C_o \quad (61)$$

$$C(L, t) = C_E \quad (62)$$

$$\partial C / \partial x(0, t) = 0 \quad (63)$$

Initially the polymer sample is at a uniform solvent concentration. The concentration of the solvent at the surface, $x = L$, is at its equilibrium value, C_E for any time, t . Also, there is no transport of the solvent through the aluminum foil at $x = 0$ for any time, t .

The exact solution of equations (60) to (63) is given by Crank [C5] as:

$$\frac{C_o - C_E}{C_E - C_o} = \sum_{n=0}^{\infty} (-1)^n \operatorname{erfc} \frac{(2n+1)L-x}{2(Dt)^{1/2}} + \sum_{n=0}^{\infty} (-1)^n \operatorname{erfc} \frac{(2n+1)L+x}{2(Dt)^{1/2}} \quad (64)$$

This concentration profile is integrated to give an expression for the weight of penetrant solvent absorbed

by the polymer sample:

$$\frac{M(t)}{M(\infty)} = 2 \left[\frac{Dt}{L^2} \right]^{\frac{1}{2}} \pi^{-\frac{1}{2}} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{erfc} \frac{nL}{(Dt)^{\frac{1}{2}}} \quad (65)$$

$M(t)$ is defined as the weight pickup at time t and $M(\infty)$ as the weight pickup at infinite time, or the equilibrium weight pickup.

For small times, the summation term in equation (65) is negligible and the ratio of weight pickup at time t to that at equilibrium can be approximated as:

$$\frac{M(t)}{M(\infty)} = \frac{2 \left[\frac{Dt}{L^2} \right]^{\frac{1}{2}}}{\sqrt{\pi}} \quad (66)$$

The average diffusion coefficient can be determined from the initial slope, $R_i = d[M(t)/M(\infty)]/d[\sqrt{t}]$, of the weight pickup versus $\sqrt{t}$.

$$D = (\pi L^2/4) R_i^2 \quad (67)$$

The initial slope of the sorption curve may be difficult to determine due to excessive vibrations of the polymer sample occurring after the solvent is injected due to the rapid boiling of the liquid. In this case the diffusion coefficient can be calculated by noting the half-time of the sorption process. The value of (t/L^2) for which $M(t)/M(\infty) = \frac{1}{2}$ is approximated by:

$$\left[\frac{t}{L^2} \right]_{\frac{1}{2}} = - \frac{1}{\pi^2 D} \ln \left[\frac{\pi^2}{16} - \frac{1}{9} \left(\frac{\pi^2}{16} \right) \right]^9 \quad (68)$$

within an error of 0.001%. Thus the diffusion coefficient is given by:

$$D = 0.049 (L^2/t)_{\frac{1}{2}} \quad (69)$$

5.4-2 Analysis of Low Solvent Concentration Data

At low solvent concentrations, the diffusivity can often be approximated by a linear function of concentration according to the expression:

$$D = D(0)[1 + (K_1 - K_2)w_1] \quad (70)$$

The values of $D(0)$ and $(K_1 - K_2)$ can be deduced from sorption data for several solvent concentration intervals using a procedure developed by Crank [C3] and summarized below.

As mentioned before, application of equation (67) or (69) to a sorption curve yields some average value $\bar{D}$ of the variable diffusion coefficient over the respective concentration interval. This average value provides a reasonable approximation to

$$\bar{D} = \frac{1}{C_1 - C_0} \int_{C_0}^{C_1} D \, dC \quad (71)$$

Crank has calculated a correction curve showing the difference between $\bar{D}/D(C_1=0)$ and

$$\frac{1}{C_1 - C_0} \int_{C_0}^{C_1} \frac{D}{D(C_1=0)} \, dC = \frac{I}{C_1 - C_0} \quad (72)$$

for diffusion coefficients which depend linearly on concentration. This correction curve can be found in Figure 1 in [C3] or Figure 10.6 in [C5]. Using this curve and either equation (67) or (69), the diffusion coefficient-concentration relationship can be deduced. The procedure is as follows:

- (1) Sorption-time curves are plotted for several

sorption experiments.

- (2) $\bar{D}$ is calculated for each curve using equation (67) or (69).
- (3) $\bar{D}$ is extrapolated to zero solvent concentration to obtain $D(C_1=0)$.
- (4) Using the correction curve as reported by Crank, the value of $I/(C_1 - C_0)$ is determined for each value of $\bar{D}/D(C_1=0)$.
- (5) I is differentiated to obtain $D/D(C_1=0)$ and hence D .
- (6) D is plotted versus solvent weight fraction and a linear best fit regression of the data will determine $D(0)$ and $(K_1 - K_2)$.

CHAPTER 6

Summary and Conclusions

Analysis of the free volume theory of Vrentas and Duda reveals that several of the assumptions made in the development of this theory place limitations on the predictive capabilities of the theory. The assumption of additivity of free volumes on mixing may not be reasonable for polymer-solvent systems with strong interactions between the polymer and the solvent. Significant volume changes on mixing are seen in numerous polymer-solvent systems. Also the calculation of a diffusion coefficient from sorption data is shown to be affected by volume changes on mixing with the greatest impact involving sorption data from experiments with large changes in solvent concentration.

The assumption that the free volume of a liquid can be related to the viscosity by the WLF equation appears invalid for many solvents especially in the experimental temperature range of interest. Several types of viscosity-temperature behavior are seen in a variety of organic solvents. An alternative method of determining the free volume parameters of the theory may be necessary for many solvents.

The jumping unit ratio and activation energy

parameters appear to lack much of the physical significance attached to them by Vrentas and Duda. The values of D_0 , E_A and ξ appear to be best determined by fitting the free volume diffusion equation to actual diffusivity data rather than using calculations with a physical interpretation. Unique values of the three parameters are not necessary to predict a diffusivity curve.

A comparison of the free volume diffusivity predictions using the Flory-Huggins and ASOG-VSP thermodynamic models reveals the following:

1. Similar diffusivity curves are predicted from both thermodynamic models for athermal polymer-solvent systems.
2. Significantly different diffusivity curves are predicted from both thermodynamic models for polymer-solvent systems exhibiting positive enthalpic interactions.
3. The differences between these predictions increase as the value of χ or Ω_1^∞ increases.
4. The free volume diffusion theory using the Flory-Huggins thermodynamic model predicts negative diffusivities at solvent weight fractions exceeding $(1/2\chi)$.

Sorption experiments to measure diffusion coefficients in polymer-solvent systems should be designed with the following considerations:

1. Large concentration gradients should be avoided to assume volume changes on mixing

to be negligible.

2. The polymer sorption chamber should be able to sustain high temperatures and pressures in order to study diffusion coefficients over wide temperature and concentration ranges.

The proposed experiments discussed in Chapter 5 meet these requirements.

CHAPTER 7

Recommendations

As a result of this study, the following recommendations for continued research are made:

1. Rather than use the WLF equation to describe the temperature dependence of the solvent viscosity, an alternative method of determining the solvent free volume parameters at the experimental temperatures of interest is necessary. Perhaps the free volume can be related to the solvent density.
2. A model to describe the temperature dependence of the infinite dilution weight fraction activity coefficient is necessary to extend the predictive capabilities of the ASOG-VSP free volume diffusion theory.
3. Extensive diffusivity data over a wide range of temperatures and solvent concentrations for polymer-solvent systems exhibiting a variety of enthalpic interactions is needed to test the applicability of both free volume diffusion theories involving the Flory-Huggins and the ASOG-VSP thermodynamic models.
4. An additional polymer-solvent system to be

considered for diffusivity studies is 1-propanol in poly(vinyl acetate) which has strong positive enthalpic interactions and a relatively high boiling point so that higher solvent concentrations can be reached at lower solvent pressures. The water-poly(vinyl acetate) system which has very strong positive enthalpic interactions should also be studied. The validity of the ASOG-VSP thermodynamic model for polymer-solvent systems with such strong interactions has not yet been verified.

