Prediction of Solvent-Diffusion Coefficient in Polymer by a Modified Free-Volume Theory

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ABSTRACT: Several versions of free-volume theory have been proposed to correlate or predict the solvent diffusion coefficient of a polymer/solvent system. The quantity of free volume is usually determined by the Williams–Landel–Ferry (WLF) equation from viscosity data of the pure component in these theories. Free volume has been extensively discussed in different equation-of-state models for a polymer. Among these models, the Simha–Somcynsky (SS) hole model is the best one to describe the crystalline polymer, because it describes it very approximately close to the real structure of a crystalline polymer. In this article, we calculated the fractions of the hole free volume for several different polymers at the glass transition temperature and found that they are very close to a constant 0.025 by the SS equation of state. It is quite consistent with the value that is determined from the WLF equation. Therefore, the free volume of a crystalline polymer below the glass transition temperature (T_g) is available from the SS equation. When above the T_g, it is assumed that the volume added in thermal expansion is the only contribution of the hole free volume. Thus, a new predictive free-volume theory was proposed. The free volume of a polymer in the new predictive equation can be estimated by the SS equation of state and the thermal expansion coefficient of a polymer instead of by the viscosity of a polymer. The new predictive theory is applied to calculate the solvent self-diffusion coefficient and the solvent mutual-diffusion coefficient at different temperatures and over most of the concentration range. The results show that the predicted values are in good agreement with the experimental data in most cases. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 428–436, 2000

Key words: solvent-diffusion coefficient; predictive theory; free-volume; polymer

INTRODUCTION

Solvent diffusion in a polymer is very important in the fields of a polymer industry and its application, such as in polymer purification,[1] polymer kinetics,[2,3] and control of drug delivery.[4] Therefore, many researchers have paid attention to this study during the past 50 years and have made great progress both in experiment and theory. Several theories had been proposed to describe the diffusion behavior, and the free-volume theory, first proposed by Fujita,[5] is known as the most successful one. Later, the free-volume theory was developed by Vrentas and colleagues[6–9] to correlate or predict accurately the self-diffusion and binary mutual-diffusion coefficients at various temperatures and over most of the concentration range. In their model, the free volume of liquid is assumed to be composed of two parts: the specific interstitial free volume and the hole free volume. It is supposed that the diffusion process depends on two factors: First, a molecule should

obtain sufficient energy to overcome attractive forces; and second, the diffusing molecule should be surrounded by a hole. When the temperature of a system is sufficiently high, for example, the temperature is close to the glass transition temperature, the second factor will control the diffusing process. Obviously, how to describe the free volume of the liquid is very important in the study of molecule diffusion behavior.

Generally, three typical kinds of description of the free volume have already been proposed to study the equation of state of a polymeric liquid. The first one is given in the cell model, where the volumetric changes in the system is restricted to changes in the cell volume, that is, the space surrounding a polymer segment is placed on a lattice framework. The second one introduces empty sites or lattice vacancies in the lattice model. The third takes into consideration both cell expansion and lattice vacancies in the hole model. Rodgers gave a review of these equations.[10] The free-volume description in the Vrentas free-volume theory belongs to the third type and the quantity of the free volume is determined by the Williams–Landel–Ferry (WLF) equation,[11] while the free-volume parameter is obtained from the viscosity data. In this article, we propose a new method to obtain the contribution of crystallizable or molten polymer to the free volume from volumetric data of a polymer and then predict the solvent-diffusion coefficient in the polymers. The free volume of a crystallizable and molten polymer is discussed in the second section of the article. The prediction principle of the solvent-diffusion coefficient is presented in the third section of the article. The application of the predictive theory is presented in the fourth section of the article.

