Effects of Thermodynamic Models on the Predictions of Free Volume Diffusion Theory for Concentrated Polymer Solutions

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Synopsis

Three thermodynamic models were used to demonstrate the effects of model choice on solvent–polymer binary diffusion coefficients predicted by free volume theory. Poly(vinyl acetate) and four solvents were used as typical solutions for these calculations. Thermodynamic models affect the predictions the most at high solvent weight fractions and for solutions which exhibit positive enthalpic interactions. For solutions dilute in solvent where Henry's law might describe phase equilibria, diffusion coefficients can be estimated without reference to thermodynamic data.

INTRODUCTION

There are a number of polymer processes in which the key problem is manipulating solvents into or out of polymer solutions. Much of the current information on solvent activity and diffusion coefficients for such processes has been developed for binary systems. Typical industrial problems include the removal of monomers from molten homopolymers at high temperatures and the removal of solvents from adhesive films. Commercial devolatilization equipment often can be operated so as to generate more gas–polymer interfacial area (bubble formation or foaming) or to move polymer fluid elements past the existing interfacial area at a higher frequency Both approaches are effective in reducing the rate limitation caused by low solute diffusivities through quiescent polymer films. The results of this study are most important to design of devolatilization processes in which bubble formation or extensive mixing are not desirable. In addition to the binary system problems, there are a number of ternary systems of industrial importance: solvent–solvent–polymer and polymer–polymer–solvent. Researchers have developed the thermodynamic and mass transfer descriptions of binary systems separately, but in free volume diffusion theory, both kinds of information are needed to predict the diffusion coefficients. The thermodynamic model choice can affect binary diffusion coefficient predictions and may also affect the extension of binary system models to ternary systems. The purpose of this article is to illustrate the impact of the thermodynamic model choice on the predicted diffusion coefficients in binary systems. The three models considered are Flory-Huggins, Henry's law, and variable size parameter (VSP).

Vrentas, Duda and co-workers 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.[1,2] 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 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 polymer.[3]

Henry's law is a popular choice of thermodynamic model for dilute solvents in molten polymers. A number of investigators have measured Henry's law constants for binary systems over a range of temperatures. These data are usually available and can be obtained by inverse phase gas chromatography.

Misovich et al.[3] 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 variable size parameter model seems to correctly describe the concentration dependence of the solvent weight fraction activity coefficient, particularly for systems with moderate enthalpic interactions. There are other thermodynamic theories which can be used to model the activity coefficient.[4-6].

We will compare the free volume diffusivity predictions made using these three thermodynamic models applied to several binary systems. Binary solvent–polymer solutions can exhibit negative enthalpic interactions, positive enthalpic interactions, or may be athermal. We have chosen poly(vinyl acetate) (PVAc) as our model polymer since there are diffusion and thermodynamic data available for solvents in this polymer over a wide range of conditions. Chloroform has negative enthalpic interactions with PVAc, acetone forms athermal solutions, toluene has moderate enthalpic interactions, and methanol has strong enthalpic interactions.

Free Volume Diffusion Theory

Cohen and Turnbull[7,8] and Fujita[9,10] developed a free volume theory for molecular diffusion based on two requirements: a void space of sufficient volume must be adjacent to the molecule and the molecule must possess enough energy to jump into it.

Vrentas and Duda removed some restrictive assumptions from Fujita's theory and have presented an improved free volume model with predictive capabilities for the determination of polymer–solvent diffusion coefficients in purely viscous diffusion which give good agreement with experimental data for several polymer–solvent systems. Modifications and improvements have been made to this model in a series of papers.[11-19]

In the Vrentas-Duda formulation, the binary mutual diffusion coefficient for a polymer–solvent system is given by:

$$D = D_1 \frac{\rho_2 \hat{V}_2^* \rho_1}{RT} \left[\frac{\partial \mu_1}{\partial \rho_1} \right]_{T_p} \tag{1}$$

where the self-diffusion coefficient of the solvent, D_1, is given by:

$$D_1 = D_{01}\exp\frac{-\zeta(w_1\hat{V}_1^* + w_2\xi\hat{V}_2^*)}{\hat{V}_{FH}} \tag{2}$$

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

$$D_{01} = D_0\exp(-E_a/RT) \tag{3}$$

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

$$\xi = \hat{V}_1^*M_1/\hat{V}_2^*M_2 \tag{4}$$

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:

$$\hat{V}_{FH}/\zeta = (K_{11}/\zeta)w_1(K_{21} + T - T_{g1}) + (K_{12}/\zeta)w_2(K_{22} + T - T_{g2}) \tag{5}$$

K_{ii}'s are physical parameters of the pure solvent and polymer related to their thermal expansion coefficients and non-hole-free volume. A detailed derivation of these equations is given by Vrentas and Duda.[14,15] Most of the parameters of Eqs. (1)–(5) can be determined by physical property and thermodynamic data on the solvent and polymer. The determination of D_0, E_a, and ξ will be discussed in the Calculations section.