APPENDIX A

APPENDIX A

Data Acquisition Program for Polymer Diffusion Apparatus

```

10 '
20 '
30 '
40 '
50 '
60 '
70 '
80 '
90 '
100 '
110 '
120 '
130 '
140 '
150 CLS
160 DEF SEG = 7936
170 SCREEN 0,1,0,0
180 DIM PV(1000), WV(1000)
190 DIM TEMMV(1000), SEC(1000)
200 DIM WPLOT(1000), STPLOT(1000), TMV(1000)
210 DIM TT(1000), TPLOT(1000), PPLOT(1000)
220 DIM TEMPLOT(1000), PMV(1000), WMV(1000)
230 CLS
240 LOCATE 9,15,0

DATA ACQUISITION FOR POLYMER DIFFUSION APPARATUS

This program collects data from the POLYMER DIFFUSION APPARATUS
and stores it in a user specified datafile for further analyzation.
Differential weight readings from a Cahn Microbalance are on
channel 1. Temperature readings from a type J thermocouple are
on channel 2. Differential pressure readings from an electronic
pressure transmitter are on channel 3.

The user information requested is 1) The DATAFILE NAME where the
time and voltage readings will be stored, 2) The total TIME for
taking readings, 3) the TIME INTERVAL between each reading and
4) plotting parameters.

' Specifies where in memory to place PCTHERM.
' Specifies the TEXT screen mode.
' Clears memory for storage of arrays.

```

```

250 '
260 '
270 '
280 PRINT "DATA ACQUISITION FOR POLYMER DIFFUSION APPARATUS"
290 FOR I = 1 TO 2000 : NEXT I
300 CLS
310 LOCATE 1,15,1,0,6 : INPUT "ENTER THE DATAFILE NAME TO BE USED: " ; D$
320 OPEN D$ FOR OUTPUT AS #1
330 LOCATE 3,15 : INPUT "ENTER THE TOTAL SAMPLING TIME (MINUTES): " ; TM
340 LOCATE 5,15 : PRINT "ENTER THE TIME INTERVALS BETWEEN READINGS (SECONDS) "
350 LOCATE 6,15 : PRINT "AND THE NUMBER OF READINGS TAKEN AT EACH INTERVAL"
360 LOCATE 7,15 : INPUT "(3 SETS) : " ; DT1,N1,DT2,N2,DT3,N3
370 LOCATE 9,15 : PRINT "ENTER TEMP, PRESS AND WEIGHT RANGES (MV)"
380 LOCATE 10,15 : INPUT "FOR Y-AXIS : ";TEMMAX, PMAX,WMAX
390 LOCATE 12,15 : PRINT "ENTER STARTING POINTS FOR TEMP, PRES"
400 LOCATE 13,15 : INPUT "AND WEIGHT PLOTS : ";PT,PP,PW
410 LOCATE 15,15 : INPUT "ENTER NUMBER OF WEIGHT READINGS : ";WW
420 '
430 TGAIN% = 500
440 PGAIN% = 10
450 WGAING% = 500
460 '
470 T = TM*60
480 TCHAN% = 2
490 PCHAN% = 3
500 WCHAN% = 1
510 ANALOG.VALUE% = 0
520 ADC.VALUE = 3
530 HIGH.V! = +10
540 LOW.V! = -10
550 RANGE! = HIGH.V! - LOW.V!
560 NOC! = 4096
570 LSB! = RANGE!/NOC!

' Gains for input voltages.

' Converts minutes to seconds.

' Initialize all variables used
' in PCTHERM call statements.

' Specify range for bipolar input.
' Specify number of divisions.
' Least significant bit.

```

```

580 '
590 '
600 '
610 LOCATE 18,15 : PRINT "HIT THE 'SPACE BAR' TO START"
620 IF INKEY$="" THEN 630 ELSE 620
630 '
640 '
650 '
660 CLS
670 Z = 0
680 N = 0
690 DT = DT1
700 TIMES$ = "00:00:00"
710 IF N = N1+1 THEN DT = DT2 ELSE 730
720 N1 = N+N2-1 : N2 = N3 : DT2 = DT3
730 HR$ = MID$(TIMES$,1,2)
740 MIN$ = MID$(TIMES$,4,2)
750 SEC$ = MID$(TIMES$,7,2)
760 H = VAL(HR$)
770 M = VAL(MIN$)
780 S = VAL(SEC$)
790 SEC(N) = H*3600 + M*60 + S
800 IF Z = 0 THEN SEC(0) = SEC(N)
810 IF Z = 0 THEN 860
820 IF (SEC(N) - SEC(N-1)) < DT THEN 710
830 TT(N) = SEC(N) - SEC(0)
840 IF (SEC(N) - SEC(0)) > T THEN 1110
850 '
860 '
870 '
880 PLAY "o2 gl6"
890 SUMT=0 : SUMP=0 : SUMW=0
900 FOR I = 1 TO 100
910 CALL ADC.VALUE(TCHAN%,TGAIN%,ANALOG.VALUE%)
920 TVOLT! = (ANALOG.VALUE*LSB! + LOW.V!)/TGAIN%
930 SUMT = SUMT + TVOLT!
940 NEXT I

```

*** Start Readings ***

LOCATE 18,15 : PRINT "HIT THE 'SPACE BAR' TO START"

IF INKEY\$="" THEN 630 ELSE 620

*** Start Clock ***

CLS

Z = 0

N = 0

DT = DT1

TIMES\$ = "00:00:00"

IF N = N1+1 THEN DT = DT2 ELSE 730

N1 = N+N2-1 : N2 = N3 : DT2 = DT3

HR\$ = MID\$(TIMES\$,1,2)

MIN\$ = MID\$(TIMES\$,4,2)

SEC\$ = MID\$(TIMES\$,7,2)

H = VAL(HR\$)

M = VAL(MIN\$)

S = VAL(SEC\$)

SEC(N) = H*3600 + M*60 + S

IF Z = 0 THEN SEC(0) = SEC(N)

IF Z = 0 THEN 860

IF (SEC(N) - SEC(N-1)) < DT THEN 710

TT(N) = SEC(N) - SEC(0)

IF (SEC(N) - SEC(0)) > T THEN 1110

*** Take Data ***

PLAY "o2 gl6"

SUMT=0 : SUMP=0 : SUMW=0

FOR I = 1 TO 100

CALL ADC.VALUE(TCHAN%,TGAIN%,ANALOG.VALUE%)

TVOLT! = (ANALOG.VALUE*LSB! + LOW.V!)/TGAIN%

SUMT = SUMT + TVOLT!

NEXT I

' 1st time through label.

' Initialize counter.

' Set time increment between reading.

' Initialize time.

' Check for change in time increment.

' Read hours.

' Read minutes.

' Read seconds.

' Change strings to variables.

' Set initial seconds reading.

' Take 1st reading.

' Check time interval.

' Check for end of sampling period.

