Predicting Ability of Free-Volume Theory for Solvent Self-Diffusion Coefficients in Rubbers

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SYNOPSIS

The effect of solvent size on the diffusion process is studied for various solvents with natural rubber and polybutadiene in terms of the free-volume theory. The importance of energy effects on the diffusion of penetrants in rubbers is examined. The critical molar volume of the polymer jumping unit is correlated with its glass transition temperature over the range 172 K to 305 K. The correlation shows a linear relationship between these two properties and can be used to predict one of the most sensitive free-volume parameters. Using this parameter in conjunction with the Vrentas–Duda free-volume theory, solvent self-diffusion coefficients in rubbers are then predicted over wide ranges of concentration and temperature. For all the systems, the predictions are comparable with experimental data. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Transport of penetrants in polymers is important in many areas where polymers are acting as barriers, and in separation processes, such as selective diffusion. Different applications of polymers have different requirements on their transport properties. Therefore, reliable predictions of diffusion coefficients for small molecules in polymer materials could be a useful tool to design appropriate materials. For many years, the Vrentas–Duda diffusion model, which was based on free-volume concepts, has been widely used in correlating and predicting diffusion coefficients for several polymer/solvent systems.[1-6] However, lack of a correct method to estimate one important parameter for certain polymers has limited our ability to predict diffusion behavior.

Recently, Zielinski and Duda investigated several polymer/solvent systems and proposed a linear relationship between the glass transition temperature of the polymer, T_{g2}, and the molar volume of a polymer jumping unit.[5] According to that correlation, the size of polymer jumping unit is predicted to equal zero at a certain temperature. Thus, as Zielinski and Duda indicated, the validity of the relationship at temperatures beyond the lower bound of the correlation is questionable. In this study, a new relation-

ship is proposed for polymers for which T_{g2} is located beyond the lower temperature bound of the previous study. In addition, solvent self-diffusion coefficients in rubbers are predicted using the new relationship.

Theory

According to the Vrentas–Duda free-volume diffusion model,[1-6] the rate of migration is the product of two probabilities: (1) the probability that a fluctuation in local density will produce a hole of sufficient size, and (2) the probability that the jumping unit will acquire sufficient energy to overcome forces attracting it to neighboring molecules. Therefore, the solvent self-diffusion coefficient, D_1, is given by eq. (1), and the polymer/solvent binary mutual diffusion coefficient, D, is expressed by eq. (2), with subscripts 1 and 2 referring to the solvent and polymer, respectively:

$$D_1 = D_o \exp\left(\frac{-E}{RT}\right)$$

$$\times \exp\left(\frac{-(\omega_1 \hat{V}_1^* + \xi \omega_2 \hat{V}_2^*)}{\omega_1\left(\dfrac{K_{11}}{\gamma_1}\right)(K_{21} - T_{g1} + T) + \omega_2\left(\dfrac{K_{12}}{\gamma_2}\right)(K_{22} - T_{g2} + T)}\right) \quad (1)$$

$$D = D_1(1 - \phi_1)^2(1 - 2_\chi\phi_1) \quad (2)$$

Here D_o is a preexponential factor, E is the critical energy that a molecule must possess to overcome the attractive forces holding it to its neighbors, and γ_i is an overlap factor for component i, which is introduced because the same free volume is available to more than one jumping unit. $\hat{V}_i^*$ is the specific hole free volume of component i required for a diffusive jump, K_{11} and K_{21} are free-volume parameters for the solvent, while K_{12} and K_{22} are those for the polymer, and ω_i is the weight fraction of component i. Finally, if a solvent moves as a single unit, the parameter ξ is defined as follows:

$$\xi = \frac{\tilde{V}_1^o(0)}{\tilde{V}_{2j}^*} = \frac{\hat{V}_1^* M_1}{\hat{V}_2^* M_{2j}} \quad (3)$$

where $\tilde{V}_1^o(0)$ and $\tilde{V}_{2j}^*$ are the solvent molar volume at 0 K and the molar volume of polymer jumping unit, respectively, while M_1 and M_{2j} are the molecular weights of solvent and polymer jumping unit, respectively.

