Single and multi-component diffusion at infinite dilution in polyisobutylene

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Abstract: In this study, diffusion coefficients of acetone, benzene, chloroform, cyclohexane and methyl ethyl ketone (MEK) in polyisobutylene (PIB) have been measured at temperatures in the range 40–70 °C using capillary column inverse gas chromatography (CCIGC). The measured diffusion coefficients for the PIB/MEK system, considered to be at infinite dilution of the solvent, agree very well with those determined previously from gravimetric and spectroscopic techniques when extrapolated to the limit of zero MEK concentration. The Vrentas–Duda free-volume theory for diffusion is used to correlate the diffusivity data at infinite dilution as a function of temperature, and the effect of solvent size on the diffusion process in PIB is studied. In addition, diffusion coefficients of MEK/toluene and MEK/ethanol mixtures in PIB have been measured at 50 °C. The CCIGC model for binary systems is used to determine diffusion coefficients for each solvent individually over a wide range of mixture compositions. The resulting values are identical to those determined from pure component data, confirming the hypothesis that the diffusion coefficient at infinite dilution is independent of a second infinitely-dilute component, with or without solvation between mixture components.
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INTRODUCTION

For many years, gravimetric vapour sorption was widely used to study the diffusion behaviour of solvents in polymers at finite solvent concentrations.[1–6] However, the use of this method is restricted to polymer/solvent binary systems, although many diffusion processes in actual application involve more than one solvent. In addition, this method becomes difficult to apply when the diffusivity and/or solubility of the solvent in the polymer are very low. In previous papers,[7,8] vapour sorption Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectroscopy was used to measure the diffusion coefficients of methyl ethyl ketone (MEK) and toluene/MEK mixtures in polyisobutylene (PIB) at various solvent activities and temperatures. The carbonyl stretching band for MEK was used in these spectroscopic measurements of the diffusion coefficient. Although this band is considered among the strongest in terms of infrared absorbance, the diffusion coefficient at conditions approximating infinite dilution of the solvent could not be obtained reliably for MEK in PIB using FTIR-ATR spectroscopy.

To investigate the transport properties of polymer/ solvent systems at infinite dilution, capillary column inverse gas chromatography (CCIGC) is often employed.[9–13] The IGC technique is based on the distribution of solvent molecules between a mobile gas phase and a stationary polymeric phase. In IGC experiments, the solvent is injected at the column inlet and is swept through the column by the carrier gas. As the solvent moves down the column, several mass transfer resistances occur and cause peak broadening. The most common contributions to peak broadening are longitudinal diffusion in a mobile gas phase and mass transfer resistance in a stationary polymeric phase. This method enables us to measure diffusion coefficients of solvents in polymers at relatively short times.

In this study, diffusion coefficients of several solvents in PIB were measured over a wide temperature range using the CCIGC technique. The Vrentas– Duda free-volume theory was used to correlate the diffusivity data at infinite dilution as a function of temperature, and the effect of solvent size on the diffusion process in PIB was investigated. In addition, diffusion coefficients of MEK/toluene and MEK/ ethanol mixtures in PIB were measured at 50 °C and

compared with those determined from pure component diffusion experiments. The mixture experiments were performed to test the hypothesis that multi-component diffusion at infinite dilution yields diffusion coefficients identical to those from single component experiments.

BACKGROUND
Capillary column inverse gas chromatography (CCIGC) model
Pawlisch et al[9] modelled the capillary column as a straight cylindrical tube with an annular film of polymer deposited on the inner wall. Using continuity equations for the solvent in the gas and polymer phases and the appropriate initial and boundary conditions, the following expressions for the concentration profile at the exit of the column in the Laplace domain can be derived:

$$Z(s) = \frac{\bar{C}L}{C_0 v}$$
$$= \exp\left(\frac{1}{2\gamma}\right) \exp\left(-\sqrt{\frac{1}{4\gamma^2} + \frac{s}{\gamma} + \frac{2\sqrt{s}}{\alpha\beta\gamma}\tanh(\beta\sqrt{s})}\right)$$
$$(1)$$