' Beep.

' Initialize sums for taking averages.

```

950 TEMMV(N) = SUMT/100*1000      ' Ave. 100 readings - convert to mv.
960 FOR I = 1 TO 100
970   CALL ADC.VALUE(PCHAN%,PGAIN%,ANALOG.VALUE%)
980   PVOLT! = (ANALOG.VALUE*LSB! + LOW.V!)/PGAIN%
990   SUMP = SUMP + PVOLT!
1000 NEXT I
1010 PMV(N) = SUMP/100*1000      ' Ave. 100 readings - convert to mv.
1020 FOR I = 1 TO WW
1030   CALL ADC.VALUE(WCHAN%,WGAIN%,ANALOG.VALUE%)
1040   WVOLT! = (ANALOG.VALUE*LSB! + LOW.V!)/WGAIN%
1050   SUMW = SUMW + WVOLT!
1060 NEXT I
1070 WMV(N) = SUMW/WW*1000
1080 WRITE #1, TT(N), TEMMV(N),
      PMV(N),WMV(N)
1090 GOSUB 1180
1100 GOTO 730
1110 CLOSE #1
1120 END
1130 ,
1140 ,
1150 ,
1160 ,
1170 ,
1180 MM = TT(N)\60
1190 SS = TT(N) MOD 60
1200 LOCATE 1,30 : PRINT "TIME = "; MM; "MIN "; SS; " SEC "
1210 LOCATE 2,30 : PRINT "TEMP = "; TEMMV(N); " MILLIVOLTS "
1220 LOCATE 3,30 : PRINT "PRES = "; PMV(N); " MILLIVOLTS "
1230 LOCATE 4,30 : PRINT "WEIGHT = "; WMV(N); " MILLIVOLTS "
1235 W = WW*10
1240 LOCATE 5,30 : PRINT "Y-AXIS = 0 TO +";W;"MG "

```

```

1250 SCREEN 2
1260 PSET(10,0)
1270 DRAW "D190 U10 R639"
1280 Y$ = "r4 l8"
1290 X$ = "u4 d8"
1300 FOR I = 180 TO 0 STEP -9
1310   PSET(10, INT(180-I))
1320   DRAW Y$
1330 NEXT I
1340 FOR I = 63 TO 630 STEP 63
1350   PSET(INT(10+I),180)
1360   DRAW X$
1370 NEXT I
1380 TMAX = TM
1390 STMAX = SQR(TM)
1400 STPLOT(N) = INT(10+SQR(TT(N)/60)*(630/STMAX) + .5) ' SQR time variable.
1410 TPLOT(N) = INT(10+(TT(N)/60)*(630/TMAX) +.5) ' Time variable.
1420 TEMPLOT(N) = INT(PT-TEMMV(N)*(PT/TEMMAX) + .5) ' Temp variable.
1430 PPLOT(N) = INT(PP-PMV(N)*(PP/PMAX) + .5) ' Pressure variable.
1440 WPLOT(N) = INT(PW-WMV(N)*(PW/WMAX) + .5) ' Weight variable.
1450 IF Z=0 THEN LINE (10,100) - (TPLOT(N), TEMPLOT(N))
      ELSE LINE (TPLOT(N-1), TEMPLOT(N-1)) - (TPLOT(N), TEMPLOT(N))
1460 IF Z=0 THEN LINE (10,100) - (TPLOT(N), PPLOT(N))
      ELSE LINE (TPLOT(N-1), PPLOT(N-1)) - (TPLOT(N), PPLOT(N))
1470 IF Z=0 THEN LINE (10,100) - (TPLOT(N), WPLOT(N))
      ELSE LINE (TPLOT(N-1), WPLOT(N-1)) - (TPLOT(N), WPLOT(N))
1480 '
1490 Z = 2
1500 N = N+1
1510 RETURN

```

APPENDIX B

APPENDIX B

Activity Data for Poly(vinyl Acetate)-Solvent SystemsTable B.1 Experimental Activity Data for Benzene, Chloroform and Toluene in Poly(vinyl Acetate)

<u>Solvent</u>	<u>Temperature</u>	<u>w_1</u>	<u>Ω_1</u>	<u>Reference</u>
Benzene	30	0.0803	4.174	[K6]
		0.0914	4.039	
		0.1113	3.764	[N1]
		0.026	9.192	
		0.116	3.698	
		0.178	3.360	
		0.215	3.247	
		0.312	2.696	
		0.407	2.214	
		0.497	1.911	
		0.551	1.782	
Chloroform	35	0.163	1.587	[J1]
		0.231	1.421	
		0.276	1.407	
		0.327	1.376	
		0.381	1.364	
		0.416	1.368	
		0.464	1.373	
Toluene	40	0.0513	6.831	[J1]
		0.0762	6.201	
		0.0890	5.936	
		0.0937	5.732	
		0.128	5.289	
		0.139	5.055	
		0.171	4.444	

Procedures for Determining Ω_1^∞ Values

The Ω_1^∞ values listed in Tables B.2 - B.4 have been determined by the following methods:

- 1a. Ω_1^∞ can be obtained from a single equilibrium solubility measurement of a trace of solvent in pure polymer using equation (45) and the following iteration procedure proposed by Misovich. Define

$$Y = w_1 + (e/\Omega_1^\infty)(1 - w_1) \quad (73)$$

and rearrange equation (45) as:

$$\Omega_1 = (1/Y) \exp \left[\frac{Y - w_1}{Y} \right] \quad (74)$$

Thus Y can be expressed as:

$$Y = \exp(1 - w_1/Y - \ln \Omega_1) \quad (75)$$

Take as an initial approximation

$$Y_0 = \exp(1 - \ln \Omega_1) \quad (76)$$

and define

$$Y_n = \exp(1 - w_1/Y_{n-1} - \ln \Omega_1) \quad (77)$$

When a convergent value is found for Y_n ,

Ω_1^∞ can be calculated from equation (73) as:

$$\Omega_1^\infty = \frac{e(1 - w_1)}{Y - w_1} \quad (78)$$

- 1b. Ω_1^∞ can also be obtained using as much activity data as possible and fitting equation (45) to the data.
2. Ω_1^∞ can be calculated from a Flory-Huggins interaction parameter, χ , using the following relation

given by Newman and Prausnitz [N3]:

$$\ln \Omega_1^\infty = \ln(\rho_2/\rho_1) + (1 - 1/r) + \chi \quad (79)$$

where r is the ratio of polymer molar volume to solvent molar volume. This relation assumes χ to be independent of concentration.

3. Ω_1^∞ can be determined experimentally by infinite dilution gas-liquid partition chromatography.

Table B.2 Infinite Dilution Weight Fraction Activity Coefficients for Poly(vinyl Acetate) Solutions Determined Using Procedures 1a and 1b.