Because ξ is one of the most sensitive free-volume parameters,[6] accurate estimation of the ξ parameter is essential to predict polymer–solvent diffusion behavior correctly. It has generally been assumed that the diffusion process is free volume driven at temperatures sufficiently close to the glass transition temperature of the system, and consequently, the contribution of the energy part to diffusion coefficients has often been ignored when studying diffusion behavior in polymer/solvent systems. In the limit of zero weight fraction of the solvent, if energy effect on the diffusion is

assumed to be negligible, eq. (1) can be written as follows:

$$\ln D = \ln D_1$$

$$= \ln D_{o1} - \frac{\dfrac{\gamma_2 \hat{V}_2^* \xi}{K_{12}}}{K_{22} - T_{g2} + T} \quad (\omega_1 \to 0) \quad (4)$$

Here, $K_{22} - T_{g2}$ and $\gamma_2 \hat{V}_2^*/K_{12}$ are simply related to the Williams–Landel–Ferry (WLF) constants of the polymer, C_{12}^{WLF} and C_{22}^{WLF}, as follows[2]:

$$K_{22} - T_{g2} = C_{22}^{\text{WLF}} - T_{g2} \quad (5)$$

$$\frac{\gamma_2 \hat{V}_2^*}{K_{12}} = 2.303 C_{12}^{\text{WLF}} C_{22}^{\text{WLF}} \quad (6)$$

and WLF constants for many polymers have been tabulated by several researchers.[7,8] Therefore, if diffusivity data are available for a polymer/solvent system in the limit of zero solvent concentration, ξ can be determined from a plot of $\ln D$ vs. $(K_{22} - T_{g2} + T)^{-1}$.

For simple gases, the temperature dependence of D is commonly reported by an effective or apparent activation energy for diffusion, E_D, which is defined by

$$E_D = RT^2 \left(\frac{\partial \ln D}{\partial T}\right)_{P,\omega_1} \quad (7)$$

Table I Free-Volume Parameters for Natural Rubber/Solvent Systems

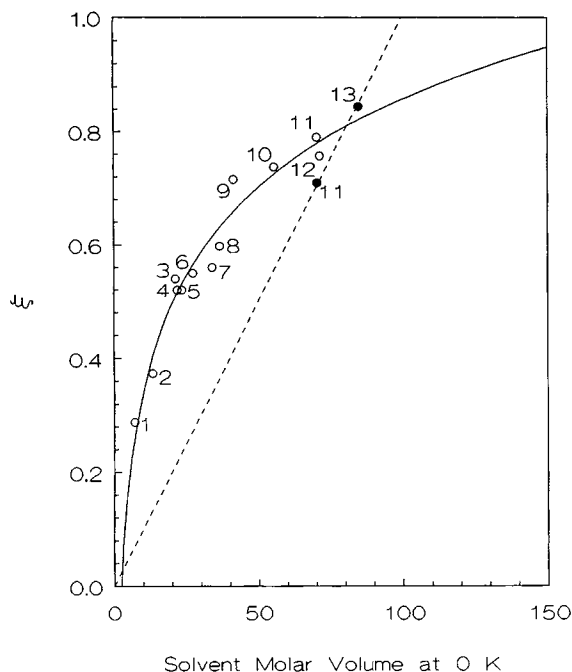|	Solvent	$\tilde{V}_1^o(0)$ (cm³/mol)	ξ	Equation	Reference
1	Helium	7.0	0.27	8	18
2	Hydrogen	13.2	0.37	8	18
3	Nitrogen	21.1	0.54	8	18
4	Oxygen	21.8	0.52	8	18
5	Argon	23.4	0.52	8	19
6	Methane	27.2	0.55	8	19
7	Carbon dioxide	33.9	0.56	8	18
8	Ethylene	36.5	0.60	8	18
9	Ethane	41.3	0.73	4	20
10	Propane	55.4	0.74	4	20
11	Benzene	70.5	0.79	4	21
12	n-Butane	71.4	0.75	4	22
13	Neopentane	84.8	0.85	4	22

Figure 1 Variation of ξ with solvent molar volume at 0 K for natural rubber/solvent systems. Numbers designating solvents correspond to those in Table I. A solid circle 11 represents a ξ value determined including the energy term, E. A dotted line is based on the solid circles.

In the limit of zero weight fraction of the solvent, this activation energy is related to the free-volume parameters by the expression

$$E_D = \frac{RT^2\left(\dfrac{\gamma_2 \hat{V}_2^* \xi}{K_{12}}\right)}{(K_{22} - T_{g2} + T)^2} \quad (\omega_1 \to 0) \qquad (8)$$

The effect of solvent size on polymer–solvent diffusion can be investigated through comparison of effective activation energies at a specific temperature for a wide variety of solvents diffusing in the same polymer. If T_{g2} and the WLF constants are known for the polymer being examined, with the help of eqs. (5) and (6), ξ can be obtained from a reported activation energy.