FREE VOLUME OF CRYSTALLIZABLE AND MOLTEN POLYMER

Although the equations of state based on various lattice models with different free-volume descriptions provide accurate fitting functions, they can be used to analyze pVT data. The hole model should be considered as the best one because its physical significance is obviously more close to the real structure of polymer, especially at the crystalline state. The Simha–Somcynsky (SS) hole model[12] has proven to be the most successful model to study the thermodynamic properties of polymer solutions and blends. Many researchers

have reported their correlation of experimental pVT data with the SS equation of state. However, most of them focused their studies on polymer liquids and the range of temperature in all their correlations was above the glass transition temperature (T_g).[10,13] In this study, the experimental pVT data of six polymers below the T_g are correlated with the SS equation of state. This equation of state in dimensionless variables is derived as[12]

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{(y\tilde{v})^{1/3}}{[(y\tilde{v})^{1/3} - 0.8909y]} - \frac{2y}{\tilde{T}}\left(\frac{1.2045}{(y\tilde{v})^2} - \frac{1.011}{(y\tilde{v})^4}\right)$$

(1)

with

$$(s/3c)[1 + y^{-1}\ln(1 - y)]$$

$$= \frac{y}{6\tilde{T}(y\tilde{v})^2}\left[2.409 - \frac{3.033}{(y\tilde{v})}\right]$$

$$+ \left(\frac{0.8909y}{(y\tilde{v})^{1/3}} - \frac{1}{3}\right)\left[1 - \frac{0.8909y}{(y\tilde{v})^{1/3}}\right]^{-1}$$ (2)

where y is the fraction of occupied sites and $\tilde{v} \equiv v/v^*$ with $v^* = \sigma^3$, $\tilde{T} \equiv T/T^*$ with $T^* = (z - 2)s\varepsilon^*/ck$, and $\tilde{P} \equiv P/P^*$ with $P^* = ckT^*/v^*$. σ is a "hard-sphere" radius, ε^*, the intersegmental potential minimum; z, the coordination number; s and $3c$, respectively, the number of segments and external degrees of freedom per segment; and k, the Boltzman constant.

The correlated results shown in Table I indicate that the SS equation of state can fit the experimental pVT data below the T_g with quite good accuracy. Meanwhile, we also give the calculated values of the fraction of hole f ($f = 1 - y$) for different polymers at their glass transition temperature. It can be found that the fraction of the hole free volume of these polymers at the T_g falls within the range of 0.02–0.03 with an averaged value of 0.025, that is, $f_{g_2} = 0.025 \pm 0.005$. It is quite consistent with the value obtained from the WLF equation,[17] which also supports the view that the fractions of the free volume at the glass transition temperature should be a constant.[18]

Many researchers have reported that the SS model equation of state can fit the pVT data of glassy or molten polymer.[10] However, the SS model is not suitable to describe the real structure of a polymer liquid because the foundation of the model is based on the crystal lattice. Here, we proposed a method to describe the changes of the

Table I   Correlated Results of *pVT* Experimental Data for Different Polymers Below T_g by SS Equation of State

Polymer[a]	Range of T (K)	Range of P (MPa)	T^* (K)	P^* (MPa)	V^* (cm³/g)	δ[b]	T_{g2} (K)	$f_{g2} \times 10^2$	Data Source
PS	281–349	0.1–200	16464	754.6	1.0033	0.043	373	2.60	14
PMMA	374–445	0.1–200	17139	788.6	0.8860	0.102	378	2.31	15
PVAc	243–303	0.1–80	13708	641.1	0.8680	0.066	304	2.37	16
PnBMA	292–371	0.1–200	12987	721.7	0.9689	0.017	293	2.56	15
PCHMA	285	0.1–200	17667	794.4	0.9568	0.043	380	2.05	15
PoMS	302–355	0.1–200	17316	760.4	1.0293	0.018	404	2.95	14

[a] PS, polystyrene; PMMA, poly(methyl methacrylate); PVAc, poly(vinyl acetate); PnBMA, poly(*n*-butyl methacrylate); PCHMA, poly(cyclohexyl methacrylate; PoMS, poly(orthomethyl styrene).
[b] $\delta = 1/N\Sigma|V_i^{calc} - V_i^{exp}|/V_i^{exp} \times 100$.