Solvent	(°C)	Correlation		Ω_1	Ω_1^∞	"best"	Data
		Point#				Ω_1^∞	Source
Chloroform	35	0.163	1.59	1.65	1.48	[L1]	(7)
	45	0.093	1.48	1.45	1.44	[L1]	(16)
Toluene	35	0.084	6.08	9.28	9.83	[L1]	(4)
	40	0.051	6.83	8.85	9.36	[L1]	(7)
	47.5	0.052	6.51	8.32	8.91	[L1]	(3)
THF	42.6	0.064	6.30	8.55	7.29	[L1]	(2)
Isooctane	110	0.025	1.91	1.93	----	[B6]	
Vinyl Acetate	30	0.074	3.35	3.82	4.46	[N1]	(9)
Benzene	30	0.062	4.03	4.66	5.87	[N1]	(11)
Water*	30	0.012	36.7	55.0	----	[L2]	
	30	0.024	30.1	71.9	----	[L2]	
	39.8	0.0096	41.8	59.9	----	[L2]	
	39.8	0.014	37.8	63.8	----	[L2]	
	39.8	0.020	31.9	64.1	----	[L2]	
	39.8	0.035	22.9	67.3	----	[L2]	
	50.5	0.013	33.2	49.2	----	[L2]	
	50.5	0.022	30.2	63.7	----	[L2]	

* The experimental data for the water-poly(vinyl acetate) solutions show a wide variation in reported Ω_1 values. The accuracy of determining Ω_1 from this method is questionable. Also the ASOG-VSP model has not been verified for systems with such large enthalpic interactions.

solvent weight fraction

THF = Tetrahydrofuran

NOTE: number in parenthesis after data source indicates the number of data points

Table B.3 Infinite Dilution Weight Fraction Activity Coefficients for Poly(vinyl Acetate) Solutions Determined Using Procedure 2

<u>Solvent</u>	<u>Temp ($^{\circ}\text{C}$)</u>	<u>χ</u>	<u>Ω_1^{∞}</u>	<u>Data Source</u>
Acetone	30	0.32	5.70	[K6]
	40	0.35	5.92	
	50	0.38	6.15	
1-Propanol	30	1.30	14.86	[K6]
	40	1.13	12.59	
	50	1.04	11.56	
Benzene	30	0.30	5.01	[K6]
	40	0.36	5.35	
	50	0.26	4.87	
Allyl Chloride	40	0.27	4.60	[K6]
Propyl Chloride	40	0.75	7.98	[K6]
Propylamine	40	0.59	8.30	[K6]
Isopropylamine	40	0.66	9.30	[K6]
Methanol	15*	1.05	11.84	[K3]
	25*	1.11	12.35	
	35	1.19	13.55	

* below T_g of the pure polymer

Table B.4 Infinite Dilution Weight Fraction Activity
Coefficients for Poly(vinyl Acetate) Solutions
Determined Using Procedure 3 [N4]

<u>Solvent</u>	<u>100 °C</u>	<u>125 °C</u>	<u>150 °C</u>	<u>175 °C</u>	<u>200 °C</u>
Benzene	5.56	5.69	5.86	6.05	6.19
Toluene	6.40	6.42	6.42	6.60	6.78
Chloroform	1.84	1.97	2.16	2.34	2.56
1,2-Dichloroethane	2.68	2.86	3.01	3.20	3.46
Isopropyl Alcohol		8.02	7.36	7.03	6.60
n-Butyl Alcohol		7.13	6.56	6.10	5.86
Methyl Ethyl Ketone		6.38	6.34	6.37	6.50
Methyl Isobutyl Ketone		8.22	8.39	8.40	8.62
Cyclohexanone		4.58	4.63	4.67	4.75
Methyl Cellusolve		6.20	6.20	6.26	6.46
Cellusolve Solvent		5.84	6.04	6.05	6.29
Ethyl Acetate		5.78	5.92	6.04	6.21
Vinyl Acetate		5.45	5.71	5.98	6.47
n-Butyl Acetate		6.55	6.88	7.10	7.25

APPENDIX C

APPENDIX C

Predicted Diffusivity Data for Poly(vinyl Acetate)-Solvent SolutionsTable C.1 Chloroform-Poly(vinyl Acetate) Diffusivity Data PredictionsT = 50 °C P^{vap} = 513 mm Hg

<u>w₁</u>	<u>a₁</u>	<u>P₁</u>	<u>D(F-H)</u>	<u>D(ASOG-VSP)</u>	<u>Δ</u>	<u>L(cm)</u>	<u>t_h</u>
0.05	1.47	38	6.11x10 ⁻¹⁰	5.96x10 ⁻¹⁰	-2%	0.03	20 hrs
0.10	1.46	75	7.27x10 ⁻⁹	6.92x10 ⁻⁹	-7%	0.03	1.8 hrs
0.20	1.44	148	1.03x10 ⁻⁷	9.43x10 ⁻⁸	-8%	0.03	8 min
0.30	1.42	219	3.93x10 ⁻⁷	3.46x10 ⁻⁷	-12%	0.15	53 min
0.40	1.39	285	8.19x10 ⁻⁷	6.96x10 ⁻⁷	-15%	0.15	26 min
0.50	1.35	346	1.20x10 ⁻⁶	9.91x10 ⁻⁷	-17%	0.15	19 min
0.60	1.30	400	1.36x10 ⁻⁶	1.10x10 ⁻⁶	-19%	0.15	17 min
0.70	1.23	442	1.21x10 ⁻⁶	9.56x10 ⁻⁷	-21%	0.15	19 min
0.80	1.17	480	7.88x10 ⁻⁷	6.14x10 ⁻⁷	-22%	0.15	30 min

T = 70 °C P^{vap} = 998 mm Hg

<u>w₁</u>	<u>a₁</u>	<u>P₁</u>	<u>D(F-H)</u>	<u>D(ASOG-VSP)</u>	<u>Δ</u>	<u>L(cm)</u>	<u>t_h</u>
0.05	1.62	81	1.04x10 ⁻⁸	1.01x10 ⁻⁸	-3%	0.20	54 hrs
0.10	1.60	160	6.01x10 ⁻⁸	5.73x10 ⁻⁸	-5%	0.20	10 hrs
0.20	1.56	311	4.44x10 ⁻⁷	4.07x10 ⁻⁷	-8%	0.20	1.3 hrs
0.30	1.52	455	1.27x10 ⁻⁶	1.13x10 ⁻⁶	-11%	0.20	30 min
0.40	1.47	587	2.28x10 ⁻⁶	1.95x10 ⁻⁶	-14%	0.20	16 min
0.50	1.41	704	3.04x10 ⁻⁶	2.59x10 ⁻⁶	-15%	0.20	13 min
0.60	1.34	802	3.23x10 ⁻⁶	2.64x10 ⁻⁶	-18%	0.20	13 min
0.70	1.27	887	2.75x10 ⁻⁶	2.21x10 ⁻⁶	-20%	0.20	15 min
0.80	1.19	950	1.73x10 ⁻⁶	1.37x10 ⁻⁶	-21%	0.20	23 min

Table C.1 (cont'd)

$T = 90^{\circ}\text{C}$ $P^{\text{vap}} = 1792 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	t_h
0.05	1.77	159	8.23×10^{-8}	8.04×10^{-8}	-2%	0.20	6.8 hrs
0.10	1.74	312	3.07×10^{-7}	2.95×10^{-7}	-4%	0.20	1.9 hrs
0.20	1.67	599	1.48×10^{-6}	1.36×10^{-6}	-8%	0.20	24 min
0.30	1.61	866	3.45×10^{-6}	3.07×10^{-6}	-11%	0.20	11 min
0.40	1.53	1097	5.49×10^{-6}	4.74×10^{-6}	-14%	0.20	6.9 min
0.50	1.47	1317	6.81×10^{-6}	5.74×10^{-6}	-16%	0.20	5.7 min
0.60	1.37	1473	6.88×10^{-6}	5.70×10^{-6}	-17%	0.20	5.7 min
0.70	1.28	1606	5.64×10^{-6}	4.61×10^{-6}	-18%	0.20	7.1 min
0.80	1.20	1720	3.45×10^{-6}	2.80×10^{-6}	-19%	0.20	12 min