The above procedures have been used successfully in studies of diffusion of trace amounts of penetrants in polystyrene, poly(vinyl acetate), poly(methyl acrylate), poly (methyl methacrylate), and poly(ethyl methacrylate).[9-12] However, because diffusion studies in rubbers are often performed at temperatures more than 100°C above the T_{g2}, the assumption that energy effects can be neglected may not be valid for those systems. In such cases, eqs. (4) and (8) become

$$\ln D = \ln D_1 = \ln D_o - \frac{E}{RT}$$

$$- \frac{\dfrac{\gamma_2 \hat{V}_2^* \xi}{K_{12}}}{K_{22} - T_{g2} + T} \quad (\omega_1 \to 0) \qquad (9)$$

$$E_D = E + \frac{RT^2\left(\dfrac{\gamma_2 \hat{V}_2^* \xi}{K_{12}}\right)}{(K_{22} - T_{g2} + T)^2} \quad (\omega_1 \to 0) \qquad (10)$$

Equation (10) implies that the relative contribution of the free-volume term (the second term on the right) decreases as temperature increases. Furthermore, for small penetrants, the contribution of the energy term is more critical at lower temperatures than it is for large penetrants.[13] Alternatively, if diffusivity data are available as a function of temperature and concentration, D_o, E, and ξ can be determined directly from the nonlinear regression of eq. (1) or (2).

According to eq. (3), ξ will be a linear function of solvent molar volume at 0 K, $\hat{V}_1^0(0)$, for solvents of any size as long as the solvent molecule moves as a single unit. The critical molar volume of a polymer jumping unit, $\hat{V}_{2j}^*$, can, thus, be obtained from the inverse of the slope of a $\hat{V}_1^0(0)$ vs. ξ plot. Recently, Zielinski and Duda proposed an linear relationship
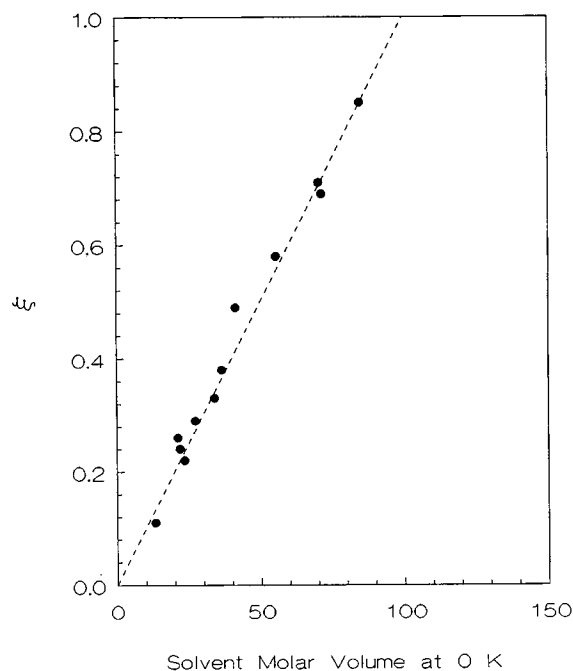

Figure 2 Variation of ξ with solvent molar volume at 0 K for solvents moving as single units in natural rubber. ξ values are determined including the energy term, E. A dotted line is the same as the one in Figure 1.

Table II Free-Volume Parameters for Polybutadiene/Solvent Systems

	Solvent	$\tilde{V}_1^0(0)$ (cm^3/mol)	ξ	Equation	Reference
1	Hydrogen	13.2	0.64	8	18
2	Nitrogen	21.1	0.91	8	18
3	Oxygen	21.8	0.86	8	18
4	Carbon dioxide	33.9	0.92	8	18
5	Methylene chloride	49.7	0.90	4	23
6	Chloroform	60.9	0.96	4	23
7	Benzene	70.5	1.00	4	23
8	Cyclohexane	84.8	1.01	1	24

between the critical molar volume of polymer jumping unit and its glass transition temperature, T_{g2}, as follows:[5]

$$\tilde{V}_{2j}^*(\text{cm}^3/\text{mol}) = 0.6224 \times T_{g2}(K) - 86.95 \quad (11)$$

Therefore, if the T_{g2} is known and the solvent moves as a single unit, the parameter ξ can be estimated, with the help of eq. (3), for a certain polymer/solvent system.

The methods for determining other free-volume parameters to estimate D_1 as a function of temperature and concentration can be summarized as follows: (1) the two critical volumes, $\hat{V}_1^*$ and $\hat{V}_2^*$, can

be estimated as the specific volumes of the solvent and polymer at 0 K. Molar volumes of the solvent and polymer at 0 K can be estimated using group contribution methods summarized by Haward,[14] and values of these parameters for a large number of solvents and polymers have been reported.[6] (2) The parameters K_{12}/γ_2 and $K_{22} - T_{g2}$ are simply related to the WLF constants of the polymers, C_{12}^{WLF} and C_{22}^{WLF}, as follows[2]:

$$\frac{K_{12}}{\gamma_2} = \frac{\hat{V}_2^*}{2.303 C_{12}^{\text{WLF}} C_{22}^{\text{WLF}}} \quad (12)$$

