

# Gas Chromatographic Measurements of Diffusion Coefficients of Trace Amounts of Benzene, Toluene, and Ethylbenzene in Polyisobutylene at Elevated Temperatures

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**ABSTRACT:** The measurements of the diffusion coefficients of trace amounts of three solvents, benzene, toluene, and ethylbenzene, in polyisobutylene (PIB) were performed at elevated temperatures by inverse gas chromatography. A packed chromatographic column was used. The Hadj-Romdhane-Danner mathematical model to describe the chromatographic process and the corresponding moment analysis were adopted to determine the diffusion coefficients. The goodness of fit of the experimental diffusion coefficient data to the Vrentas-Duda free-volume relationship indicates that the free-volume theory is a very good description of the relationship of the observed solvent diffusion coefficient with temperature. Furthermore, the solvent diffusivity data were compared, by using the free-volume theory, with those determined by nuclear magnetic resonance method for the systems of PIB/benzene and PIB/toluene. The good agreements show that these diffusivity data obtained by inverse gas chromatography measurement are reliable. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 529–538, 2001

**Key words:** inverse gas chromatography; diffusion coefficient; polyisobutylene; solvent; free volume

## INTRODUCTION

Most of the available diffusion coefficient data<sup>1,2</sup> of small weight molecules in polymers were obtained by sorption experiments. However, the sorption experiments become difficult to use in a polymer-solvent system in the case of very small amounts of solvent. Therefore, only a few data for highly concentrated polymer solutions can be found in the literature. However, such data are very important to chemical engineers and of particular interest in production and applications of polymer membranes. In the last twenty years,

inverse gas chromatographic (IGC) techniques have been developed to measure rapidly the diffusion coefficient of trace amounts of small-weight molecules in polymer. Previously, a packed-column IGC was usually used and diffusion coefficient estimation was extracted from the elution curve data by using the van Deemter equation.<sup>3–6</sup> Recently, the IGC method for the measurement of diffusivity has been developed by several different researchers. Pawlisch et al.<sup>7</sup> presented a significant improvement where capillary chromatographic columns with highly uniform coatings of polymer were used instead of packed columns, and a new mathematical model was established to describe capillary column IGC. Meanwhile, a moment analysis procedure was proposed to analyze the chromatographic eluting curves and correct the asymmetry of the chro-

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matographic peaks. Therefore, the measurement accuracy is greatly improved. Hadj-Romdhane and Danner<sup>8</sup> proposed a new mathematical model to describe the chromatographic process in a packed column where the diffusions of solvent both in polymer and gas phase were considered, and a moment analysis procedure was developed from this model. In the moment analysis procedure, the asymmetry of chromatographic peaks was accounted for. This improvement overcomes the two main defects in the established mathematical model on which the van Deemter equation is based. One is that the diffusion of solvent molecules in the gas phase is neglected, and the other is that the asymmetry of the chromatographic peaks eluting from the packed column is not considered. Therefore, the diffusion coefficients obtained have a better accuracy than those determined from the van Deemter equation. In this work, the diffusion coefficient of trace amounts of three solvents (benzene, toluene, and ethylbenzene) in polyisobutylene (PIB) at elevated temperatures were measured by using the Hadj-Romdhane-Danner model to analyze the chromatographic data in the packed column. Because the film thickness coated on particles in the packed column has great influence on the measurement accuracy of the diffusion coefficient, the method, which was proposed by Braun and Guillet<sup>9</sup> to accurately determine the film thickness, was adopted. In addition, the experimental data were analyzed using the Vrentas-Duda free-volume relationship and compared with the data determined from the nuclear magnetic resonance (NMR) method.

## EXPERIMENTAL

### Materials

The sample of PIB ( $\bar{M}_v = 1.2 \times 10^6$ ) was purchased from Aldrich Chemical Co. Benzene, toluene, ethylbenzene, and propione were of analytical grade reagents, and they were all rectified before use.

### Preparation of Packed Columns

Two packed columns were prepared; one was a Chromosorb-W column that was used to measure the diffusion coefficient, and the other was a glass-bead column that was used in the determination of absorption parameters of the probe mol-

**Table I** Column Characteristics

Support Type	<i>L</i> /cm	<i>W<sub>s</sub></i> /g <sup>a</sup>	<i>W<sub>p</sub></i> /g <sup>b</sup>
Chromosorb-W	198	5.8067	0.3015
Glass bead	198	17.4438	0.1480

<sup>a</sup> Weight of support.

<sup>b</sup> Weight of polymer.

ecule in polymer. Samples of Chromosorb-W and glass bead, of mesh size 60/80, were obtained from Shanghai No. 1 Reagent Manufactory of China and the Center of Measurement and Test of Tongji University of China, respectively. The PIB was coated onto these two particles by solvent evaporation. A solution of the polymer in benzene was mixed with the solid support and solvent was removed by slow evaporation; the particles were then dried under vacuum to constant weight. The coated Chromosorb-W and glass beads were then placed in solvent-washed 195-cm-long, 5-mm i.d. stainless steel tubes with the aid of a mechanical vibrator. The ends of the tubes were loosely plugged with steel wool. The column characteristics are shown in Table I.