Thermodynamic Models

Flory-Huggins. The underlined term in Eq. (1), the chemical potential derivative, represents the effect of thermodynamic changes on the diffusion coefficient. Vrentas, Duda, and co-workers used the Flory-Huggins theory to obtain the following equation for the thermodynamic term:

$$\frac{\rho_2\hat{V}_2^*\rho_1}{RT}\left[\frac{\partial\mu_1}{\partial\rho_1}\right]_{T,P} = x_2\frac{d\ln a_1}{d\ln x_1}$$

$$= (1 - \phi_1)^2(1 - 2\chi\phi_1) \tag{6}$$

χ is usually assumed to be constant, although it has been found to be a function of temperature and concentration. The derivative in Eq. (6) is based on χ being constant: models which include a concentration variation would give a different derivative. The Flory-Huggins expression for the solvent activity is:

$$\ln a_1 = \ln\gamma_1x_1 = \ln\phi_1 + \phi_2 + \chi\phi_2^2 \tag{7}$$

The assumption of χ being constant is approximately correct for athermal systems where the enthalpy change on mixing is zero. The polymer–solvent

interaction parameter has been written as a sum of entropic and enthalpic components:

$$\chi = \chi_S + \chi_H = 0.34 + V_1/RT(\delta_1 - \delta_2)^2 \qquad (8)$$

where the enthalpic term has been expressed in terms of solubility parameters to illustrate expected temperature dependence of χ_H. χ_S, the entropic term, is usually taken to be a constant between .3 and .4 for nonpolar systems (0.34 is suggested by Blanks and Prausnitz[20]). Equation (8) may be adequate over some temperature ranges, but it will not predict the lower critical solution temperature (LCST) due to the large χ_S value. The LCST has been explained by using free volume concepts.[21,22] The entropic component of the interaction parameter can be separated into a combinatorial and free volume component. Both the enthalpic term and the free volume term are positive, but the enthalpic term decreases with temperature while the free volume term increases with temperature. χ should exhibit a minimum as a function of temperature due to these two competing effects.

Nakajima et al.[23] have shown that χ is concentration dependent for some poly(vinyl acetate) systems. Kokes et al.[24] have shown that χ is temperature dependent for poly(vinyl acetate) systems. There is no generally accepted model for describing the concentration dependence of the interaction parameter. Equation (8) describes the temperature dependence of some systems near room temperature.

Henry's Law. This popular model for describing polymer–solvent equilibrium applies at low solvent concentrations, usually less than 10 wt%. However, the Henry's law coefficients of a particular system are often available in the absence of other data. For example, several investigators[25–29] have taken much data over wide temperature ranges. In many cases, these are the only thermodynamic data available at typical devolatilization temperatures of molten homopolymers.

The activity of the solute in the gas phase is:

$$a_1 = \frac{p_1}{p_1^0} = \frac{Hw_1}{p_1^0} = \frac{H}{p_1^0}\frac{x_1M_1}{x_1M_1 + x_2M_2} \qquad (9)$$

where the Henry's law coefficient is given in terms of the solvent weight fraction. The expression for solvent activity can be differentiated to give the thermodynamic factor in Eq. (1):

$$x_2\frac{d \ln a_1}{d \ln x_1} = w_2 \qquad (10)$$

This simple result only applies at concentrations where Henry's law describes the equilibrium. At these concentrations, however, the binary diffusivity may be estimated in the absence of a specific value for the thermodynamic coefficient. The limit of Eq. (10) as solute concentration goes to zero is 1: the same limit as the Flory-Huggins and VSP models.