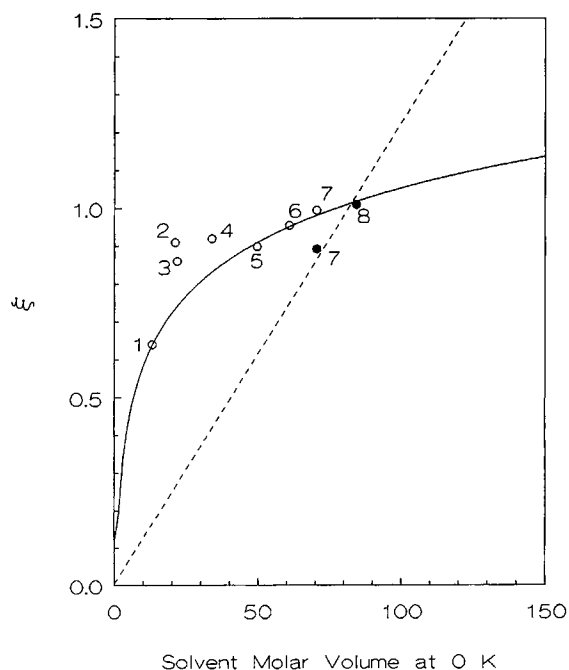$$K_{22} - T_{g2} = C_{22}^{\text{WLF}} - T_{g2} \quad (5)$$

Figure 3 Variation of ξ with solvent molar volume at 0 K for polybutadiene/solvent systems. Numbers designating solvents correspond to those in Table II. A solid circle 7 represents a ξ value determined including the energy term, E. A dotted line is based on the solid circles.
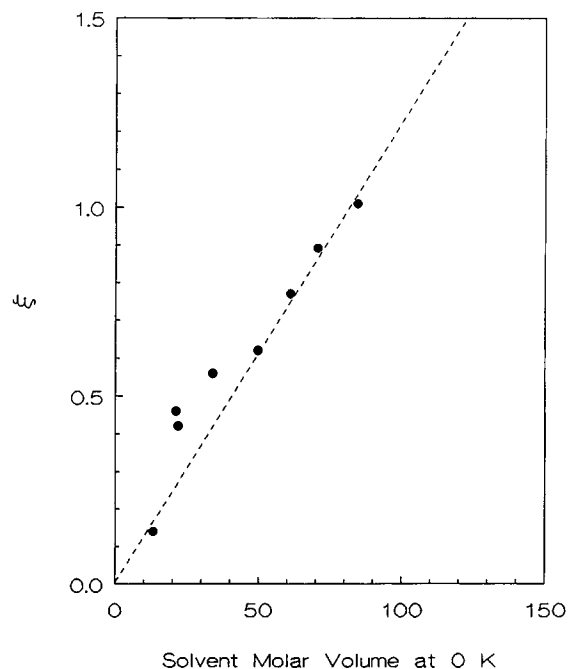

Figure 4 Variation of ξ with solvent molar volume at 0 K for solvents moving as single units in polybutadiene. ξ values are determined including the energy term, E. A dotted line is the same as the one in Figure 3.
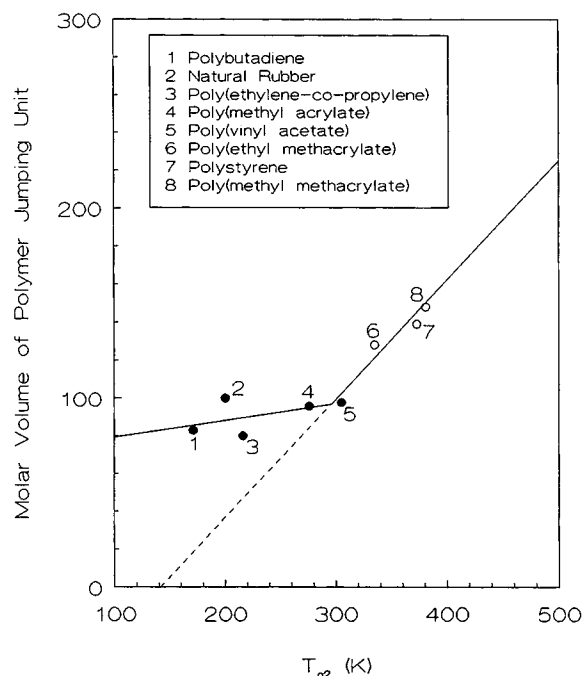
Figure 5 Correlations of the critical molar volume of a polymer jumping unit, $\hat{V}_{2j}^*$, with its glass transition temperature, T_{g2}. Solid circles represent polymers used in the new correlation, while a dotted line indicates the extension of the previous correlation from Zielinski and Duda to the lower T_{g2} range.