### Apparatus and Procedure

The gas chromatograph used was the HPSF1490 (HP-Shanghai Analytical Instrument Limited Co.) equipped with a thermal conductivity detector. Hydrogen was used as the carrier gas in all experiments. The temperature of injection block and the detector were set about 40 K above the column temperature to avoid condensation. Small amounts of solvent (0.4  $\mu$ L) were injected through a silicone rubber septum using a 10- $\mu$ L syringe. Usually, about 6  $\mu$ L of air were injected along with the liquid samples as the inlet component to determine the average velocity of carrier gas in the column. The output from the thermal conductivity detector was fed to a chromatographic workstation for further analysis of the chromatographic peaks. The carrier gas flow rate was measured by means of a soap-bubble flowmeter. At each temperature, measurements were made over a wide range of flow rates. In addition, replicate experiments were done at each flow rate to ensure that the results were reproducible at a fixed set of conditions. After each flow-rate study, the pressure drop across the column was measured by a highly accurate manometer and the column set to the next flow rate.

## CALCULATIONS

### Determination of the Thickness of Polymer Film on the Particles Chromosorb-W

The method proposed by Braun and Guillet<sup>9</sup> was applied to evaluate the film thickness  $d_f$  on the particles Chromosorb-W. Here, propione, a non-solvent for PIB, was used as a probe molecule on a polymeric stationary phase with support particles of glass beads. The propione was used to obtain the retention volume in a glass-bead column at temperatures ranging from 318.2 to 341.2 K under a constant carrier gas velocity of 50 cm/min. An average value of  $1.26 \times 10^{-7}$  was obtained for the absorption constant  $K_{a,0}$  and a value of  $-27.78 \text{ kJ} \cdot \text{mol}^{-1}$  for the absorption heat,  $\Delta H$ . Then, the specific surface area of Chromosorb-W accessible to PIB was available from the retention volume of probe molecules in the packed column of Chromosorb-W. An averaged value of  $4.98 \times 10^{-5} \text{ cm}$  was obtained for the film thickness  $d_f$  in the Chromosorb-W column used in this work.

### Diffusion Equation of the Solvent in a Packed Column

Hadj-Romdhane and Danner<sup>8</sup> had derived the solvent diffusion equation in a packed column from their model as:

$$H_{\text{eff}}/v = C_p \frac{j}{f} + C_{g0} \quad (1)$$

where  $j$  is the James-Martin compressibility factor,  $f$  is the compressibility factor of Giddings et al.,<sup>8</sup> and  $v$  is the average value of the velocity of the carrier gas.  $C_p$  and  $C_{g0}$  are the resistance to mass transfer in the polymer and the gas phase, respectively.  $H_{\text{eff}}$  is defined as:

$$H_{\text{eff}} = L \frac{\mu_2^* j}{\mu_1^2 f} - Aj - \frac{B_0}{v} j^2 \quad (2)$$

where  $A$ , the multi-path factor, is equal to  $2 \lambda d_p$ ,  $\lambda$  is a packing characterization factor, and  $d_p$  is the particle diameter.  $L$  is the length of the column.  $B_0$ , the longitudinal diffusion term, is equal to  $2 \tau D_{m0}$ , where  $\tau$  is the tortuosity factor that takes into account the irregular pattern along the particles, and has a value in the range of 0.6 ~ 1.0.<sup>10</sup>  $D_{m0}$  is the value of the molecular diffu-

sion coefficient evaluated at the outlet pressure,  $P_0$ .  $L\mu_2^*/\mu_1^2$  is the theoretical plate height, where  $\mu_1$  is the first temporal moment or the mean residence time and  $\mu_2^*$  is the second central moment or variance of the concentration distribution, which are defined as:

$$\mu_1 = \int_0^\infty tC(t) dt / \int_0^\infty C(t) dt \quad (3)$$

$$\mu_2^* = \int_0^\infty (t - \mu_1)^2 C(t) dt / \int_0^\infty C(t) dt \quad (4)$$

where  $C(t)$  is the eluting concentration of solvent at the moment of  $t$ .

### Determination of Solvent Diffusion Coefficient

The left-hand side of eq. (1),  $H_{\text{eff}}/v$ , vs  $j/f$  should yield a straight line with a slope  $C_p$  and an intercept  $C_{g0}$ . According to the definitions of  $C_p$  and  $C_{g0}$ :

$$C_p = \frac{2}{3} \frac{k}{(1+k)^2} \frac{d_f^2}{D_1} \quad (5)$$

$$C_{g0} = \frac{2}{3} \frac{k}{(1+k)^2} \frac{KR_p}{k_{f0}} \left( \frac{R_p^3 - R_s^3}{R_p^3} \right) \quad (6)$$

If the capacity ratio  $k$  and the film thickness  $d_f$  are evaluated, the diffusion coefficient of solvent in polymer  $D_1$  will be obtained from  $C_p$ . Here,  $k$  is equal to  $K\epsilon_p/\epsilon_g$  where  $K$  is the equilibrium partition coefficient and  $\epsilon_p$  and  $\epsilon_g$  are fractional volumes of polymer and gas phases, respectively.  $R_s$  and  $R_p$  are the radius of the support particles and the polymer film.  $k_{f0}$  is the value of external fluid-film mass-transfer coefficient evaluated at the outlet pressure.