free volume in crystallizable and molten polymer: (1) At low temperature, the free volume (including hole free volume and cell free volume) changes in the rule of the SS model. (2) When the temperature increases to the glass transition temperature, the cell free volume will no longer increase with the temperature and arrive at a maximum value, so the expansion volume is due to increase of the hole free volume of the polymer liquid. The second assumption is consistent with the point of view advanced by Turnbull and Cohen[19] that the volume added in the thermal expansion can be considered the hole free volume at the glass transition temperature. Thus, the hole free volume of a polymer below T_{g2} can be available from the SS equation of state and that of a polymer liquid can be estimated as

$$V_{FH_2} = V_2(T_{g2})[f_{g2} + \alpha_2(T - T_{g2})] \quad (3)$$

where V_{FH_2} is the hole free volume of a polymer liquid; $V_2(T_{g2})$, the specific volume of a polymer liquid at T_{g2}; and α_2, the thermal expansion coefficient of a polymer liquid. Table II gives the averaged values of two polymers within a certain range of temperature.

Table II   Thermal Expansion Coefficient of PS and PVAc

Polymer	$\hat{V}_2^*$ (cm³/g)	Range of T (K)	$\alpha_2 \times 10^4$	Data Source
PS	0.850	388.6–468.8	5.39	14
PVAc	0.749	308.2–373.2	7.02	16

PREDICTIVE THEORY OF DIFFUSION COEFFICIENT FOR SOLVENT–POLYMER SYSTEM

Predictive Theory

According to the free-volume theory, the mechanism of molecule diffusion is assumed as the following: (1) A vacancy of sufficient size appears adjacent to the molecule, and (2) the diffusing molecule possesses enough energy to break contacts with neighboring molecules. Vrentas and colleague[9] proposed the solvent self-diffusion expression D_1 as

$$D_1 = \bar{D}_0\exp\left(-\frac{E^*}{RT}\right)\exp\left(-\frac{\omega_1\hat{V}_1^* + \omega_2\xi\hat{V}_2^*}{\hat{V}_{FH}/\gamma}\right) \quad (4)$$

$$E^* = E_p - E_s \quad (5)$$

where $\bar{D}_0$ is an effectively constant preexponential factor; $\hat{V}_i^*$, the specific critical hole free volume of component i required for a jump; ω_i, the mass fraction of component i; $\hat{V}_{FH}$, the average hole free volume per gram of polymer; γ, an overlap factor; and ξ, the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit. E_p and E_s represent energies that molecules per mole need to overcome attractive forces which constrain them to their neighbors. The assumption of a negligible energy effect is often acceptable in the predictive version of the theory,[20] so eq. (4) can be simplified as

$$D_1 = \bar{D}_0\exp\left(-\frac{\omega_1\hat{V}_1^* + \omega_2\xi\hat{V}_2^*}{\hat{V}_{FH}/\gamma}\right) \quad (6)$$

The definition of the solvent mutual-diffusion co-efficient is[21]

$$D = \frac{D_1 \rho_1 \hat{V}_2 \rho_2}{RT} \left(\frac{\partial \mu_1}{\partial \rho_1} \right)_{T,P} \qquad (7)$$

The solvent chemical potential in mixture is given by the Flory–Huggins equation

$$\mu_1 = \mu_1^0 + RT[\ln(1 - \phi_2) + \chi \phi_2^2 + \phi_2] \qquad (8)$$

If the Flory–Huggins model is accurate enough to describe the chemical potential of a solvent in a mixture, the polymer/solvent binary mutual-diffusion D can be derived as[22]

$$D = D_1(1 - \phi_1)^2(1 - 2\chi\phi_1) \qquad (9)$$

where χ is the polymer–solvent interaction parameter, and ϕ_1, the solvent volume fraction, which can be estimated by

$$\phi_1 = \frac{\omega_1 \hat{V}_1^0}{\omega_1 \hat{V}_1^0 + \omega_2 \hat{V}_2^0} \qquad (10)$$

where $\hat{V}_1^0$ and $\hat{V}_2^0$ are the equilibrium liquid volume at 0 K for a solvent and polymer. The partial specific volumes of a polymer and solvent are assumed independent of concentration, so that the influence of the volume change in the mixing process on the free volume of a system is considered negligible, that is,