Variable Size Parameter. Misovich et al.[3] have 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 solvent activity coefficients.[30, 31] The approach was first applied to athermal systems and also was found to model systems with moderate enthalpic interactions. The correlation depends on a variable size parameter which is related to the solvent infinite dilution weight fraction activity coefficient at a given temperature. The weight fraction activity coefficient is:

$$\Omega_1 = \exp \frac{\dfrac{e}{\Omega_1^\infty}(1-w_1)}{\dfrac{w_1 + \dfrac{e}{\Omega_1^\infty}(1-w_1)}{w_1 + \dfrac{e}{\Omega_1^\infty}(1-w_1)}} \tag{11}$$

This result is restricted to solvents of low molecular weight compared to polymer and to solutions where Ω_1^∞ is not very large. Ω_1^∞ is the only adjustable parameter in Eq. (11) and can be determined experimentally by a variety of means, including inverse phase gas chromatography. This coefficient can also be calculated from the Flory-Huggins interaction parameter[32]

$$\ln \Omega_1^\infty = \ln(\rho_2/\rho_1) + (1 - 1/r) + \chi \tag{12}$$

where r is the ratio of polymer molar volume to solvent molar volume. Equation (11) gives a good representation for the concentration dependence of the activity coefficient for a number of polymer–solvent systems. The thermodynamic factor in Eq. (1) can be represented as:

$$x_2 \frac{d \ln a_1}{d \ln x_1} = \left[\frac{(e/\Omega_1^\infty)w_2}{w_1 + (e/\Omega_1^\infty)w_2} \right]^2 \tag{13}$$

Figure 1 compares the term, $x_2 d \ln a_1/d \ln x_1$, for the three models. The first pair of curves below the Henry's law curve is for $\Omega_1^\infty = 5$ and $\chi = 0.42$ (with $\rho_2/\rho_1 = 1.2$). Equation (12) was used to calculate the comparable value for χ. This pair of curves represents an athermal system and there is little difference between the predictions. The lowest pair of curves represents a system with moderate enthalpic interactions and shows that there can be significant differences between the predictions. The polymer–solvent density ratio also affects the Flory-Huggins calculations. For example, if the curve for $\chi = 1.2$ were based on $\rho_2/\rho_1 = 0.8$, the thermodynamic factor would be 12% higher at $w_1 = 0.1$. In general, the value of the thermodynamic factor is within 1% of 1.00 for solvent weight fractions less than 0.001. For these low weight fractions, free volume diffusivity predictions are insensitive to the thermodynamic model choice. Equation (11) can be used to estimate the thermodynamic factor and no other thermodynamic data are needed. At $w_1 = .01$, there is approximately 7% difference between the Henry's law and VSP ($\Omega_1^\infty = 11$) models and the Henry's law estimate is less reliable.
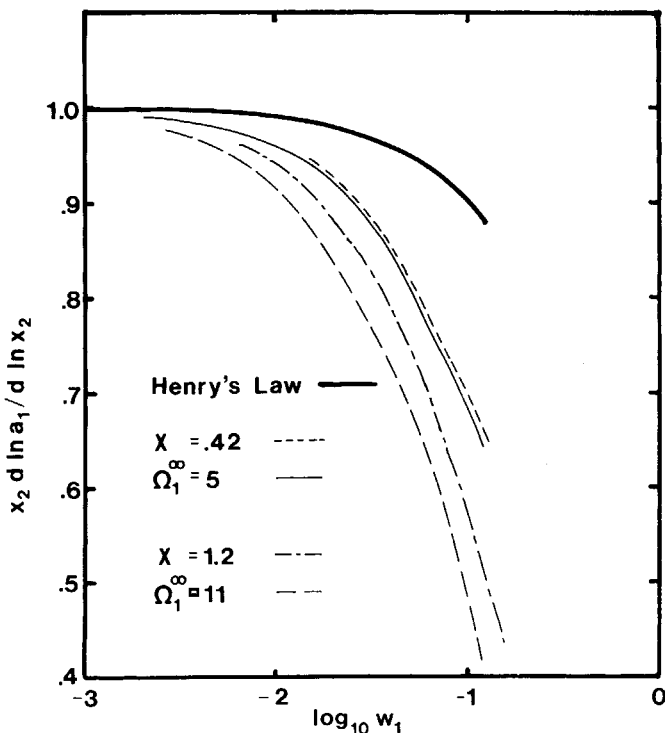
Fig. 1.   Thermodynamic factor as a function of solvent weight fraction.

CALCULATION METHODS

There is sufficient information on the four solvents chosen to estimate the parameters for the free volume theory and the thermodynamic models. The suggestions of Vrentas and Duda were followed to determine the value of the jumping unit ratio, activation energy and D_o. Ju[1] gives free volume constants for chloroform and toluene. The constants for acetone and methanol had to be estimated. The jumping unit ratio was determined in conjunction with fitting the other constants to as much data as possible rather than by ratio from other solvent diffusion data.