Two parameters of the diffusion model,  $A$  and  $B_0$ , should be determined before linear regress of eq. (1) in  $H_{\text{eff}}/v$  vs  $j/f$ . Here, assuming the value of  $\tau$  to be unity in all case, the values of  $B_0$  can be evaluated by calculation of  $D_{m0}$  from the Fuller-Schettler-Giddings equation<sup>11</sup> at any temperature. At high velocity of the carrier gas, eq. (1) can be simplified to be:

$$L\mu_2^*/\mu_1^2 = Af + cv \quad (7)$$

**Table II Diffusion Coefficients of Trace Amounts of Benzene, Toluene, and Ethylbenzene in Polyisobutylene and the Corresponding Parameters of the Diffusion Model**

$T$ (K)	$D_1 \times 10^9$ (cm <sup>2</sup> /s)	$C_p$ (s)	$k$	$\ln D_1$	$10^3/T + K_{22} - T_{g2}$	$\ln D_1\lambda$	$1/T_{RF}$
Benzene							
323.2	0.75	0.293	5.33	-21.01	5.30	-23.85	2.98
341.2	2.05	0.138	3.57	-20.01	4.84	-22.84	2.72
348.2	3.05	0.101	3.08	-19.62	4.68	-22.45	2.63
356.2	3.34	0.075	2.68	-19.25	4.51	-22.36	2.54
363.2	6.27	0.054	2.44	-18.88	4.37	-21.73	2.46
373.2	8.99	0.038	2.15	-18.48	4.19	-21.37	2.36
Toluene							
323.2	0.35	0.310	13.19	-21.77	5.30	-24.62	3.14
341.2	1.59	0.150	7.09	-20.55	4.84	-23.11	2.86
348.2	1.92	0.125	6.17	-20.26	4.68	-22.92	2.77
356.2	2.35	0.098	4.92	-19.86	4.51	-22.72	2.67
363.2	3.03	0.080	4.38	-19.58	4.37	-22.46	2.59
373.2	4.24	0.050	3.53	-18.98	4.19	-22.13	2.48
Ethylbenzene							
341.2	1.01	0.135	15.36	-21.08	4.84	-23.57	2.49
348.2	1.39	0.103	11.97	-20.59	4.68	-23.25	2.89
356.2	1.79	0.083	9.08	-20.15	4.51	-23.00	2.79
363.2	2.28	0.073	7.60	-19.88	4.37	-22.76	2.70

Therefore, the value of  $A$  can be obtained from high-velocity data by linear regression. To determine the diffusion coefficient of solvent  $D_1$  from the regressed value of  $C_p$ , the capacity ratio  $k$  and the film thickness  $d_f$  must first be evaluated.

Applying moment analysis of the eluting curve of the concentration time, the value of  $k$  can be obtained from linear regression in  $\mu_1$  vs the time of the carrier gas passing the column to need,  $L/v$ , with the moment equation:

$$\mu_1 = \frac{L}{v} (1 + k) \quad (8)$$

Here, no interaction between air and polymer is assumed, so the retention time of air,  $t_a$ , is identical to  $L/v$ . From the slopes of the linear plots of  $\mu_1$  vs  $t_a$ , the values of the capacity ratio  $k$  at different temperatures for three solvents (benzene, toluene, and ethylbenzene) were determined. These values are listed in Table II.