where

$$\alpha = \frac{r}{K\tau} \tag{2a}$$

$$\beta^2 = \frac{\tau^2}{D_{\text{inf}} t_c} \tag{2b}$$

and

$$\gamma = \frac{D_g}{vL} \tag{2c}$$

In eqns (1) and (2), $\bar{C}$ is the concentration at the exit of the column in the Laplace domain, C_0 is the strength of the inlet pulse, r is the radius of the polymer–gas interface, K is the partition coefficient, v is the average linear velocity of the carrier gas, τ is the polymer film thickness, L is the length of the column, t_c ($=L/v$) is the residence time for the carrier gas, D_g is the solvent diffusion coefficient in the gas phase, and D_{inf} is the solvent diffusion coefficient in the polymer phase at infinite dilution.

By employing the moment-generating property of Laplace transforms, the following equations can be obtained:

$$\mu_1 = t_c\left(1 + \frac{2\tau}{r}K\right) \tag{3}$$

$$\mu_2^* = t_c^2\left[\frac{4\tau^3 K}{3t_c D_{\text{inf}} r} + \frac{2D_g t_c}{L^2}\left(1 + \frac{2\tau}{r}K\right)^2\right] \tag{4}$$

where μ_1 is the first temporal moment or mean residence time, and μ_2^* is the second central moment or variance of the concentration distribution.

Estimation of model parameters
The parameters in the CCIGC model can be evaluated either by a moment analysis or a time-domain fitting analysis. In the moment analysis, μ_1 and μ_2^* are first computed by numerical integration of the outlet peak, and the partition coefficient K is determined from eqn (3). The value of K is then used to estimate the solvent diffusion coefficient in the polymer phase (D_{inf}), from eqn (4). The use of the moment analysis is restricted to symmetric or nearly symmetric elution curves.

For asymmetric peaks, a time-domain fitting analysis should be used. In this method, the left side of eqn (1) is inverted numerically using a fast Fourier transform algorithm with initial estimates for K and D_{inf}, obtained usually from the moment analysis. The resulting theoretical profile is then compared with the experimental profile, and non-linear least squares regression is used to obtain those values of K and D_{inf} which minimize the residual.

Correlation of diffusion coefficients
According to the Vrentas–Duda free-volume theory for diffusion, the polymer/solvent mutual diffusion coefficient D can be expressed as[14]

$$D = D_0 \exp\left(\frac{-E}{RT}\right)$$
$$\exp\left(\frac{-(\omega_1 \hat{V}_1^* + \xi\omega_2 \hat{V}_2^*)}{\hat{V}_{\text{FH}}/\gamma}\right)(1 - \phi_1)^2(1 - 2\chi\phi_1) \tag{5}$$

$$\frac{\hat{V}_{\text{FH}}}{\gamma} = \omega_1\left(\frac{K_{11}}{\gamma_1}\right)(K_{21} - T_{g1} + T)$$
$$+ \omega_2\left(\frac{K_{12}}{\gamma_2}\right)(K_{22} - T_{g2} + T) \tag{6}$$

Here, D_0 is a pre-exponential factor, E is the critical energy that a molecule must possess to overcome the attractive forces holding it to its neighbours, γ_i is an overlap factor which is introduced because the same free-volume is available to more than one molecule, $\hat{V}_i^*$ is the specific hole free-volume of component i required for a diffusive jump, and ω_i is the weight fraction of component i. ξ is the ratio of the molar volume of the jumping unit of solvent to that of the polymer, K_{11} and K_{21} are free-volume parameters for the solvent while K_{12} and K_{22} are those for polymer, ϕ_1 is the solvent volume fraction, and T_{gi} is the glass transition temperature of component i.