$$\hat{V}_{FH}/\gamma = \hat{V}_{FH1}/\gamma_1 + \hat{V}_{FH2}/\gamma_2 \qquad (11)$$

where γ_i represents the overlap factor for the free volume of the pure component i. $\hat{V}_{FH1}$ and $\hat{V}_{FH2}$ are hole free volumes for a pure solvent and polymer, respectively. The term of $\hat{V}_{FH1}/\gamma_1$ is estimated from the WLF equation

$$\hat{V}_{FH1}/\gamma_1 = K_{11}/\gamma_1 \omega_1 (K_{21} + T - T_{g1}) \qquad (12)$$

where T_{g1} is the glass transition temperature of a pure solvent, K_{11} and K_{21} are free-volume parameters for a solvent, and the term of $\hat{V}_{FH2}/\gamma_2$ is calculated by eq. (3) above T_{g2} or available from the SS equation below T_{g2}; here, γ_2 is assumed to be equal to a unit.

When $\omega_1 \rightarrow 0$, the prediction eq. (6) can be rewritten as

$$D_1 = \bar{D}_0 \exp\left(-\frac{\xi \hat{V}_2^*}{\hat{V}_{FH2}/\gamma_2} \right) \qquad (13)$$

Equation (13) can be applied to predict the solvent self-diffusion coefficient of trace amounts of a solvent in a polymer.

Estimation of Equation Parameter

1. $\hat{V}_1^*$ and $\hat{V}_2^*$.

The specific critical hole free volume, $\hat{V}_1^*$ and $\hat{V}_2^*$, can be estimated as the specific volumes of a solvent and polymer at absolute zero temperature, that is,

$$\hat{V}_1^* = \hat{V}_1(0) \qquad (14)$$

$$\hat{V}_2^* = \hat{V}_2(0) \qquad (15)$$

$\hat{V}_1(0)$ and $\hat{V}_2(0)$ can be calculated by using a group contribution method developed by Sugden.[23]

2. $\bar{D}_0$, K_{11}/γ_1, and $K_{21} - T_{g1}$.

Dullien[24] first proposed a simple predictive equation of the self-diffusion coefficient D_1^0 for a pure solvent; it is

$$\frac{\eta_1 D_1^0}{RT\, d_1} = 0.124 \times 10^{-16} V_c^{2/3} \qquad (16)$$

where d_1 and η_1 are the density and viscosity of a pure solvent, and V_c, the critical molar volume. When $\omega_1 \rightarrow 1$, eq. (6) can be simplified as

$$D_1^0 = \bar{D}_0 \exp\left(-\frac{\hat{V}_1^*}{\hat{V}_{FH1}/\gamma_1} \right) \qquad (17)$$

Substituting eqs. (11) and (17) into eq. (16) yields

$$\ln\left(\frac{0.124 \times 10^{-16} V_c^{2/3} RT\, d_1}{\eta_1 M_1} \right)$$

$$= \ln \bar{D}_0 - \frac{\hat{V}_1^*/(K_{11}/\gamma_1)}{K_{21} - T_{g1} + T} \qquad (18)$$

where M_1 is the molecular weight of a solvent. According to eq. (16), it is possible to determine the quantities $\bar{D}_0$, K_{11}/γ_1, and $K_{21} - T_{g1}$ using

viscosity–temperature and density–temperature data for the solvent.

3. ξ.

This parameter can be defined as

$$\xi = \frac{M_1 \hat{V}_1^*}{\hat{V}_{2j}} \qquad (19)$$

where $\hat{V}_{2j}$ is the molar volume of the polymer-jumping unit, which is related to the stiffness of the polymer chain. Because the glass transition temperature is considered as an indicator of chain stiffness, Lipatov and Privalko[25,26] studied the relationship between the quantity $\hat{V}_{2j}$ and the glass transition temperature of a polymer and gave a linear correlated expression:

$$V_{2j}\left(\frac{cm^3}{mol}\right) = 0.6224 T_{g2}(K) - 86.95 \qquad (20)$$

Another method to estimate the quantity ξ was proposed by Ju et al.[27] It is possible to determine ξ using the result

$$\xi = \beta \hat{V}_1(0)/[2.303(C_1^g)_2(C_2^g)_2] \qquad (21)$$

where $(C_1^g)_2$ and $(C_2^g)_2$ are the WLF constants for a polymer. β is a constant for a certain polymer, whose values have been reported for a number of polymers.