Values of K_{12}/γ_2 and $K_{22} - T_{g2}$ have been calculated by several researchers.[5,6] (3) In 1921, Vogel proposed an empirical equation to describe the viscosity–temperature relationship.[15] Thirty years later Doolittle postulated that viscosity should be related to the amount of free volume in a system and derived the Vogel equation from free-volume concepts.[16] Adopting Doolittle's expression and using the nomenclature of Vrentas and Duda leads to eq. (13) for solvent viscosity, η_1, by the equation

$$\ln \eta_1 = \ln A_1 + \frac{\left(\dfrac{\gamma_1 \hat{V}_1^*}{K_{11}}\right)}{(K_{21} - T_{g1}) + T} \tag{13}$$

where A_1 is considered to be effectively constant. Hence, the parameters K_{11}/γ_1 and $K_{21} - T_{g1}$ can be determined, using solvent viscosity data as a function of temperature, from a nonlinear regression analysis of eq. (13). Values of these parameters for a large number of solvents have been reported.[6] (4) Finally, D_o and E can be estimated by combining the Dullien equation[17] for the self-diffusion coefficient of pure solvents with the Vrentas–Duda free-volume equation evaluated in the limit of pure solvents. Thus,

$$\ln\left(\frac{0.124 \times 10^{-16} \tilde{V}_c^{2/3} RT}{\eta_1 M_1 \hat{V}_1}\right)$$

$$= \ln D_o - \frac{E(\omega_1 \to 1)}{RT} - \frac{\dfrac{\gamma_1 \hat{V}_1^*}{K_{11}}}{K_{21} - T_{g1} + T} \tag{14}$$

Here, $\tilde{V}_c$ (cm^3/mol) and M_1 (g/mol) are the solvent's critical molar volume and molecular weight, respectively, and 0.124×10^{-16} is a constant that has a unit of mol$^{2/3}$. η_1 (g/cm^{-s}) and $\hat{V}_1$ (cm^3/g) are the viscosity and specific volume of the pure solvent, respectively, and are the only temperature-dependent parameters in the expression. Because solvent free-volume parameters have been determined previously from eq. (13), with pure solvent viscosity and specific volume data as a function of temperature, D_o and E ($\omega_1 \to 1$) can be estimated from a nonlinear regression of eq. (14).[6] If one assumes that E does not vary much with concentration, E ($\omega_1 \to 1$) can be used over the entire concentration range.

Table III   Parameters Used in Diffusion Coefficient Predictions

Parameter	PBD/Cyclohexane	PIB/Benzene	PIB/Toluene
$\hat{V}_1^*$ (cm^3/g)	1.008	0.901	0.917
$\hat{V}_2^*$ (cm^3/g)	0.954	1.004	1.004
K_{11}/γ_1 (cm^3/g $-$ K)	3.02×10^{-3}	1.51×10^{-3}	2.20×10^{-3}
$K_{21} - T_{g1}$ (K)	-157.81	-94.32	-102.72
K_{12}/γ_2 (cm^3/g $-$ K)	6.10×10^{-4}	4.42×10^{-4}	4.42×10^{-4}
$K_{22} - T_{g2}$ (K)	-111.5	-134.6	-134.6
T_{g2}	172	203	205
D_o (cm^2/s)	2.01×10^{-4}	4.47×10^{-4}	1.87×10^{-4}
ξ	0.993	0.796	0.955
E (cal/mol)	0	0	0

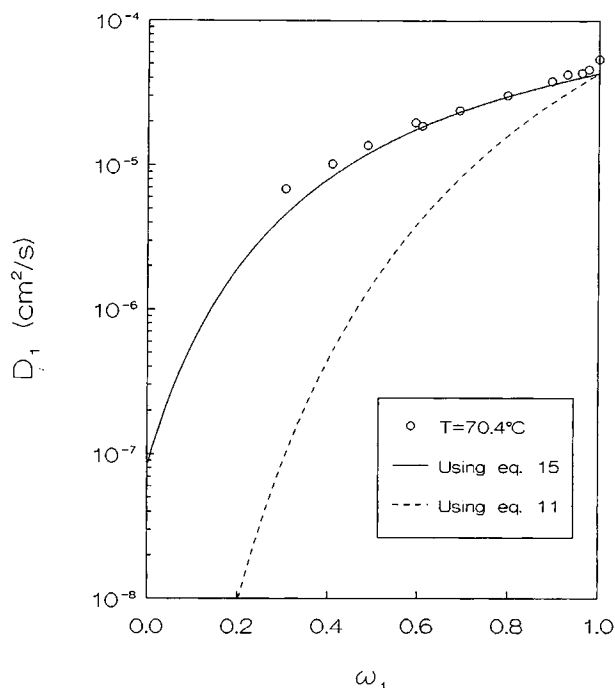Abbreviations: PBD, polybutadiene; PIB, polyisobutylene.