At the limit of zero solvent concentration, if the energy term E is neglected, eqn (5) becomes

$$D_{\text{inf}} = D_{01} \exp\left(\frac{-\xi\omega_2 \hat{V}_2^*}{\frac{K_{12}}{\gamma_2}(K_{22} - T_{g2} + T)}\right) \tag{7}$$

where D_{01} is a pre-exponential factor when E is set equal to zero. In the application of free-volume theory as defined by eqn (7), only five parameters ultimately need to be evaluated: D_{01}, ξ, $\hat{V}_2^*$, K_{12}/γ_2, and $K_{22} - T_{g2}$.
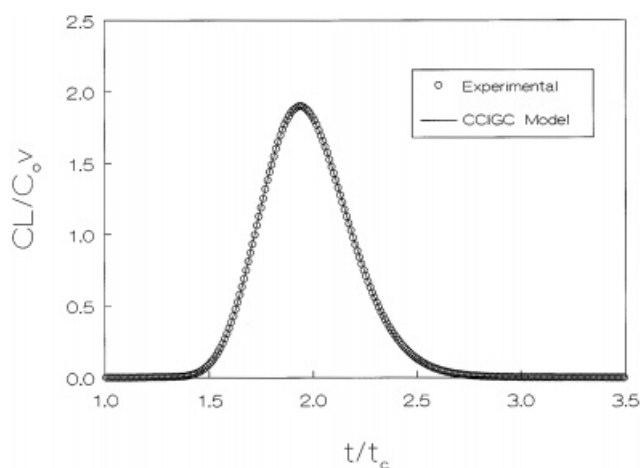
Figure 1. Comparison of experimental and theoretical elution profiles for MEK in PIB at 50 °C.

The specific critical hole free-volume of the polymer $\hat{V}_2^*$ can be estimated as the specific volume of the polymer at a temperature of absolute zero from established group contribution methods.[15] K_{12}/γ_2, and $K_{22} - T_{g2}$ can be estimated directly from zero shear rate viscosity or indirectly from tabulated values of Williams–Landel–Ferry (WLF) constants.[16,17] Finally, D_{01} and ξ can be evaluated by regressing diffusivity data with eqn (7).

EXPERIMENTAL
Materials and sample preparation
The solvents used in this study were acetone, benzene, chloroform, cyclohexane and methyl ethyl ketone (MEK). All solvents were of HPLC grade, purchased from Aldrich Co (Milwaukee, WI, USA), and were used without further purification. Polyisobutylene (PIB) was purchased from Scientific Polymer Products, Inc (Ontario, NY, USA) and was characterized by the manufacturer as follows: $M_v = 4\,700\,000$ [GPC], density = 0.92 g cm^{-3}, and $T_g = -64$ °C. The capillary column used in this study was prepared by Supelco, Inc (Bellefonte, PA, USA), from PIB supplied by the authors. The column had an inside diameter of 530 μm and was 15 m long, and the PIB coating thickness was 3 μm.

Diffusion experiments
Chromatograms were obtained using a Hewlett Packard 6890 gas chromatograph (Hewlett Packard, Wilmington, DE, USA) equipped with a flame ionization detector (FID), a splitless capillary injector, and a circulating air oven. Dry-grade air and high-purity hydrogen were used for the FID detector. Small amounts of solvent (<0.1 μl) were injected in the column as liquids. Diffusion coefficients were determined using the time-domain fitting analysis described above, starting with initial estimates from the moment analysis. Further details of the data analysis procedure are described elsewhere.[11–13] Inverse gas chromatography (IGC) experiments for the diffusion of five

solvents in PIB were carried out at temperatures in the range 40–70 °C, whereas, for diffusion of MEK/toluene and MEK/ethanol mixtures in PIB, the experiments were conducted at 50 °C over a wide range of mixture compositions. Two experiments were done at each condition and averaged. The difference between repeated experiments was less than or equal to 3%.

RESULTS AND DISCUSSION
An elution profile for methyl ethyl ketone (MEK) in polyisobutylene (PIB) at 50 °C is shown in Fig 1, with the regressed fit of the data indicated by the solid line. The experimental points were obtained through digitization of the chromatogram. The CCIGC model gives an excellent fit of the experimental data. Next, the assumption that measurements were made at conditions approximating infinite dilution of the solvent was checked for the PIB/acetone system at 40 °C. In this test, sample amounts of acetone were varied from about 0.2 μl to essentially residual vapours. Partition and diffusion coefficients for the PIB/actone system at 50 °C were determined using the CCIGC model (data not shown). The results suggest that partition and diffusion coefficients are independent of the amount injected and that the IGC experiments were carried out at conditions approximating infinite dilution of the solvent in the stationary polymeric phase.