Thermodynamic data were available from Ju[1] (toluene and chloroform), Kokes et al.[24] (acetone), Newman and Prausnitz[32] (toluene, chloroform, iso-propyl alcohol, and methyl ethyl ketone) and Kishimoto[33] (methanol). The infinite dilution weight fraction activity coefficient can be obtained from a single physical measurement, but the accuracy of this method is questionable. Slight differences in the measurement of solvent weight fractions can lead to significant deviations in calculated values of Ω_1^∞. Typical data used are shown in Figures 2–4. The benzene- and chloroform-poly(vinyl acetate) data appear to have an outlying data point at the lowest solvent weight fraction. The variable size parameter model seems to fit the available data for the concentration dependence of the activity coefficient. However, using only one point could lead to errors as large as 20% about a mean value representing the best curve. For most of the calculations, only a single value of an activity
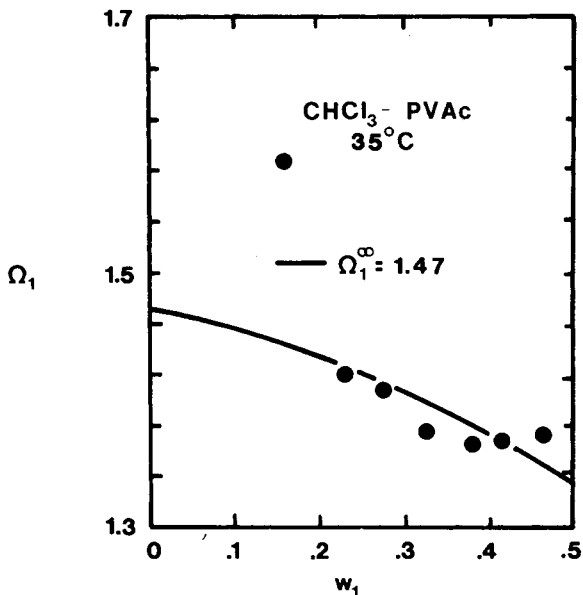
Fig. 2.   Predicted solvent weight fraction activity coefficients for chloroform-poly(vinyl acetate) solutions. Data of Ju[1].

coefficient was available, since multiple data are usually available only for lower temperatures.

The temperature range of the calculations is 50–130°C. This is a temperature ratio range, T/T_g, of 1.07 to 1.33, a typical range over which commercial devolatilization processes are operated. The variable size parameter model was assumed to correctly predict the concentration dependence of the weight
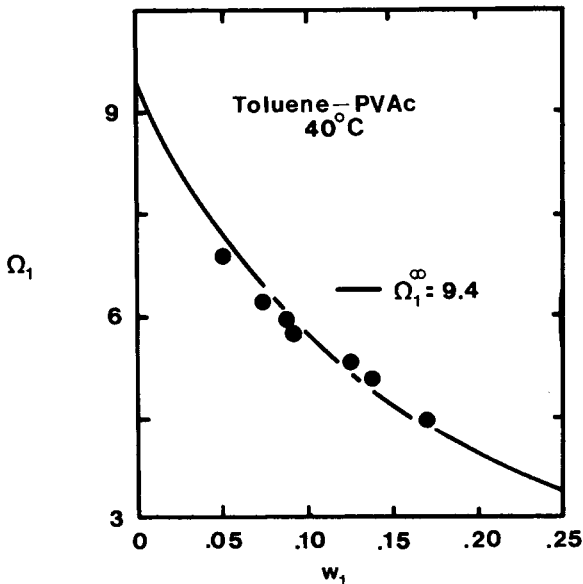
Fig. 3.   Predicted solvent weight fraction activity coefficients for toluene-poly(vinyl acetate) solutions. Data of Ju[1].
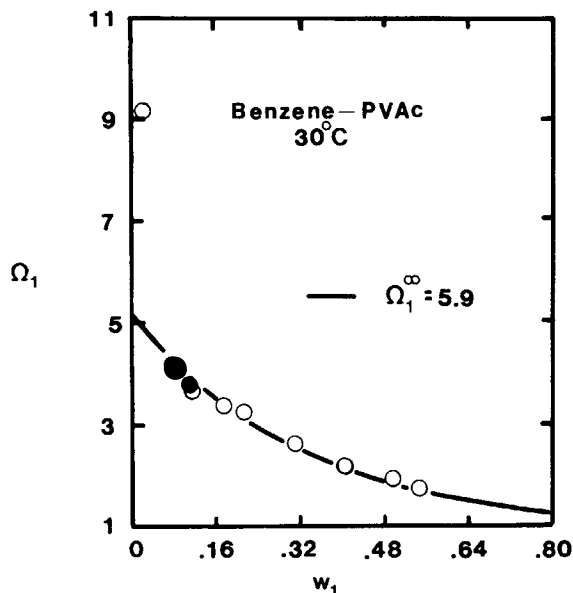
Fig. 4.   Predicted solvent weight fraction activity coefficients for benzene-poly(vinyl acetate) solutions. Solid circles—Kokes et al.[24] Open circles—Nakajima et al.[23]