$T = 110^{\circ}\text{C}$ $P^{\text{vap}} = 3035 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	t_h
0.05	1.85	281	4.08×10^{-7}	3.99×10^{-7}	-2%	0.25	2.1 hrs
0.10	1.80	546	1.14×10^{-6}	1.09×10^{-6}	-4%	0.25	47 min
0.20	1.73	1050	4.05×10^{-6}	3.74×10^{-6}	-8%	0.25	14 min
0.30	1.65	1502	8.12×10^{-6}	7.26×10^{-6}	-11%	0.25	7.0 min
0.40	1.57	1906	1.18×10^{-5}	1.03×10^{-5}	-13%	0.25	5.0 min
0.50	1.49	2261	1.38×10^{-5}	1.18×10^{-5}	-14%	0.25	4.3 min
0.60	1.39	2531	1.24×10^{-5}	1.13×10^{-5}	-16%	0.25	4.5 min
0.70	1.29	2741	1.06×10^{-5}	8.86×10^{-6}	-16%	0.25	5.8 min
0.80	1.20	2914	6.32×10^{-6}	5.26×10^{-6}	-17%	0.25	9.7 min

Table C.1 (cont'd)

$T = 130^{\circ}\text{C}$ $P^{\text{vap}} = 4818 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	$t_{\frac{1}{2}}$
0.05	2.01	484	1.47×10^{-6}	1.44×10^{-6}	-2%	0.30	51 min
0.10	1.91	920	3.38×10^{-6}	3.25×10^{-6}	-4%	0.30	23 min
0.20	1.81	1744	9.60×10^{-6}	8.90×10^{-6}	-7%	0.30	8.3 min
0.30	1.72	2486	1.71×10^{-5}	1.54×10^{-5}	-10%	0.30	4.8 min
0.40	1.61	3103	2.31×10^{-5}	2.04×10^{-5}	-12%	0.30	3.6 min
0.50	1.52	3662	2.57×10^{-5}	2.23×10^{-5}	-13%	0.30	3.3 min
0.60	1.42	4105	2.40×10^{-5}	2.07×10^{-5}	-14%	0.30	3.6 min
0.70	1.31	4418	1.85×10^{-5}	1.59×10^{-5}	-14%	0.30	4.6 min
0.80	1.20	4625	1.08×10^{-5}	9.27×10^{-6}	-14%	0.30	7.9 min

- NOTE:
1. Units on P_1 are mm Hg.
 2. Δ = difference between $D(\text{ASOG-VSP})$ and $D(\text{F-H})$.
 3. $t_{\frac{1}{2}} = (0.049L^2/D)$ using $D(\text{ASOG-VSP})$.
 4. Units on D are cm^2/sec .

Table C.2 Acetone-Poly(vinyl Acetate) Diffusivity Data Predictions

$T = 50^{\circ}\text{C}$ $P^{\text{vap}} = 613 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	$t_{\frac{1}{2}}$
0.05	5.27	162	1.80×10^{-9}	1.57×10^{-9}	-13%	0.04	14 hrs
0.10	4.51	276	1.14×10^{-8}	1.06×10^{-8}	-7%	0.04	2.1 hrs
0.20	3.44	422	4.18×10^{-8}	4.48×10^{-8}	+7%	0.04	29 min
0.30	2.74	504	5.64×10^{-8}	6.93×10^{-8}	+23%	0.04	19 min
0.40	2.25	552	5.19×10^{-8}	7.33×10^{-8}	+41%	0.04	18 min
0.50	1.89	579	3.85×10^{-8}	6.26×10^{-8}	+63%	0.04	21 min
0.60	1.62	596	2.41×10^{-8}	4.53×10^{-8}	+88%	0.04	29 min
0.70	1.41	605	1.25×10^{-8}	2.74×10^{-8}	+119%	0.04	48 min
0.80	1.24	608	4.92×10^{-9}	1.27×10^{-8}	+158%	0.04	1.7 hrs

$T = 70^{\circ}\text{C}$ $P^{\text{vap}} = 1190 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	$t_{\frac{1}{2}}$
0.05	5.27	314	2.87×10^{-8}	2.71×10^{-8}	-6%	0.10	5.0 hrs
0.10	4.51	537	1.09×10^{-7}	1.10×10^{-7}	+1%	0.10	1.2 hrs
0.20	3.44	819	2.85×10^{-7}	3.31×10^{-7}	+16%	0.10	25 min
0.30	2.74	978	3.39×10^{-7}	4.52×10^{-7}	+33%	0.10	18 min
0.40	2.25	1071	2.92×10^{-7}	4.49×10^{-7}	+54%	0.10	18 min
0.50	1.89	1125	2.09×10^{-7}	3.70×10^{-7}	+77%	0.10	22 min
0.60	1.62	1157	1.27×10^{-7}	2.26×10^{-7}	+106%	0.10	31 min
0.70	1.41	1175	6.47×10^{-7}	1.56×10^{-7}	+141%	0.10	52 min
0.80	1.24	1180	2.51×10^{-8}	7.12×10^{-8}	+184%	0.10	1.9 hrs

Table C.2 (cont'd)

$T = 90^{\circ}\text{C}$ $p^{\text{vap}} = 2142 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	t_h
0.05	5.27	564	2.73×10^{-7}	2.76×10^{-7}	+1%	0.15	1.1 hrs
0.10	4.51	966	7.45×10^{-7}	8.08×10^{-7}	+8%	0.15	23 min
0.20	3.44	1474	1.51×10^{-6}	1.90×10^{-6}	+26%	0.15	9.7 min
0.30	2.74	1761	1.62×10^{-6}	2.36×10^{-6}	+46%	0.15	7.8 min
0.40	2.25	1928	1.33×10^{-6}	2.23×10^{-6}	+68%	0.15	8.2 min
0.50	1.89	2024	9.16×10^{-7}	1.79×10^{-6}	+95%	0.15	10 min
0.60	1.62	2082	5.45×10^{-7}	1.24×10^{-6}	+133%	0.15	15 min
0.70	1.41	2114	2.73×10^{-7}	7.26×10^{-7}	+166%	0.15	25 min
0.80	1.24	2125	1.05×10^{-7}	3.29×10^{-7}	+213%	0.15	56 min

$T = 110^{\circ}\text{C}$ $p^{\text{vap}} = 3594 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	t_h
0.05	5.27	947	1.80×10^{-6}	1.94×10^{-6}	+8%	0.25	26 min
0.10	4.51	1621	3.91×10^{-6}	4.52×10^{-6}	+16%	0.25	11 min
0.20	3.44	2473	6.56×10^{-6}	8.86×10^{-6}	+35%	0.25	5.8 min
0.30	2.74	2954	6.50×10^{-6}	1.02×10^{-5}	+57%	0.25	5.0 min
0.40	2.25	3235	5.08×10^{-6}	9.31×10^{-6}	+83%	0.25	5.5 min
0.50	1.89	3396	3.41×10^{-6}	7.27×10^{-6}	+113%	0.25	7.0 min
0.60	1.62	3493	1.99×10^{-6}	4.96×10^{-6}	+149%	0.25	10 min
0.70	1.41	3547	9.81×10^{-7}	2.88×10^{-6}	+194%	0.25	18 min
0.80	1.24	3565	3.72×10^{-7}	1.29×10^{-6}	+247%	0.25	40 min