The regressed values of D_{inf} at temperatures in the range 40–70 °C for five solvents in PIB are provided in Table 1. Among the solvents investigated in this study, acetone has the highest diffusion coefficient in PIB at experimental temperatures. This is reasonable, considering that the size of acetone for the diffusion

Table 1. Diffusion coefficients of solvents in polyisobutylene at infinite dilution

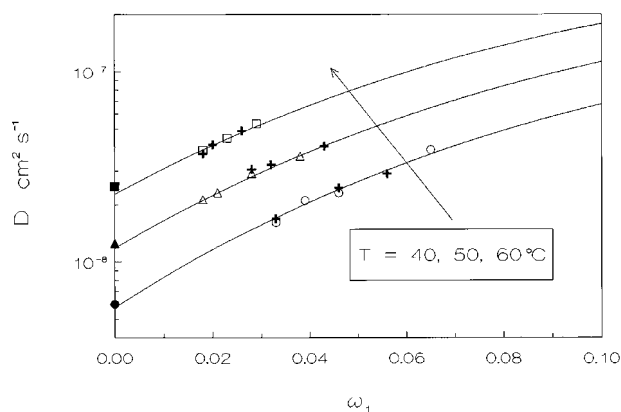| Solvent	T (°C)	$D_{inf} \times 10^9$ (cm^2 s^{-1})
Acetone	40	8.00
	50	16.8
	60	31.1
	70	54.7
Benzene	40	4.46
	50	9.70
	60	19.5
	70	36.7
Chloroform	40	1.77
	50	3.61
	60	6.83
	70	12.2
Cyclohexane	40	1.33
	50	3.00
	60	6.28
	70	12.3
MEK	40	6.10
	50	12.5
	60	25.6
	70	46.9

Figure 2. Mutual diffusion coefficients and theoretical correlations for the PIB/MEK system. Open and solid symbols represent data measured from FTIR-ATR and IGC experiments, respectively, while the values from gravimetric sorption experiments are shown as crosses.

process is the smallest. To verify the PIB coating thickness inside the capillary column, the measured diffusion coefficients for the PIB/MEK system at temperatures in the range 40–60 °C are compared with those determined previously from other techniques[7] in Fig 2. The diffusion coefficients measured using IGC, considered to be at infinite dilution, agreed very well with those determined from gravimetric and spectroscopic techniques when extrapolated using the Vrentas–Duda free-volume theory to the limit of zero MEK concentration. For example, the diffusion coefficient of MEK in PIB at 50 °C using IGC was $1.25 \times 10^{-8} \, \mathrm{cm}^{-1}$, while the value from free-volume correlations was $1.18 \times 10^{-8} \, \mathrm{cm}^2 \, \mathrm{s}^{-1}$. The temperature dependence of D_{inf} for the PIB/solvent systems is shown in Fig 3. In this figure, solid lines represent the theoretical correlations using the Vrentas–Duda free-volume theory. The parameters used in the correlations are provided in Table 2. The Vrentas–Duda free-volume theory is able to describe the temperature dependence of the diffusivity data at infinite dilution.

In the Vrentas–Duda free-volume theory, if a solvent moves as a single unit, the parameter ξ is defined as

$$\xi = \frac{\tilde{V}_1^0(0)}{\tilde{V}_{2j}^*} = \frac{\hat{V}_1^* M_1}{\hat{V}_2^* M_{2j}} \tag{8}$$