## RESULTS AND DISCUSSION

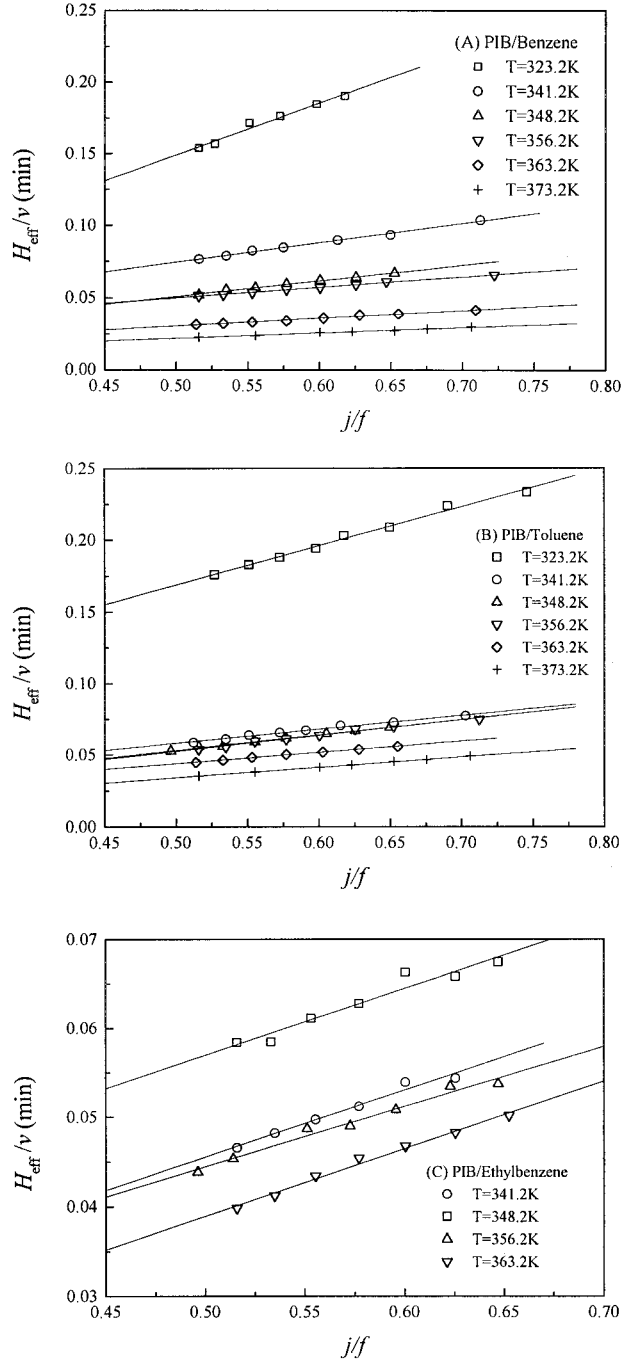
The theoretical plate height in eq. (2),  $L\mu_2^*/\mu_1^2$ , can be determined either according to eqs. (3) and (4) or directly from the retention time at peak maximum

and the peak width at half-height, as suggested by Conder and Young<sup>12</sup>

$$L \frac{\mu_2^*}{\mu_1^2} = \frac{L}{5.54} \left( \frac{W_{1/2}}{t_r} \right) \quad (9)$$

where  $W_{1/2}$  is the peak width at half-height and  $t_r$  is the retention time of solvent obtained at the maximum of the peak. These two approaches have no significant difference. The latter was applied in this work. Thus, using eq. (2),  $H_{\text{eff}}$  can be calculated from the values of the model parameters,  $A$  and  $B_0$ , and chromatographic data  $L\mu_2^*/\mu_1^2$  at different inlet pressures of the Chromosorb-W column that correspond to velocity of carrier gas,  $v$ . The plots of  $H_{\text{eff}}/v$  vs  $j/f$  were prepared at different temperatures for benzene, toluene, and ethylbenzene. As shown in Figure 1, the data are in good agreement with eq. (1). The value of the parameter  $C_p$  at each temperature was obtained by linear regression in  $H_{\text{eff}}/v$  vs  $j/f$ .

According to the definition of  $C_p$ , the diffusion coefficients,  $D_1$ , of trace amounts of benzene, toluene, and ethylbenzene in PIB were determined combining the capacity ratio  $k$  and the film thickness  $d_f$ . The results of  $C_p$  and  $D_1$  are all listed in Table II.



**Figure 1** Estimation of  $D_1$  for benzene, toluene, and ethylbenzene in PIB (A) benzene in PIB, (B) toluene in PIB, (C) ethylbenzene in PIB.

### Test of the Vrentas-Duda Free-Volume Theory

For a polymer-solvent system, the concentration or temperature dependence of solvent diffusion coefficient  $D_1$  can be expressed using the Vrentas-Duda<sup>13,14</sup> free-volume equation:

$$D_1 = D_{01} \exp \left[ -\frac{E^*}{RT} \right] \exp \left[ \frac{-(\omega_1 \hat{V}_1^* + \omega_2 \hat{V}_2^* \xi)}{\omega_1 (K_{11}/\gamma)(K_{21} - T_{g1} + T) + \omega_2 (K_{12}/\gamma)(K_{22} - T_{g2} + T)} \right] \quad (10)$$

where  $V_i^*$  is the specific critical hole-free volume of component  $i$  required for a jumping ( $i$  can be 1 or 2; 1 for solvent and 2 for polymer),  $\gamma$  is an overlap factor,  $K_{11}$  and  $K_{21}$  are the free-volume parameters for the solvent, whereas  $K_{12}$  and  $K_{22}$  for the polymer,  $T_{gi}$  is the glass transition temperature of component  $i$ ,  $\omega_i$  is the mass fraction of component  $i$ ,  $D_{01}$  is a pre-exponential factor which is assumed to be independent of temperature, and  $\xi$  is the ratio of molar volume of the solvent jumping unit to the molar volume of the polymer jumping unit.  $E^*$  is the energy per mol that a molecule needs to overcome attractive forces from neighboring molecules. There are nine independent parameters that need to be determined in eq. (10):  $D_{01}$ ,  $E^*$ ,  $\xi$ ,  $K_{11}/\gamma$ ,  $K_{21} - T_{g1}$ ,  $K_{12}/\gamma$ ,  $K_{22} - T_{g2}$ ,  $\hat{V}_1^*$  and  $\hat{V}_2^*$ . However, most of them can conceivably be set from other data than diffusion data. For example,  $K_{12}/\gamma$  and  $K_{22} - T_{g2}$  can be estimated from zero shear rate viscosity or indirectly from the tabulated values of the Williams-Landel-Ferry (WLF) constant.<sup>15</sup> The two critical volumes  $\hat{V}_1^*$  and  $\hat{V}_2^*$  can be estimated as the specific volume of the solvent and polymer at temperature  $T = 0\text{K}$  from established group contribution methods.<sup>16</sup> For the systems under study, PIB and its solvents (benzene, toluene, and ethylbenzene), the values of parameters  $K_{12}/\gamma$ ,  $K_{22} - T_{g2}$  and  $\hat{V}_2^*$  for PIB and  $\hat{V}_1^*$  for solvents are collected from Refs. 17 and 18, and they are listed in Table III. Usually, the term of  $E^*$  is set to zero because the solvent diffusion is dominated by free volume rather than by energy effects.<sup>18</sup>