Figure 6 Concentration dependence of self-diffusion coefficients of benzene in polyisobutylene. Lines represent theoretical predictions and points are experimental data.[27]

However, it has been found that calculated values of E ($\omega_1 \to 1$) are relatively small compared to the E values determined from diffusion experiments and don't vary much among the solvents. Therefore, only D_{o1} (D_o when E is set equal to zero) is usually calculated from eq. (14), and the values for commonly employed solvents have been tabulated elsewhere.[6]

RESULTS AND DISCUSSION

Values of the ξ parameter have been determined for diffusion of several solvents in two rubbers using data in the literature.[18–24] If diffusivity data at zero solvent weight fraction were available in the literature, eq. (4) was used to estimate ξ. If the data were reported in the form of apparent activation energy for the diffusion, E_D, then, eq. (8) had to be used to obtain ξ. Values of solvent molar volume at 0 K, $\tilde{V}_1^0(0)$, and ξ for 13 penetrants diffusing in natural rubber are given in Table I. All the solvents studied here are assumed to move as single units. The equation used in the calculation of ξ for each solvent is also provided. The parameter ξ is plotted vs. $\tilde{V}_1^0(0)$ in Figure 1. ξ is not a linear function of $\tilde{V}_1^0(0)$ even for solvents moving as single units.

This kind of behavior was previously reported for polyisobutylene, which has almost the same T_{g2} as that of natural rubber. The nonlinearity for poly-

isobutylene was explained by the importance of the energy term, E, for the diffusion of small molecules at temperatures far above T_{g2}.[13] Because diffusivity data for benzene in natural rubber were available as a function of solvent concentration as well as temperature, the nonlinear regression analysis, using eq. (2), which includes the energy term, E, was also used to determine ξ for benzene in natural rubber. The resulting values were 0.71 and 1070 (cal/mol) for ξ and E, respectively, and this ξ value appears as a solid circle 11 in Figure 1. Although the ξ value for neopentane was determined without considering energy effect, the point was on a straight line through the origin and the new point for benzene. This fact may imply that it is reasonable to expect that the energy effect becomes less significant as solvent size increases and is negligible for neopentane. Therefore, a straight line through the origin is constructed using these two points and shown as a dotted line in Figure 1. The value of $\tilde{V}_{2j}^*$ was determined from the inverse of the slope of the line and was valued at 100 (cm³/mol). It is obvious that additional data on solvents with widely different ξ values are required to determine the value of $\tilde{V}_{2j}^*$ more precisely.

To prove that ξ is a linear function of $\tilde{V}_1^0(0)$ for solvents moving as single units and the $\tilde{V}_{2j}^*$ value for natural rubber was evaluated correctly, E value for each solvent in natural rubber was determined, using values for benzene and neopentane, with an
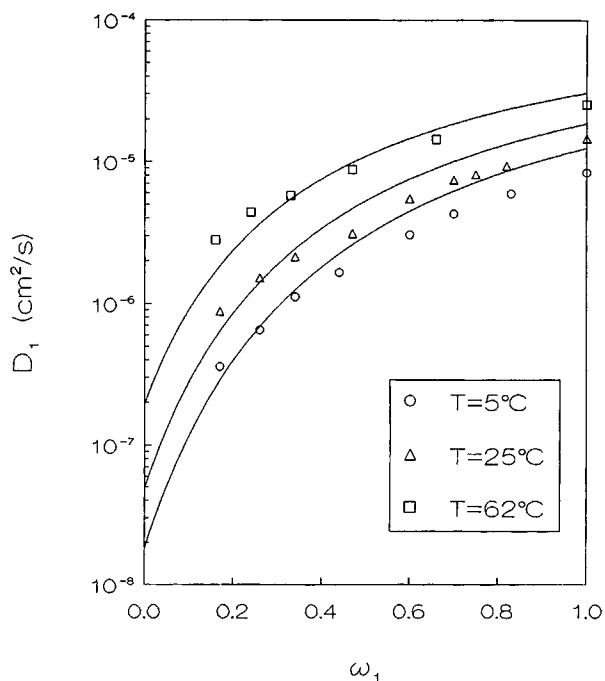