4. χ.

The values of the polymer–solvent interaction parameter χ were compiled by Steehan and Bisio and by Orwoll for many common polymers and solvents.[28,29] χ can be determined by many methods,[30,31] such as the solubility data measurement, inverse gas chromatography, and phase equilibrium measurement.

RESULTS AND DISCUSSION

Prediction of Self-diffusion Coefficient for Trace Amounts of Solvent in Polymer

According to eq. (13), the solvent self-diffusion coefficient for trace amounts of solvent depends on the following four parameters: $\hat{V}_{FH2}$, $\bar{D}_0$, ξ, and $\hat{V}_2^*$. The values of these parameters can be estimated by the
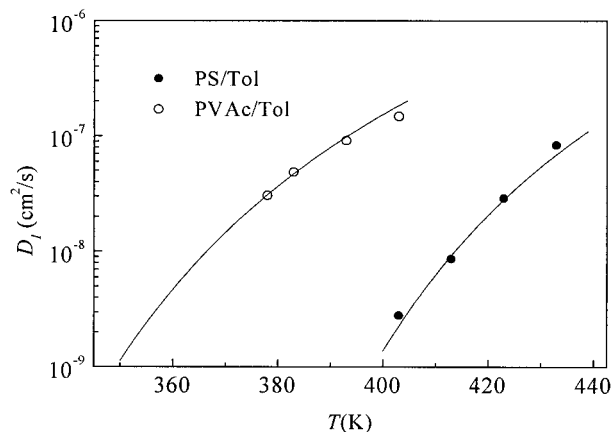

Figure 1 Comparison of experimental data[32,33] and predicted values of solvent self-diffusion coefficient of trace amounts of solvent in polymers for PS/Tol and PVAc/Tol systems.

method discussed in the second and third sections of this article. Figure 1 shows the predicted values of self-diffusion for a trace amount of toluene (Tol) in two polymers (PS and PVAc) at different temperatures.

The values of corresponding parameters are given in Tables II–IV. Because the ranges of temperature in this study for PVAc/Tol and PS/Tol systems are all above the glass transition temperatures of the corresponding polymers, the quantity of $\hat{V}_{FH2}$ can be calculated from eq. (3). Thus, the prediction of a self-diffusion coefficient of trace amounts of solvent in a polymer does not need the viscosity of the polymers. However, in other predictive versions of the free-volume theory, the viscosity of the polymer must be known to determine the WLF constant and to obtain the free-volume parameter. Figure 1 also shows that

Table III Solvent Free-volume Parameters

Solvent[a]	$\hat{V}_1^*$ (cm^3/g)	$\bar{D}_{01} \times 10^4$ (cm^2/s)	$K_{11}/\gamma_1 \times 10^4$ (K^{-1})	$K_{21} - T_{g1}$ (K)
Tol	0.917	4.17	15.7	−90.5
Ben	0.901	11.3	10.7	−73.79
EB	0.946	4.61	14.0	−80.01
ClFrm	0.510	5.49	6.52	−37.90
THF	0.899	14.4	7.50	10.45

Data collected from refs. 9 and 34.
Tol, toluene; Ben, benzene; EB, ethylbenzene; ClFrm, chloroform; THF, tetrahydrofuran.

Table IV χ and ξ Values Needed for Theory Prediction

Polymer	Solvent	χ	ξ
PS	Tol	0.40	0.58
	Ben	—	0.48
	EB	0.363	0.69
	THF	—	0.45
PVAc	Tol	0.393	0.82
	ClFrm	0.351	0.65

Data collected from refs. 21 and 34.

the predicted values are in good agreement with the experimental data.