In various versions of the Vrentas-Duda predictive theory, the free-volume parameters  $D_{01}$ ,  $K_{11}/\gamma$ , and  $K_{21} - T_{g1}$  are evaluated by combining the expression developed by Dullien<sup>19</sup> for self-diffusion  $D_1^0$  of pure solvents:

$$\frac{\eta_1 D_1^0}{RT} = 0.124 \times 10^{-16} V_c^{2/3} \quad (11)$$

with the Vrentas-Duda equation evaluated in the pure solvent limit, i.e.,

$$D_1^0 = D_{01} \exp \left[ -\frac{\hat{V}_1^*}{K_{11}/\gamma_1 (K_{21} - T_{g1} + T)} \right] \quad (12)$$

**Table III Free-Volume Parameters of PIB, Benzene, Toluene, and Ethylbenzene**

Parameter	PIB/Benzene	PIB/Toluene	PIB/Ethylbenzene
$\hat{V}_1^*$ (cm <sup>3</sup> /g)	0.901	0.917	0.946
$\hat{V}_2^*$ (cm <sup>3</sup> /g)	1.004	1.004	1.004
$K_{11}/\gamma$ (cm <sup>3</sup> /g·K)	$5.55 \times 10^{-3}$	$4.44 \times 10^{-3}$	$3.28 \times 10^{-3}$
$K_{21} - T_{g1}$ (K)	-205.1	-175.0	-159.1
$K_{12}/\gamma$ (cm <sup>3</sup> /g·K)	$4.42 \times 10^{-4}$	$4.42 \times 10^{-4}$	$4.42 \times 10^{-4}$
$K_{22} - T_{g2}$ (K)	-134.6	-134.6	-134.6
$T_{g2}$ (K)	205	205	205
$D_{01}$ (cm <sup>2</sup> /s)	$1.36 \times 10^{-4}$	$1.42 \times 10^{-4}$	$1.79 \times 10^{-4}$
$\xi$	1.01	1.07	1.13
$E^*$ (J/mol)	0	0	0

so that,

$$\ln\left(\frac{0.124 \times 10^{-16} V_c^{2/3} RT d_1}{\eta_1 M_1}\right) = \ln D_{01} - \frac{\hat{V}_1^*/(K_{11}/\gamma)}{K_{21} - T_{g1} + T} \quad (13)$$

where  $d_1$  and  $\eta_1$  are the density and viscosity of a pure solvent respectively,  $V_c$  is the molar volume of a solvent at its critical temperature, and  $M_1$  is the molecular weight of a solvent. In principle, the quantities  $D_{01}$ ,  $K_{11}/\gamma$ , and  $K_{21} - T_{g1}$  of a solvent can be determined, from the solvent viscosity and density as a function of temperature, by using a nonlinear regression analysis based on eq. (13). However, the fitting in this case cannot yield a unique set of parameter values. For example, three different sets of such parameter values for toluene were reported in literature, although they all are estimated from the viscosity-temperature and density-temperature data, i.e.:

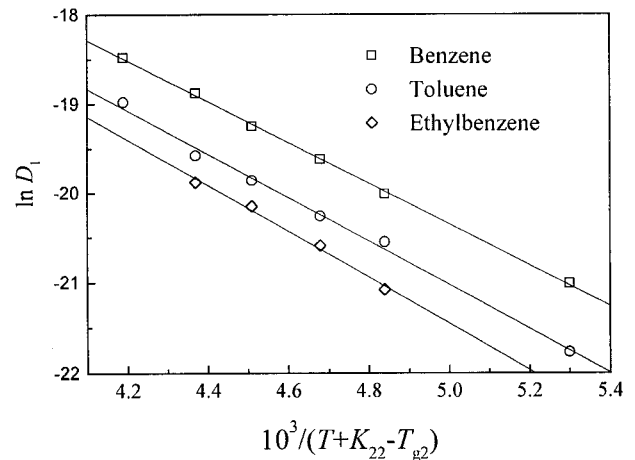
1. In Ref. 17:  $D_{01} = 4.82 \times 10^{-4}$  cm<sup>2</sup>/s,  $K_{11}/\gamma = 1.45 \times 10^{-3}$  cm<sup>2</sup>/(g · K) and  $K_{21} - T_{g1} = -86.32$  K.
2. In Ref. 18:  $D_{01} = 1.87 \times 10^{-4}$  cm<sup>2</sup>/s,  $K_{11}/\gamma = 2.20 \times 10^{-3}$  cm<sup>2</sup>/(g · K) and  $K_{21} - T_{g1} = -102.72$  K.
3. In Ref. 20:  $D_{01} = 4.17 \times 10^{-4}$  cm<sup>2</sup>/s,  $K_{11}/\gamma = 1.57 \times 10^{-3}$  cm<sup>2</sup>/(g · K) and  $K_{21} - T_{g1} = -90.5$  K.