fraction activity coefficients over this range of temperatures. Figure 5 shows the calculated concentration dependence of χ at 90°C. Values of Ω_1^∞ were obtained in several ways. As shown in Figure 6, there are some variations in Ω_1^∞ with temperature. The data for chloroform and toluene were interpolated from the curves joining the separate data sets at low (30–50°C) and high (100–200°C) temperatures. The values for acetone were assumed to be con-
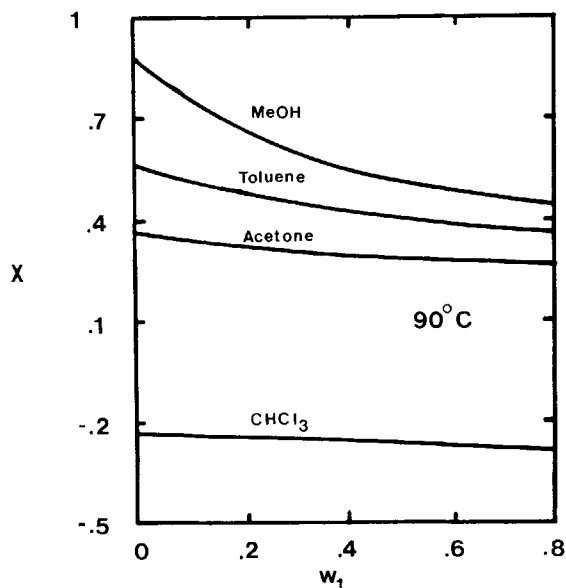

Fig. 5.   Variation of χ with concentration for four solvents in PVAc at 90°C.
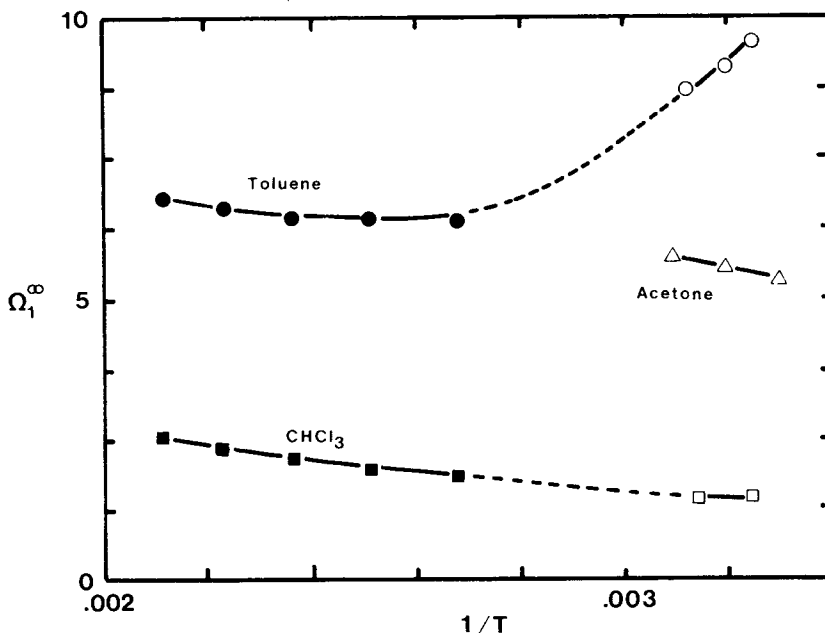
Fig. 6. Temperature dependence of Ω_1^∞. Solid circles (Newman and Prausnitz[32]). Open circles (chloroform—Ju[1]; acetone—Kokes et al.[24]; toluene—Ju[1]).