Prediction of Self-diffusion Coefficient of Solvent in Polymer at Different Temperatures and Solvent Concentrations

Four systems, PS/Ben, PS/Tol, PS/EB, and PS/THF, are selected to prove the predictive ability of

eq. (6). Figure 2 shows a comparison of the predicted values with the experimental data of the solvent self-diffusion coefficient of polymer/solvent systems. The contribution to the hole free volume of a solvent in eq. (6) is treated the as same as the Vrentas–Duda free-volume theory, and the corresponding free-volume parameters of a solvent are given in Tables III. The contributions to the free volume of a polymer at different temperatures are evaluated by different methods. When $T \geq T_g$, the free volume of a molten polymer is calculated by eq. (3), while when $T < T_g$, that of a polymer crystalline is calculated by the SS model equation of state, whose parameters are shown in Table I. Although there is a certain deviation between the predicted values and the experimental data, the predicted results are still satisfactory because the prediction equation need not any D_1 data to determine the parameters of the predictive equation.

Comparisons of some theories and solvent self-diffusion data for polymer–solvent systems were
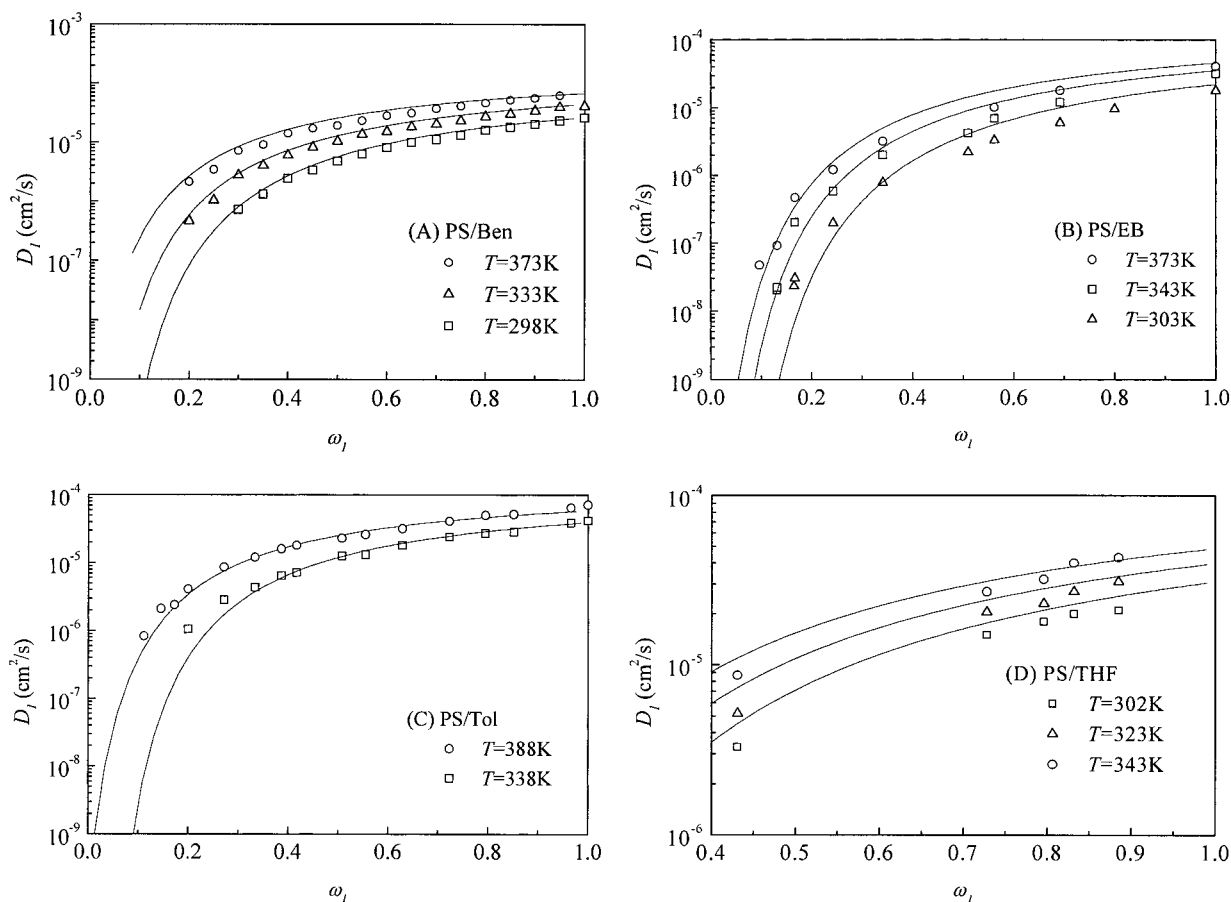