In this work, the three above-mentioned parameters are evaluated by a way as follows. At zero solvent mass fractions, if energy effect on the diffusion is assumed to be negligible, eq. (10) can be rewritten as:

$$\ln D_1 = \ln D_{01} - \frac{\hat{V}_2^* \xi}{(K_{12}/\gamma)(K_{22} - T_{g2} + T)} \quad (14)$$

The parameters,  $D_{01}$  and  $\xi$ , can be obtained by linear regression in  $\ln D_1$  vs  $(K_{22} - T_{g2} + T)^{-1}$ . The correlation, as shown in Figure 2, indicates that the temperature dependence of the solvent diffusion coefficients obtained in this study is well captured by the Vrentas-Duda free-volume theory. The regressed values of  $D_{01}$  and  $\xi$  for each system are given in Table III.

When  $D_{01}$  is determined from the solvent diffusivity data as a function of temperature, parameters  $K_{11}/\gamma$  and  $K_{21} - T_{g1}$  can be estimated from the viscosity-temperature and density-temperature data by using linear regression analysis based on a reformed expression:



**Figure 2** Free-volume correlation of the diffusion coefficient data of benzene, toluene, and ethylbenzene in PIB.

$$\left\{ \ln \left( \frac{0.124 \times 10^{-16} V_c^{2/3} R T d_1}{\eta_1 M_1} \right) - \ln D_{01} \right\}^{-1} = - \frac{K_{21} - T_{g1}}{\hat{V}_1^*/(K_{11}/\gamma)} - \frac{T}{\hat{V}_1^*/(K_{11}/\gamma)} \quad (15)$$

of eq. (13). The quantities  $K_{11}/\gamma_1$  and  $K_{21} - T_{g1}$  for benzene, toluene, and ethylbenzene were determined using viscosity-temperature and density-temperature data<sup>21</sup> of pure solvents, and they are listed in Table III.

If a solvent moves as a single unit, the parameter  $\xi$  is defined as follows:

$$\xi = \frac{\hat{V}_1^0(0)}{\hat{V}_{2j}^*} = \frac{\hat{V}_1^* \cdot M_1}{\hat{V}_2^* \cdot M_{2j}} \quad (16)$$

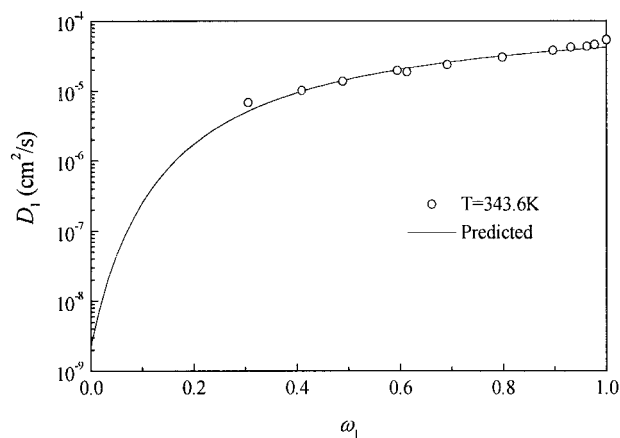
where  $\hat{V}_1^0(0)$  and  $\hat{V}_{2j}^*$  are the solvent molar volume at 0 K and the molar volume of polymer jumping unit, whereas  $M_{2j}$  is the molar weight of the polymer jumping unit. Because  $\xi$  is one of the most sensitive free-volume parameters, accurate estimation of the  $\xi$  parameter is very important. Two kinds of empirical methods had been proposed to estimate the  $\xi$  parameter. One was developed by Ju et al., i.e.,  $\gamma \hat{V}_2^* \xi / K_{12}$  was found to be a linear function of the solvent molar volume at 0 K  $\hat{V}_1^0(0)$ :

$$\frac{\gamma \hat{V}_2^* \xi}{K_{12}} = B \cdot \hat{V}_1^0(0) \quad (17)$$

where  $B$  is a constant dependent on polymer and independent of solvent. Therefore, once  $B$  is known for a particular polymer, the value of  $\xi$  for any solvent in that polymer can be determined accurately. Recently, Bandis et al.<sup>23</sup> found that the linear relationship between  $\gamma \hat{V}_2^* \xi / K_{12}$  and  $\hat{V}_1^0(0)$  is not true for some polymers such as PIB. The other is to estimate the molar volume of the polymer jumping unit  $\hat{V}_{2j}^*$  from an empirical linear relationship between  $\hat{V}_{2j}^*$  and the glass transition temperature  $T_{g2}$  of polymer:

$$\hat{V}_{2j}^* = 0.6224 \cdot T_{g2}(K) - 86.95 \quad (18)$$

However, Hong<sup>18</sup> found that the values of  $\hat{V}_{2j}^*$  of some polymers, such as polybutadiene, PIB, poly(ethylene-co-propylene) etc., have great deviations from the above-mentioned linear relationship. Although another relationship between  $\hat{V}_{2j}^*$  and  $T_{g2}$  has been proposed by some researchers,<sup>18</sup> the predictive accuracy of  $\xi$  still cannot be ensured.