Table C.2 (cont'd)

$T = 130^{\circ}\text{C}$ $P^{\text{vap}} = 5670 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	$t_{\frac{1}{2}}$
0.05	5.27	1494	9.11×10^{-6}	1.04×10^{-5}	+13%	0.40	13 min
0.10	4.51	2557	1.66×10^{-5}	2.04×10^{-5}	+23%	0.40	6.4 min
0.20	3.44	3901	2.41×10^{-5}	3.49×10^{-5}	+45%	0.40	3.7 min
0.30	2.74	4661	2.23×10^{-5}	3.80×10^{-5}	+70%	0.40	3.4 min
0.40	2.25	5103	1.68×10^{-5}	3.35×10^{-5}	+99%	0.40	3.9 min
0.50	1.89	5358	1.10×10^{-5}	2.56×10^{-5}	+133%	0.40	5.1 min
0.60	1.62	5511	6.27×10^{-5}	1.73×10^{-5}	+176%	0.40	7.6 min
0.70	1.41	5596	3.06×10^{-5}	9.92×10^{-6}	+224%	0.40	13 min
0.80	1.24	5625	1.15×10^{-5}	4.42×10^{-6}	+284%	0.40	30 min

- NOTE:
1. Units on P_1 are mm Hg.
 2. Δ = difference between $D(\text{ASOG-VSP})$ and $D(\text{F-H})$.
 3. $t_{\frac{1}{2}} = (0.049L^2/D)$ using $D(\text{ASOG-VSP})$.
 4. Units on D are cm^2/sec .

Table C.2 Toluene-Poly(vinyl Acetate) Diffusivity Data Predictions

$T = 50^{\circ}\text{C}$ $P^{\text{vap}} = 91.6 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	t_z
0.05	5.43	24.9	1.76×10^{-10}	1.64×10^{-10}	-7%	0.01	8.3 hrs
0.10	4.63	42.4	5.13×10^{-9}	4.61×10^{-9}	-10%	0.01	18 min
0.20	3.50	64.1	6.82×10^{-8}	6.13×10^{-8}	-10 ⁵	0.10	2.2 hrs
0.30	2.76	75.8	1.46×10^{-7}	1.47×10^{-7}	+1%	0.10	55 min
0.40	2.26	82.8	1.43×10^{-7}	1.90×10^{-7}	+33%	0.10	43 min
0.50	1.89	86.6	7.16×10^{-8}	1.78×10^{-7}	+149%	0.10	46 min
0.60	1.62	89.0		1.35×10^{-7}		0.10	60 min
0.70	1.41	90.4		8.28×10^{-8}		0.10	1.6 hrs
0.80	1.24	90.9		3.84×10^{-8}		0.10	3.5 hrs

$T = 70^{\circ}\text{C}$ $P^{\text{vap}} = 203 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	t_z
0.05	5.43	55.1	1.57×10^{-9}	1.53×10^{-9}	-3%	0.01	53 min
0.10	4.63	94.0	1.94×10^{-8}	1.90×10^{-8}	-2%	0.10	43 min
0.20	3.50	142	1.42×10^{-7}	1.48×10^{-7}	+4%	0.10	55 min
0.30	2.76	168	2.43×10^{-7}	2.97×10^{-7}	+22%	0.10	28 min
0.40	2.26	184	2.12×10^{-7}	3.55×10^{-7}	+67%	0.10	23 min
0.50	1.89	192	9.79×10^{-8}	3.21×10^{-7}	+228%	0.10	25 min
0.60	1.62	197		2.37×10^{-7}		0.10	34 min
0.70	1.41	200		1.44×10^{-7}		0.10	57 min
0.80	1.24	201		6.63×10^{-8}		0.10	2.1 hrs

Table C.3 (cont'd)

$T = 90^{\circ}\text{C}$ $P^{\text{vap}} = 404 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	t_z
0.05	5.43	110	7.53×10^{-9}	7.58×10^{-9}	+1%	0.02	43 min
0.10	4.63	187	5.33×10^{-8}	5.50×10^{-8}	+3%	0.10	2.5 hrs
0.20	3.50	283	2.56×10^{-7}	2.93×10^{-7}	+14%	0.10	28 min
0.30	2.76	335	3.69×10^{-7}	5.15×10^{-7}	+40%	0.10	16 min
0.40	2.26	365	2.93×10^{-7}	5.78×10^{-7}	+97%	0.10	14 min
0.50	1.89	382	1.27×10^{-7}	5.06×10^{-7}	+298%	0.10	16 min
0.60	1.62	393		3.68×10^{-7}		0.10	22 min
0.70	1.41	399		2.21×10^{-7}		0.10	36 min
0.80	1.24	401		1.01×10^{-7}		0.10	1.3 hrs

$T = 110^{\circ}\text{C}$ $P^{\text{vap}} = 743 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	t_z
0.05	5.43	202	2.45×10^{-8}	2.52×10^{-8}	+2%	0.10	5.4 hrs
0.10	4.63	344	1.18×10^{-7}	1.25×10^{-7}	+9%	0.10	1.1 hrs
0.20	3.50	520	4.11×10^{-7}	4.99×10^{-7}	+21%	0.10	17 min
0.30	2.76	615	5.20×10^{-7}	7.85×10^{-7}	+51%	0.10	10 min
0.40	2.26	672	3.83×10^{-7}	8.35×10^{-7}	+118%	0.10	10 min
0.50	1.89	702	1.55×10^{-7}	7.09×10^{-7}	+357%	0.10	12 min
0.60	1.62	722		5.06×10^{-7}		0.10	16 min
0.70	1.41	733		3.00×10^{-7}		0.10	28 min
0.80	1.24	737		1.36×10^{-7}		0.10	61 min

Table C.3 (cont'd)

$T = 130^{\circ}\text{C}$ $P^{\text{vap}} = 2260 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	$t_{\frac{1}{2}}$
0.05	5.43	614	6.17×10^{-8}	6.34×10^{-8}	+3%	0.15	4.8 hrs
0.10	4.63	1046	2.23×10^{-7}	2.39×10^{-7}	+7%	0.15	1.3 hrs
0.20	3.50	1582	6.09×10^{-7}	7.51×10^{-7}	+23%	0.15	24 min
0.30	2.76	1871	6.90×10^{-7}	1.07×10^{-6}	+55%	0.15	17 min
0.40	2.26	2043	4.75×10^{-7}	1.07×10^{-6}	+125%	0.15	17 min
0.50	1.89	2136	1.81×10^{-7}	8.81×10^{-7}	+387%	0.15	21 min
0.60	1.62	2197		6.14×10^{-7}		0.15	30 min
0.70	1.41	2231		3.59×10^{-7}		0.15	51 min
0.80	1.24	2242		1.61×10^{-7}		0.15	1.9 hrs

- NOTE:
1. Units on P_1 are mm Hg.
 2. Δ = difference between $D(\text{ASOG-VSP})$ and $D(\text{F-H})$.
 3. $t_{\frac{1}{2}} = (0.049L^2/D)$ using $D(\text{ASOG-VSP})$.
 4. Units on D are cm^2sec .