stant, even though the low temperature data suggest a significant temperature dependence. The χ value of acetone-PVAc at 50°C is 0.38, so the system is nearly athermal. Methyl ethyl ketone, (MEK) which has a solubility parameter near that of acetone ($\delta = 9.3$ for MEK vs. $\delta = 9.9$ for acetone) has a nearly constant Ω_1^∞ over the temperature range, 100–200°C.[32] The estimates for methanol were based on low temperature data for methanol and the slope of the Ω_1^∞ vs. temperature curve for propanol in PVAc.[32]

DISCUSSION OF BINARY DIFFUSION COEFFICIENT CALCULATIONS

The predicted diffusivities of chloroform, acetone, toluene, and methanol in poly(vinyl acetate) using the Flory-Huggins and ASOG-VSP models are shown in Figures 7–10. The diffusion coefficients are calculated for a range of temperatures from 50 to 130°C using parameters for the free volume theory.[34] The curves based on the different thermodynamic models are similar in shape for chloroform and acetone and slightly different in magnitude at high solvent weight fractions. For chloroform at .8 solvent weight fraction, the difference between the two curves is about 20% for each of the temperatures. For acetone, the values differ by about the same order of magnitude. In general, the differences increase as the solvent weight fraction increases. The results of the two models for chloroform are within the expected error of prediction of the free volume model. This is in part due to the small value of the thermodynamic correction to the diffusion coefficient [Eqs. (7) and (14)]. Even though there is a concentration dependence to the thermodynamic term, its total impact on the calculations is quite small. In the case of acetone, both models assume a constant value for the thermodynamic term. Small differ-
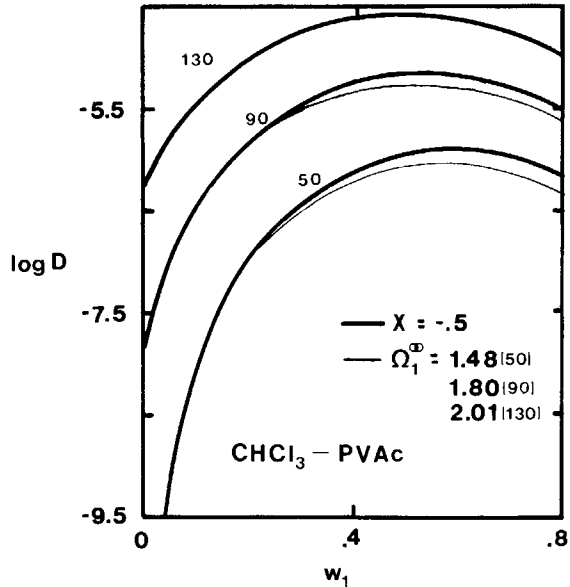
Fig. 7. Comparison of Flory-Huggins and ASOG-VSP thermodynamic models in free volume diffusion theory for chloroform-poly(vinyl acetate) solutions.

ences between these values become apparent at higher solvent weight fractions.

The diffusivity curves for toluene and methanol show distinct differences at higher solvent concentrations in both the magnitude and shape of the curves. Free volume effects dominate at temperatures near T_g while thermodynamic effects become more apparent at higher temperatures.[35] As shown in Figure 5,
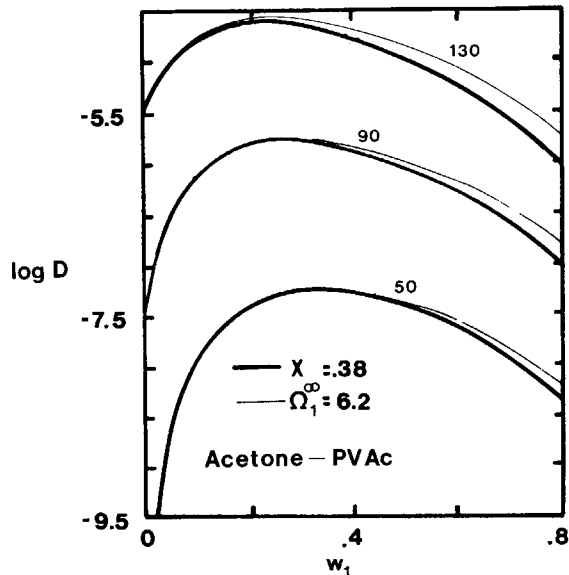