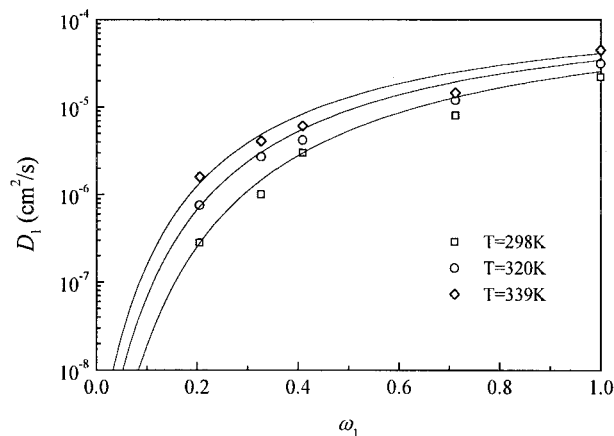


**Figure 3** Concentration dependence of diffusion coefficients of benzene in PIB. Lines represent theoretical predictions and points are experimental data.<sup>22</sup>

Therefore, the regressed values of  $\xi$  from the diffusivity-temperature data measured in this work were selected for further discussion.

#### A Comparison of the Diffusion Coefficient Measured by the IGC Method with Those Obtained by NMR Experiment Using the Vrentas-Duda Theory

In previous articles,<sup>22,23</sup> the diffusion coefficients for the systems of PIB/benzene and PIB/toluene were measured at various solvent concentrations and temperatures by means of NMR experiment. To verify the solvent diffusion coefficients measured in this work, a comparison was performed using the Vrentas-Duda free-volume theory. Temperature and concentration dependence of the solvent diffusion coefficients for two polymer/solvent systems: PIB/benzene and PIB/toluene were predicted by using the Vrentas-Duda free-volume theory. These predictions are shown in Figures 3 and 4, and the parameters used to generate the theoretical curves are provided in Table III. Two of these parameters,  $D_{01}$  and  $\xi$ , are obtained by regression of the diffusivity data at infinite dilution measured in this work. Figures 3 and 4 also show a comparison of the theoretical predictions with the experimental data reported by other researchers.<sup>22,23</sup> The good agreement between the predictions and the experimental data obtained by NMR experiment indicate that the diffusivity data measured in this work by the IGC method are reliable.



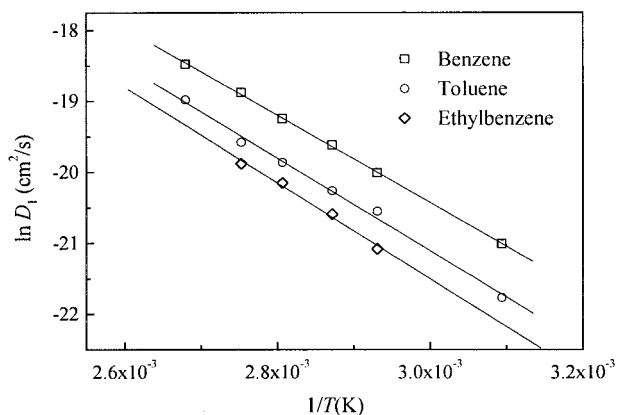
**Figure 4** Concentration dependence of diffusion coefficients of toluene in PIB. Lines represent theoretical predictions and points are experimental data.<sup>23</sup>

#### Calculation of Activation Energy for Diffusion

As to activation energy for diffusion  $\Delta H_D$ , an Arrhenius temperature dependence was given to the solvent diffusion coefficients:

$$D_1 = D_0 \exp(-\Delta H_D/RT) \quad (19)$$

Here,  $D_0$  is a constant for each solvent and it is independent of temperature. Plotting  $\ln D_1$  as a function of  $1/T$  should yield a straight line. Figure 5 shows these relationships for the three PIB/solvent systems. Table IV illustrates the values of the activation energy regressed from the experimental diffusivity data at infinite dilution measured in this work. For a comparison, the activa-



**Figure 5** Plots of the logarithm of diffusion coefficient,  $\ln D_1$ , vs  $1/T$  for benzene, toluene, and ethylbenzene in PIB.