Figure 7 Concentration dependence of self-diffusion coefficients of cyclohexane in polybutadiene. Lines are theoretical predictions and points are experimental data.[26]
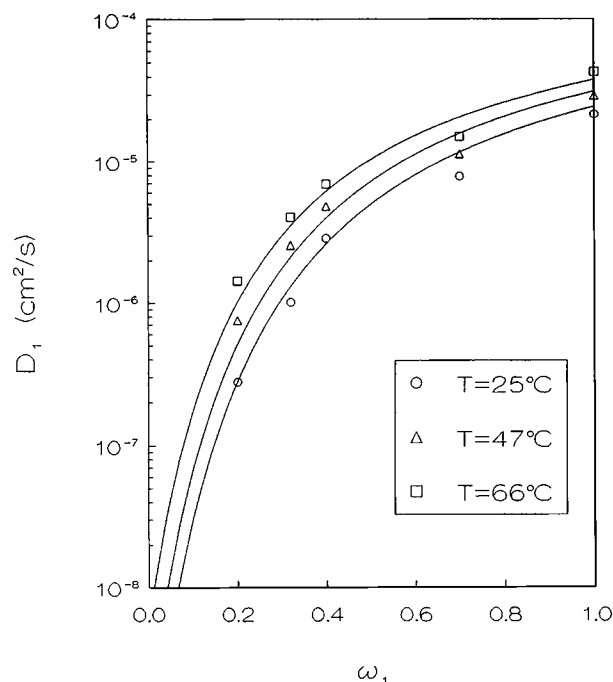
Figure 8 Concentration dependence of self-diffusion coefficients of toluene in polyisobutylene. Lines are theoretical predictions and points are experimental data.[28]

assumption that the energy term, E, varies linearly with the solvent molar volume at 0 K. ξ values for solvents represented as the open circles in Figure 1 were then recalculated, including E values, with the help of eqs. (9) and (10). The new ξ values are plotted vs. $\tilde{V}_1^0(0)$ in Figure 2. The dotted line is the same as the one in Figure 1, which was based on two points for benzene and neopentane. Surprisingly, all but two of these points are on the straight line.

ξ values for solvents with polybutadiene are also tabulated in Table II, while a plot of $\tilde{V}_1^0(0)$ vs. ξ is shown in Figure 3. Same as the case of natural rubber, the plot for polybutadiene shows a nonlinear relationship between $\tilde{V}_1^0(0)$ and ξ. Because diffusivity data for benzene in polybutadiene were available as a function of solvent concentration at various temperatures, the nonlinear regression method using eq. (2) was also used to determine ξ value for benzene. The resulting values were 0.89 and 830 (cal/mol) for ξ and E, respectively. This ξ value appears as a solid circle 7 in Figure 3. Same as the case of natural rubber, cyclohexane (which has the same molar volume as that of neopentane) was assumed to be free from energy effect ($E = 0$). A straight line through the origin is drawn using these two points and shown as a dotted line in Figure 3. The value of $\tilde{V}_{2j}^*$ was determined from the inverse of the slope of the line and was valued at 82 (cm³/mol). Based on the same assumptions for natural rubber, E value

was calculated for each solvent. ξ values were then recalculated using the same procedures for natural rubber and are plotted vs. $\tilde{V}_1^0(0)$ in Figure 4. Again, same as the case of natural rubber, most points are on the straight line based on two points for benzene and cyclohexane.

Values of $\tilde{V}_{2j}^*$ for poly(vinyl acetate), poly-(methyl acrylate), and poly(ethylene-co-propylene) have been reported in the literature,[5,25] while those for polybutadiene and natural rubber were determined in this study. The values of $\tilde{V}_{2j}^*$ for these polymers are correlated with glass transition temperatures of the polymers, and a linear regression of the data yields

$$\tilde{V}_{2j}^*(\text{cm}^3/\text{mol}) = 0.0925 \times T_{g2}(K) + 69.47 \quad (15)$$

The new correlation as well as the one from Zielinski and Duda [eq. (11)] are shown in Figure 5 with the values of $\tilde{V}_{2j}^*$ for eight polymers. The solid circles represent the polymers used for the new correlation, while the dotted line indicates the extension of the previous correlation to the lower temperature range. The result indicates that two correlations meet each other at near room temperature (295 K). Although a single correlation can be obtained if a polynomial function is used, two linear correlations are proposed in this study due to their simplicity. Therefore, eq. (15) can be used for polymers having
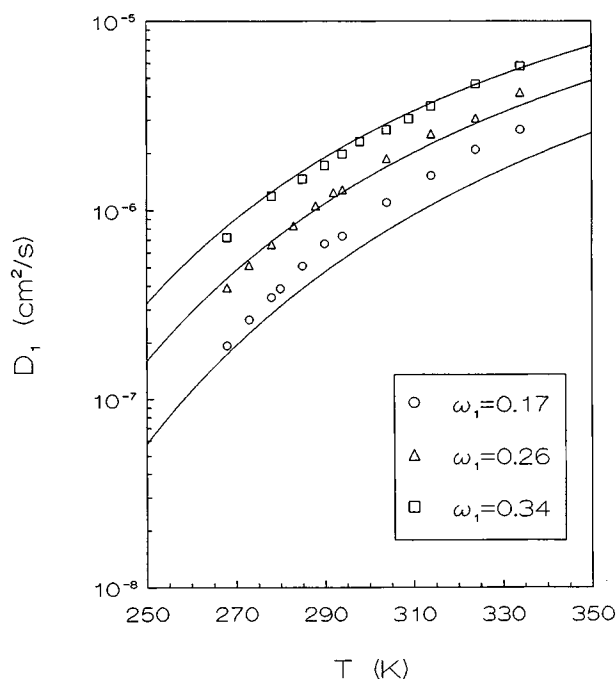