Fig. 8. Comparison of Flory-Huggins and ASOG-VSP thermodynamic models in free volume diffusion theory for acetone-poly(vinyl acetate) solutions.
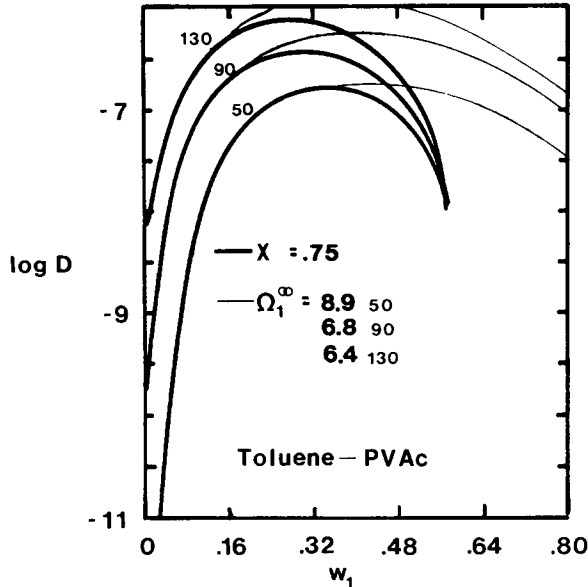
Fig. 9. Comparison of Flory-Huggins and ASOG-VSP thermodynamic models in free volume diffusion theory for toluene-poly(vinyl acetate) solutions.

the values of χ for toluene in poly(vinyl acetate) show a marked decrease as solvent weight fraction increases. The data in Figure 6 show that the infinite dilution weight fraction activity coefficient changes with temperature, so that χ should not be constant. χ was assumed to be constant in all the calculations for Figures 7–10. The calculations for methanol show these effects even more sharply.
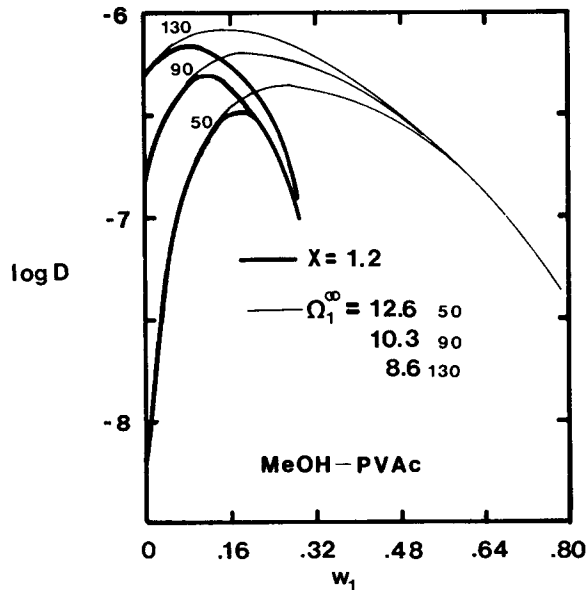

Fig. 10. Comparison of Flory-Huggins and ASOG-VSP thermodynamic models in free volume diffusion theory for methanol-poly(vinyl acetate) solutions.

The diffusion coefficients based on the Flory-Huggins theory actually become negative. From Eq. (2), it can be shown that this will occur when $\phi_1 = 1/2\chi$. The conditions for the spinodal curve when phase separation should occur are:

$$\frac{\partial \Delta\mu_1/RT}{\partial \phi_2} = 1/\phi_1 + 1 - 1/x + 2\chi\phi_2 = 0 \qquad (14)$$

The spinodal condition is also met when $\phi_1 = 1/2\chi$ if the degree of polymerization is high. Since χ decreases as solvent weight fraction increases, phase separation should occur at higher values of ϕ_1 than predicted by Eq. (14) using a constant χ evaluated at infinite dilution of solvent. For example, based on the χ for toluene at 50°C and infinite dilution of solvent, phase separation should occur at a solvent volume fraction of .67. However, at a volume fraction of 0.67, the χ value should be below 0.50 and phase separation should not occur.