Table C.4 Methanol-Poly(vinyl Acetate) Diffusivity Data Predictions

$T = 50^{\circ}\text{C}$ $p^{\text{vap}} = 413 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	$t_{1/2}$
0.05	9.18	190	7.53×10^{-8}	5.76×10^{-8}	-24%	0.10	2.4 hrs
0.10	6.78	280	2.82×10^{-7}	1.77×10^{-7}	-37%	0.10	46 min
0.20	4.33	358	8.02×10^{-7}	4.02×10^{-7}	-50%	0.10	20 min
0.30	3.12	387	9.24×10^{-7}	4.53×10^{-7}	-51%	0.10	18 min
0.40	2.42	400	6.19×10^{-7}	3.83×10^{-7}	-38%	0.10	21 min
0.50	1.97	407	1.78×10^{-7}	2.75×10^{-7}	+96%	0.10	30 min
0.60	1.65	409		1.72×10^{-7}		0.10	47 min
0.70	1.42	411		9.21×10^{-8}		0.10	1.5 hrs
0.80	1.25	413		3.83×10^{-8}		0.10	3.6 hrs

$T = 70^{\circ}\text{C}$ $p^{\text{vap}} = 932 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	$t_{1/2}$
0.05	9.18	428	2.12×10^{-7}	1.69×10^{-7}	-20%	0.10	48 min
0.10	6.78	632	4.97×10^{-7}	3.34×10^{-7}	-33%	0.10	24 min
0.20	4.33	807	9.52×10^{-7}	5.35×10^{-7}	-44%	0.10	15 min
0.30	3.12	872	9.24×10^{-7}	5.25×10^{-7}	-43%	0.10	16 min
0.40	2.42	902	5.61×10^{-7}	4.14×10^{-7}	-26%	0.10	20 min
0.50	1.97	918	1.46×10^{-7}	2.86×10^{-7}	+96%	0.10	29 min
0.60	1.65	923		1.74×10^{-7}		0.10	47 min
0.70	1.42	926		9.16×10^{-8}		0.10	1.5 hrs
0.80	1.25	932		3.77×10^{-8}		0.10	3.6 hrs

Table C.4 (cont'd)

$T = 90^{\circ}\text{C}$ $P^{\text{vap}} = 1901 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	t_b
0.05	9.18	873	4.01×10^{-7}	3.31×10^{-7}	-17%	0.10	25 min
0.10	6.78	1289	7.08×10^{-7}	5.10×10^{-7}	-28%	0.10	16 min
0.20	4.33	1646	1.04×10^{-6}	6.53×10^{-7}	-37%	0.10	13 min
0.30	3.12	1779	8.90×10^{-7}	5.85×10^{-7}	-34%	0.10	14 min
0.40	2.42	1840	4.99×10^{-7}	4.41×10^{-7}	-12%	0.10	19 min
0.50	1.97	1872	1.18×10^{-7}	2.96×10^{-7}	+151%	0.10	28 min
0.60	1.65	1882		1.78×10^{-7}		0.10	46 min
0.70	1.42	1890		9.25×10^{-8}		0.10	1.5 hrs
0.80	1.25	1901		3.77×10^{-8}		0.10	3.6 hrs

$T = 110^{\circ}\text{C}$ $P^{\text{vap}} = 3566 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	t_b
0.05	9.18	1637	6.03×10^{-7}	5.14×10^{-7}	-15%	0.10	16 min
0.10	6.78	2418	8.83×10^{-7}	6.75×10^{-7}	-24%	0.10	12 min
0.20	4.33	3088	1.07×10^{-6}	7.47×10^{-7}	-30%	0.10	11 min
0.30	3.12	3338	8.31×10^{-7}	6.62×10^{-7}	-24%	0.10	13 min
0.40	2.42	3452	4.34×10^{-7}	4.59×10^{-7}	+6%	0.10	18 min
0.50	1.97	3513	9.05×10^{-8}	3.03×10^{-7}	+235%	0.10	27 min
0.60	1.65	3530		1.80×10^{-7}		0.10	45 min
0.70	1.42	3545		9.27×10^{-8}		0.10	1.5 hrs
0.80	1.25	3566		3.76×10^{-8}		0.10	3.6 hrs

Table C.4 (cont'd)

$T = 130^{\circ}\text{C}$ $p^{\text{vap}} = 6237 \text{ mm Hg}$

w_1	a_1	P_1	$D(\text{F-H})$	$D(\text{ASOG-VSP})$	Δ	$L(\text{cm})$	$t_{\frac{1}{2}}$
0.05	9.18	2863	7.86×10^{-7}	6.92×10^{-7}	-12%	0.10	12 min
0.10	6.78	4229	1.01×10^{-6}	8.17×10^{-7}	-19%	0.10	10 min
0.20	4.33	5401	1.06×10^{-6}	8.20×10^{-7}	-23%	0.10	10 min
0.30	3.12	5857	7.61×10^{-7}	6.61×10^{-7}	-13%	0.10	12 min
0.40	2.42	6037	3.33×10^{-7}	4.73×10^{-7}	+27%	0.10	17 min
0.50	1.97	6143	6.69×10^{-8}	3.08×10^{-7}	+360%	0.10	27 min
0.60	1.65	6175		1.82×10^{-7}		0.10	45 min
0.70	1.42	6200		9.34×10^{-8}		0.10	1.5 hrs
0.80	1.25	6237		3.78×10^{-8}		0.10	3.6 hrs

- NOTE:
1. Units on P_1 are mm Hg.
 2. Δ = difference between $D(\text{ASOG-VSP})$ and $D(\text{F-H})$.
 3. $t_{\frac{1}{2}} = (0.049L^2/D)$ using $D(\text{ASOG-VSP})$.
 4. Units on D are cm^2/sec .

Table C.5 Free Volume Parameters for Figures 4.7 - 4.10 and Tables C.1 - C.4

	Chloroform- PVAC	Acetone- PVAC	Toluene- PVAC	Methanol- PVAC
$\hat{V}_1^*$ (cm^3/g)	0.510 a	0.978 b	0.917 a	0.963 c
$\hat{V}_2^*$ (cm^3/g)	0.749 a	0.749 a	0.749 a	0.749 a
K_{11}/β ($\text{cm}^3/\text{g K}$)	9.73×10^{-4} a	1.92×10^{-3} d	2.21×10^{-3} a	1.17×10^{-3} c
K_{12}/β ($\text{cm}^3/\text{g K}$)	4.45×10^{-4} a	4.45×10^{-4} a	4.45×10^{-4} a	4.45×10^{-4} a
K_{21}^{-T} (K)	-61.2 a	-53.3 a	-103 a	-47.9 a
K_{22}^{-T} (K)	-256 a	-256 a	-256 a	-256 a
β	0.65 a	0.53 f	0.87 a	0.45 c
E_A (kcal/gmole)	6.850 a	16.664 f	0.740 a	-4.800 c
D_O (cm^2/sec)	3.90 a	$1.07 \times 10^{+6}$ f	2.15×10^{-4} a	1.99×10^{-7} c
χ	-0.5 a	0.38 g	0.75 a	1.19 h
Ω_1^∞ (130 °C)	2.01 i	6.25 j	6.4 k	8.6 l
	(110 °C)	6.25 j	6.4 k	9.4 l
	(90 °C)	6.25 j	6.8 k	10.3 l
	(70 °C)	6.25 j	7.6 k	11.4 l
	(50 °C)	6.25 j	8.9 k	12.6 l

Table C.5 (cont'd)