Figure 9 Temperature dependence of self-diffusion coefficients of cyclohexane in polybutadiene. Lines are theoretical predictions and points are experimental data.[26]
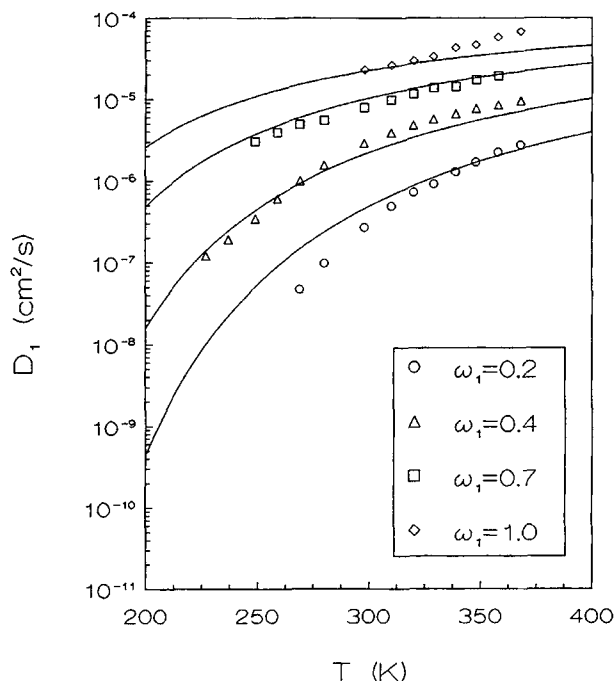
Figure 10 Temperature dependence of self-diffusion coefficients of toluene in polyisobutylene. Lines are theoretical predictions and points are experimental data.[28]

T_{g2} lower than 295 K, while eq. (11) for polymers possessing T_{g2} higher than 295 K.

Solvent self-diffusion coefficients have been predicted as a function of temperature and concentration for three polymer/solvent systems: polybutadiene/cyclohexane,[26] polyisobutylene/ benzene,[27] and polyisobutylene/toluene.[28] These predictions are shown in Figures 6-10, while the parameters used to generate the theoretical curves are provided in Table III. All the parameters have been estimated without using any diffusion data, and the values (except for ξ and E) can be found in the literature.[6] In this study, the ξ parameter was estimated using eqs. (3) and (15) because the glass transition temperatures of the polymers studied were well below 295 K. Because the solvents studied are assumed being large enough to neglect the energy effect, and the E parameter cannot be estimated without using diffusion data at the present time, E is set equal to zero.

In Figure 6, the prediction results, using ξ values from eq. (11) as well as eq. (15), are presented. The value of the ξ parameter using eq. (11) was 1.735. As we can see, the prediction can be improved a lot when eq. (15) instead of eq. (11) was used for rubbers. For all the systems investigated, the predictions are comparable with experimental data. The Vrentas-Duda theory can reasonably predict both temperature and concentration dependencies of solvent

self-diffusion coefficients. For the polybutadiene/cyclohexane system, although the ratios of cis-, trans-, and vinyl-polybutadiene used in the diffusion experiment and in the calculation of the polymer free-volume parameters were somewhat different, the predictions are still reasonable.

CONCLUSIONS

The plots of $\tilde{V}_1^0(0)$ vs. ξ for rubber/solvent systems show a nonlinear behavior if the energy effect on diffusion was not considered in the calculation of ξ. The ξ values for solvents moving as single units are located on the straight line, however, when the energy term, E, was included in the calculation of ξ. In order to confirm the importance of the energy effect further, additional diffusion data are required over wide ranges of temperature and concentration for solvents with widely different ξ values. The correlation of $\tilde{V}_{2j}^*$ with T_{g2} for five polymers in this study shows a linear relationship between these two properties and meets the previous correlation from Zielinski and Duda at 295 K. Depending on the T_{g2} of polymer interested, therefore, one of the correlations can be used to calculate $\tilde{V}_{2j}^*$. Once $\tilde{V}_{2j}^*$ has been evaluated for a particular polymer, ξ can be determined for any solvent that moves as a single unit.

When the relationship proposed in this study was used to calculate the ξ parameter, the Vrentas-Duda theory can reasonably predict solvent self-diffusion coefficients in rubbers. Although the experimental data were reported as early as in 1967, this is the first time that solvent self-diffusion coefficients for these systems are predicted successfully using free-volume theory because the correct method to estimate the ξ parameter for rubbers was not available before. The results indicate that the new correlation to estimate the ξ parameter is valid and can be used to predict diffusion behavior of other polymer/solvent systems.

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