Figure 2   Comparison of experimental data[20,35–37] and predicted values of solvent self-diffusion coefficient in polymer/solvent mixtures.

Table V   Comparisons of Theory and Solvent Self-diffusion Data for PS/Tol and PS/EB Systems

Method Used to Estimate D_1	Average Absolute Error (%)	D_1 Data Used
	PS/EB	
Vrentas–Duda correlative theory	21.6	All points in temperature range 388.7–451.2 K
Vrentas–Duda predictive theory	193	No D_1 data used
Vrentas–Duda semipredictive theory	24.3	Four points at 403.2 K and four points at 451.2 K
Vrentas–Duda semipredictive theory	190	Four points at 388.7 K and three points at 403.2 K
Theory proposed in this work	44.2	No D_1 data used
	PS/Tol	
Vrentas–Duda correlative theory	25.2	All points in temperature range 298.2–451.2 K
Vrentas–Duda predictive theory	34.5	No D_1 data used
Vrentas–Duda semipredictive theory	32.8	Three points at 298.2 K and three points at 383.2 K
Vrentas–Duda semipredictive theory	567	All points at 443.2 and 451.2 K
Theory proposed in this work	12.6	No D_1 data used

All the results, estimated by using the Vrentas–Duda theories, are collected from ref. 7.

given by Vrentas et al.[7] The Vrentas–Duda theory is proved to be the most successful in the correlation or prediction of D_1. Table V shows the esti-