**Table IV** Activation Energy for Diffusion of Benzene, Toluene, and Ethylbenzene in PIB at  $\omega_1 = 0$

Solvent	$\Delta H_D$ (kJ/mol)	
	This Work	Literature <sup>23</sup>
Benzene	51.1	—
Toluene	54.3	50.4
Ethylbenzene	56.2	—

tion energy for the PIB/toluene system at the limit of zero toluene concentration obtained by other researchers is also listed in Table IV. The activation energy determined in this work is very close to the value reported in Ref. 23.

#### Correlation of the Solvent Coefficients with Temperature Using the Generalized Vrentas-Duda Free-Volume Relationship

To make the various quantities in eq. (14) dimensionless, Hu et al.<sup>5</sup> proposed the following parameter  $\lambda$ :

$$\lambda = \frac{(M_1)^{1/2}}{(T_c)^{1/2}(V_c)^{1/3}} \quad (20)$$

where  $M_1$  is the molecular weight of solvent,  $T_c$  is the critical temperature of solvent, and  $V_c$  is the critical volume of solvent. By using the parameter  $\lambda$  and the critical temperature  $T_c$  of solvent, the generalized Vrentas-Duda free-volume relationship can be obtained from eq. (14).

$$\ln D_1 \lambda = a - b/T_{RF} \quad (21)$$

where

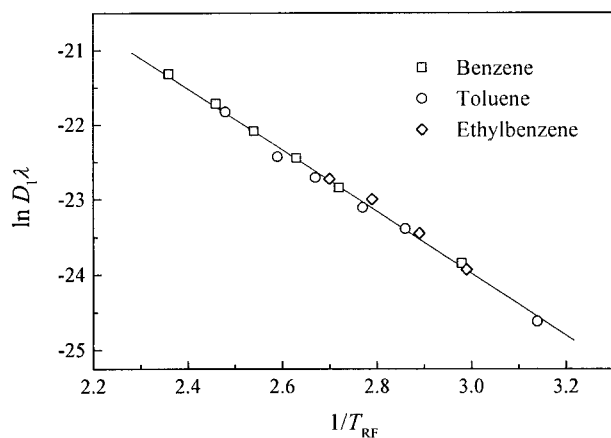
$$a = \ln D_{01} \lambda \quad (22)$$

$$b = \gamma V_{2\xi}^* / K_{12} T_c \quad (23)$$

$$T_{RF} = (K_{22} - T_{g2} + T)/T_c \quad (24)$$

Obviously, the influence of the diffusion coefficient on the size of solvent molecule is corrected in the generalized Vrentas-Duda free-volume equation. The logarithm of the reduced diffusion coefficient,  $\ln D_1 \lambda$ , is the linear function of  $1/T_{RF}$ .





**Figure 6** Plots of the logarithm of reduced diffusion coefficient,  $\ln D_1\lambda$ , vs  $1/T_{RF}$  for benzene, toluene, and ethylbenzene in PIB.

Using the experimental data (as shown in Table II) obtained in this study, plots of  $\ln(D_1\lambda)$  vs  $1/T_{RF}$  are presented in Figure 6. Within uncertainties of experimental data, all the points of  $\ln D_1\lambda$  for different solvents fall on a straight line. By regression of the experimental data, the linear dependence of  $\ln D_1\lambda$  on  $1/T_{RF}$  for the PIB-solvent system can be formulated as follows:

$$\ln D_1\lambda = -11.67 - 4.104/T_{RF} \quad (25)$$

Similar discussion of the dependence of reduced diffusion coefficient on temperature for PS-solvent and PVAc-solvent systems can be found in other literature.<sup>5</sup> Furthermore, the slope and intercept in eq. (21) are independent on solvent, so eq. (21) can be used to predict the diffusion coefficients of trace amounts of other solvents besides the above-mentioned ones in PIB at the elevated temperatures in the range studied in this work.

## CONCLUSIONS

In the present investigation, the solvent diffusion coefficients of trace amounts of benzene, toluene, and ethylbenzene in PIB were measured at several different temperatures by IGC based on the Hadj-Romdhane-Danner model of chromatographic process. These diffusivity data were correlated with temperature by using the Vrentas-Duda free-volume equation in the limit of zero solvent concentration. This good correlation shows that the free-volume theory can well describe the temperature dependence of solvent dif-

fusion coefficient at infinite dilution. Once the equation parameters  $D_{01}$  and  $\xi$  were determined from the diffusivity data at zero solvent concentration, the free-volume theory can be used to predict accurately the diffusivity data at different concentrations and temperatures. Therefore, the solvent diffusion coefficient for the polymer/solvent system can be obtained conveniently and reliably from a few experimental solvent diffusivity data measured by using the IGC techniques.

Meanwhile, the good correlation of the experimental diffusivity data with temperature using the generalized Vrentas-Duda free-volume equation shows that this equation can be well used to describe the relationship of reduced diffusion coefficient with temperature at infinite solvent concentration. In particular, the parameter, either  $a$  or  $b$ , in the generalized Vrentas-Duda free-volume equation is found to be constant and independent of the solvent. Therefore, if the values of  $a$  and  $b$  are determined by some experimental data of diffusion coefficient for one solvent, the equation can be extended to predict the diffusion coefficient for other solvents.

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