Solvent	$\hat{V}_1^o$ (50 °C)	$\hat{V}_1^o$ (70 °C)	$\hat{V}_1^o$ (90 °C)	$\hat{V}_1^o$ (110 °C)	$\hat{V}_1^o$ (130 °C)
Chloroform ^m	0.701	0.721	0.743	0.768	0.796
Acetone ^m	1.323 ⁿ	1.362 ^o	1.416 ^o	1.473 ^o	1.538 ^o
Toluene ^m	1.193	1.221	1.252	1.285	1.323
Methanol ⁿ	1.307	1.340	1.379	1.425	1.477
PVAc ^p	0.855	0.867	0.881	0.894	0.907

NOTE:

PVAc = poly(vinyl acetate)

a - [J1]

b - calculated using equation (12) and Goldheimer's method of estimating densities [L4]:

$$\rho_{mp} = \rho_{bp} (1 - T_r) / (1 - T_{br})^n \quad (80)$$

where $T_r = T/T_c$ and $T_{br} = T_b/T_c$

for acetone:

$$T_c = 509.1 \text{ K}$$

$$T_b = 329.7 \text{ K}$$

$$n = 0.31$$

c - [J2]

Table C.5 (cont'd)

d - calculated using $\hat{V}_1^*/K_{11} = 508 \text{ K}$ and $\hat{V}_1^0$ calculated above in b
e - [L1]
f - calculated using equations (2), (3), (4), (6), (10) and (11) and three diffusivity data points from [K5]:

$D(\text{cm}^2/\text{sec})$	$T(\text{K})$	w_1
2.52×10^{-10}	303.15	0.08
1.26×10^{-9}	313.15	0.08
7.94×10^{-10}	323.15	0.04

g - [K6]
h - [K3]
i - interpolated from experimental Ω_1^∞ data from [N4]
j - determined by fitting equation (45) to experimental activity data for acetone-poly(vinyl acetate) solutions from [K6]
k - interpolated from experimental Ω_1^∞ data at high temperatures from [N4] and calculated Ω_1^∞ data from Table B.2
l - estimated using the following technique:

- 1) combined infinite dilution activity coefficient data for n-propyl alcohol and isopropyl alcohol are fit to a model of the form

$$\Omega_1^\infty = G_3 + G_4/T \tag{81}$$

Table C.5 (cont'd)

2) a curve for methanol Ω_1^∞ values versus temperature is generated using G_1 calculated above and one data point for methanol ($\Omega_1^\infty = 13.455$ at $T = 35^\circ\text{C}$ from Table B.3) to compute a value of G_3 for methanol

m - calculated using density equation given in [Y1]

$$\rho = [\text{QB}]^{-(1 - T_r)^{2/7}} \quad (82)$$

for chloroform	$Q = 0.5165$	$B = 0.2666$	$T_c = 536.6 \text{ K}$
for toluene	$Q = 0.2883$	$B = 0.2624$	$T_c = 591.3 \text{ K}$

n - [P4]

o - [L1]

p - [B8]

APPENDIX D

APPENDIX D

Maximum in Diffusivity versus Solvent Weight Fraction CurvesASOG-VSP Free Volume Theory

The binary mutual diffusion coefficient is given as:

$$D = D_o \exp(-E_A/RT) \left[\frac{(e/\Omega_1^\infty)w_2}{w_1 + (e/\Omega_1^\infty)w_2} \right]^2 \exp \left[- \frac{w_1 \hat{V}_1^* + w_2 \xi \hat{V}_2^*}{\hat{V}_{FH}/\xi} \right] \quad (83)$$

where

$$\hat{V}_{FH}/\xi = w_1 (K_{11}/\xi) (K_{21} + T - T_{g1}) + w_2 (K_{12}/\xi) (K_{22} + T - T_{g2}) \quad (84)$$

Equations (83) and (84) can be rewritten as:

$$D = c \left[\frac{d(1-w_1)}{d + (1-d)w_1} \right] \exp \left[\frac{(f-g)w_1 + g}{b + (a-b)w_1} \right] \quad (85)$$

$$\text{where } a = (K_{11}/\xi) (K_{21} + T - T_{g1}) \quad (86)$$

$$b = (K_{12}/\xi) (K_{22} + T - T_{g2}) \quad (87)$$

$$c = D_o \exp(E_A/RT) \quad (88)$$

$$d = (e/\Omega_1^\infty) \quad (89)$$

$$f = - \hat{V}_1^* \quad (90)$$

$$g = - \xi \hat{V}_2^* \quad (91)$$

Thus the partial derivative of equation (85) with respect to solvent weight fraction is:

$$\frac{\partial D}{\partial w_1} = c \exp \left[\frac{(f-g)w_1 + g}{b + (a-b)w_1} \right] \left[\frac{d(1-w_1)}{d + (1-d)w_1} \right] \times \left\{ d(1-w_1) \left[\frac{bf - ga}{[b + (a-b)w_1]^2} \right] - \left[\frac{2d}{d + (1-d)w_1} \right] \right\} \quad (92)$$

Equation (92) is set equal to zero and solved for w_1 to find the solvent weight fraction at the maximum diffusivity

yielding the following result:

$$w_1 = \frac{-i \pm \sqrt{i^2 - 4hj}}{2h} \quad (93)$$

$$\text{where } h = 2(a-b)^2 + (bf - ga)(1-d) \quad (94)$$

$$i = 4b(a-b) - (bf - ga)(1-2d) \quad (95)$$

$$j = 2b^2 - d(bf - ga) \quad (96)$$

Flory-Huggins Free Volume Theory

The binary mutual diffusion coefficient is given as:

$$D = D_0 \exp(-E_A/RT) (1-\phi_1)^2 (1-2\chi\phi_1) \exp \left[- \frac{w_1 \hat{V}_1^* + w_2 \hat{V}_2^*}{\hat{V}_{FH}/\xi} \right] \quad (97)$$

where $\hat{V}_{FH}/\xi$ is as defined above and

$$\phi_1 = \frac{w_1 \hat{V}_1^0}{w_1 \hat{V}_1^0 + w_2 \hat{V}_2^0} \quad (98)$$

Equations (84), (97) and (98) can be rewritten as:

$$D = c \left[1 - \frac{kw_1}{m + (k-m)w_1} \right]^2 \left[1 - \frac{2\chi kw_1}{m + (k-m)w_1} \right] \times \exp \left[\frac{(f-g)w_1 + g}{b + (a-b)w_1} \right] \quad (99)$$

where a, b, c, f , and g are as defined above and

$$k = \hat{V}_1^0 \quad (100)$$

$$m = \hat{V}_2^0 \quad (101)$$

Thus the partial derivative of equation (99) with respect to solvent weight fraction is:

$$\frac{\partial D}{\partial w_1} = n[p^2(qr + s) + 2qt] \quad (102)$$

where

$$n = c \exp \left[\frac{(f-g)w_1 + g}{b + (a-b)w_1} \right] \quad (103)$$

$$p = 1 - \frac{kw_1}{m + (k-m)w_1} \quad (104)$$

$$q = 1 - \frac{2\chi kw_1}{m + (k-m)w_1} \quad (105)$$

$$r = \frac{bf - ga}{[b + (a-b)w_1]^2} \quad (106)$$

$$s = - \frac{2\chi km}{[m + (k-m)w_1]^2} \quad (107)$$

$$t = - \frac{km}{[m + (k-m)w_1]^2} \quad (108)$$

Equation (102) is set equal to zero and solved for w_1 to find the solvent weight fraction at the maximum diffusivity.

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