mated results of D_1 for PS/EB and PS/Tol systems by using the Vrentas–Duda theory and the new theory proposed in this work. Obviously, the new
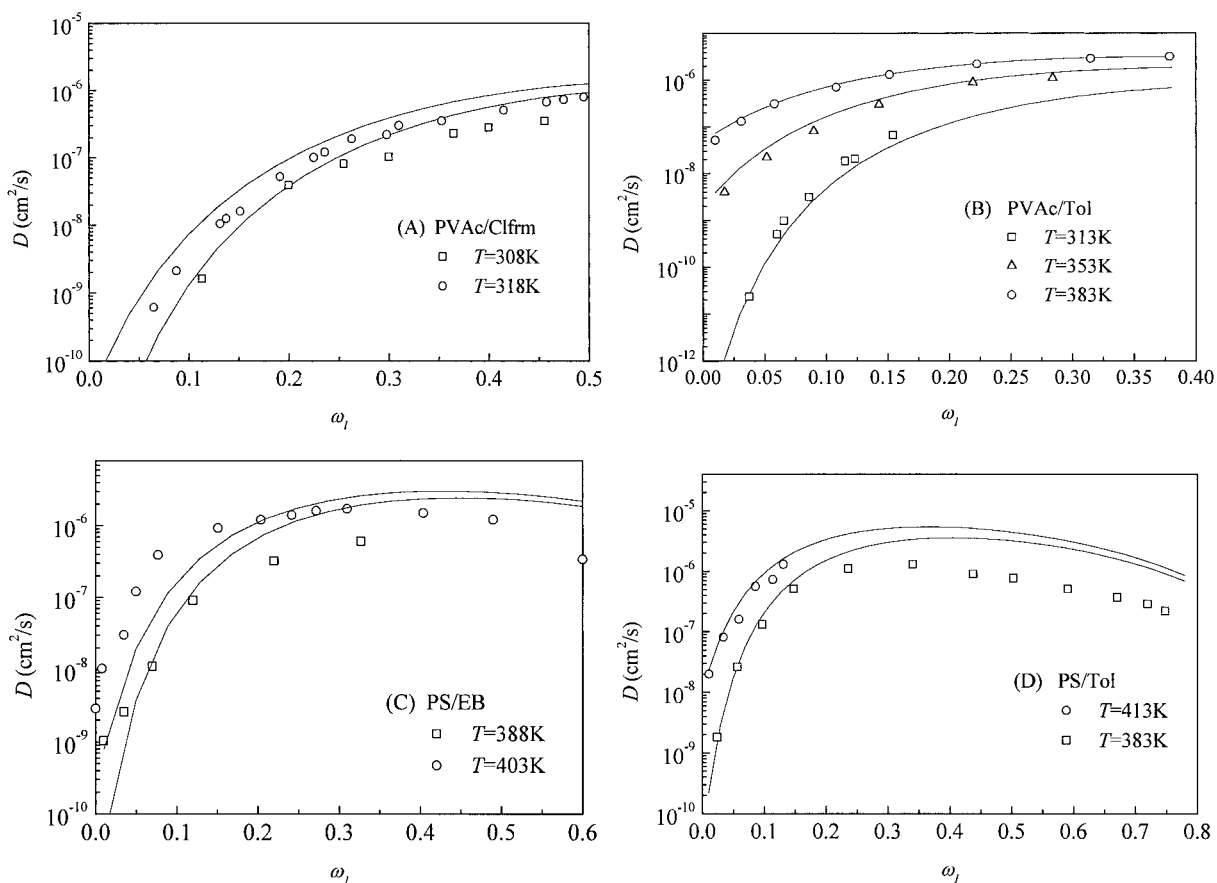

Figure 3   Comparison of experimental data[38–40] and predicted values of solvent mutual-diffusion coefficient in polymer/solvent mixtures.

theory also has good predictive capabilities, especially in the absence of D_1 data.

Prediction of Mutual-diffusion Coefficient of Solvent in Polymer at Different Temperatures and Solvent Concentrations

Figure 3 shows a comparison between predicted values and experimental data of the solvent mutual-diffusion coefficient for four systems: PVAc/ClFrm, PVAc/Tol, PS/EB, and PS/Tol, at different temperatures and concentrations. Except for PVAc/Tol, the prediction is not as good as expected. It may due to the treating of the Flory–Huggins interaction parameter χ as a constant independent of temperature and concentration. However, it is well known that χ will slightly change with temperature and concentration. Some researchers studied the dependence of χ on temperature and concentration, for example, Qian[41] and Bae[42] obtained an expression to describe this relationship by regressing the vapor–liquid equilibrium data. However, this expression seems too complex to be used in an application. Meanwhile, this expression has five adjustable parameters, so its reliability cannot be assured. Although the quantity χ has a great effect on the prediction, the treatment of χ as a constant is acceptable in predictive versions of a theory.

CONCLUSIONS

According to the molecule-diffusion mechanism of a solvent in a polymer, the free volume of a mixture dominates the diffusing process at higher temperature. The assumption that the free volume of a system obeys the added law of the free volume of pure components makes it possible to predict the solvent-diffusion coefficient from the properties of pure components. This is the basis of several predictive versions of the free-volume theory. In most of these theories, the free volume of a pure polymer is evaluated by the viscosity data by the WLF equation. In our method, the free volume of a pure polymer is calculated by the SS equation of state and the thermal expansion coefficient and has been proved to be satisfactory to predict solvent self-diffusion and mutual diffusion. All the parameters required for the modified free-volume diffusion models can be estimated without the knowledge of any diffusion experimental data. Prediction of diffusion coefficients at

various conditions of temperature and concentration is in good agreement with experimental data in most cases. The modified free-volume theory provides a way to predict the solvent-diffusion coefficient in a polymer using the volumetric data instead of the viscosity data of the polymer.

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