It can be convenient to use a linearized model for the diffusion coefficient:[35]

$$D(w_1) = D_{w_1=0} + (\partial D/\partial w_1)_{w_1=0} * (w_1 - 0)$$

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

$$D(0) = D_0 \exp\left[-(E_a/RT + \hat{V}_2^* \xi/A_2)\right]$$

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

$$K_2 = 2/(e/\Omega_1^\infty): \qquad \text{ASOG-VSP}$$

$$= 2(\hat{V}_1/\hat{V}_2)(1 + \chi): \qquad \text{Flory-Huggins}$$

$$= 1: \qquad \text{Henry's law}$$

Each thermodynamic model results in a similar linearization. These models are useful at temperatures well above T_g and at low solvent weight fractions
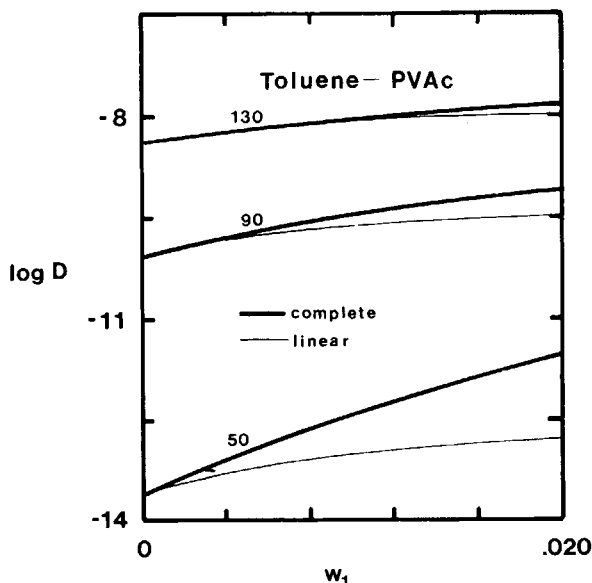

Fig. 11. Comparison of linearized and complete free volume diffusion models for toluene-PVAc.
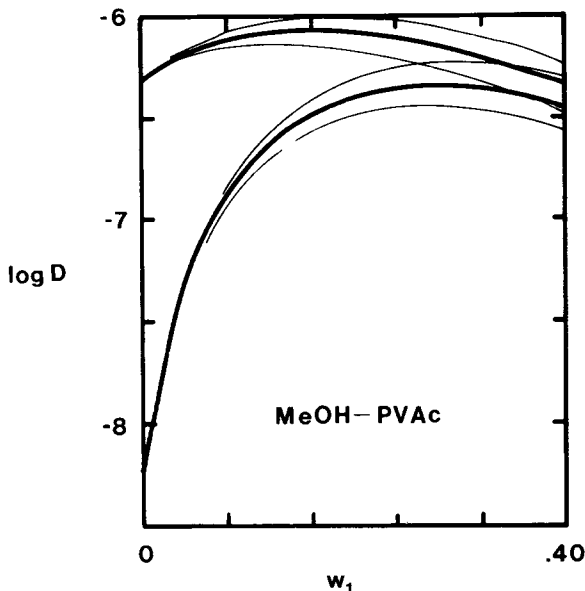
Fig. 12. Effect of 20% variation in Ω_1^∞ on D for methanol-PVAc.

for systems with enthalpic interactions (Fig. 11). As discussed before, the variable size parameter model might vary 20% about a mean curve depending on the data point selected. Figure 12 illustrates the expected variations about a mean curve for 50 and 130°C for this model.

LIST OF SYMBOLS

a_1 solvent activity
A_i combined free volume coefficient of component i

$$A_1 = \frac{K_{11}}{\xi}(K_{21} + T - T_{g1}), \qquad A_2 = \frac{K_{12}}{\xi}(K_{22} + T - T_{g2})$$

D binary mutual diffusion coefficient
D_0 pre-exponential factor
D_1 self-diffusion coefficient of solvent
D_{01} pre-exponential factor
E_a activation energy for diffusion
H   Henry's law constant based on weight fraction
K_{ii} free volume parameters of component i
M_i molecular weight of component i
p_i vapor pressure of component i
p_i^0 saturated vapor pressure of component i
r ratio of polymer molar volume to solvent molar volume
R gas constant
T absolute temperature
T_g glass transition temperature
$\hat{V}_i^*$ specific critical volume of pure component i
$\hat{V}_{FH}$ specific hole-free volume

x_i mole fraction of component i
γ_i solvent mole fraction activity coefficient
ζ overlap factor in free volume diffusion model
μ_1 chemical potential of component i
ξ ratio of molar critical volume of solvent jumping unit to that of the polymer jumping unit
ρ_i mass density of component i
ϕ_i volume fraction of component i
χ polymer-solvent interaction parameter
Ω_1^∞ solvent weight fraction activity coefficient at infinite dilution
Ω_1 solvent weight fraction activity coefficient

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