where $\tilde{V}_1^0(0)$ 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. According to eqn (8), ξ will be a linear function of $\tilde{V}_1^0(0)$ for solvents of any size if the solvent molecule moves as a single unit. Therefore, $\tilde{V}_{2j}^*$ can be obtained from the inverse of the slope of a $\tilde{V}_1^0(0)$ versus ξ plot. In this study, the variation of the parameter ξ with solvent size was investigated for five solvents in PIB. Among the five solvents studied here, four solvents (acetone, benzene, chloroform and cyclohexane) are assumed to move as single units owing to their small
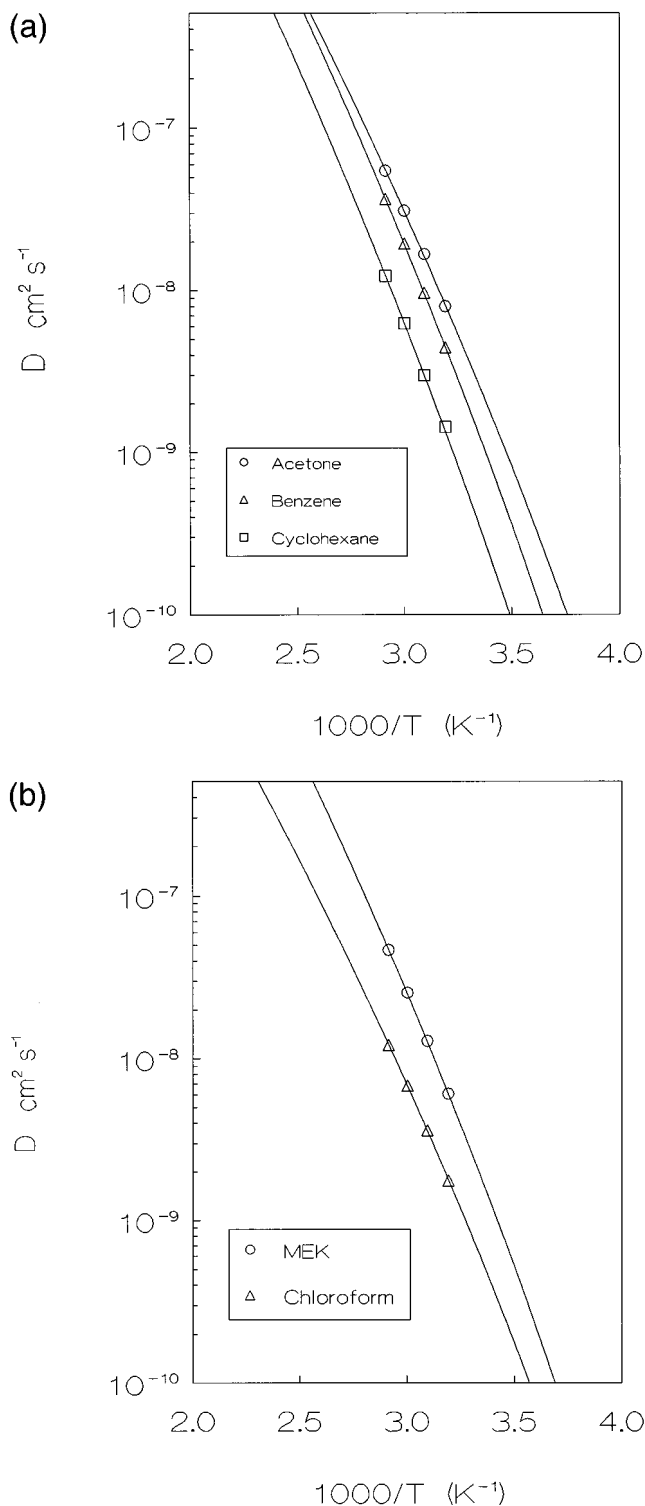

Figure 3. Mutual diffusion coefficients in PIB at infinite dilution for (a) acetone, benzene, and cyclohexane, and (b) MEK and chloroform. The lines represent theoretical correlations using the Vrentas–Duda free-volume theory.

size or spherical shape. Values of $\tilde{V}_1^0(0)$ and ξ for the solvents diffusing as single units in PIB are provided in Table 3, while the parameter ξ is plotted versus $\tilde{V}_1^0(0)$ in Fig 4 in which ξ values for simple gases reported in the literature[18] are also provided for comparison. The results show that ξ is not a linear function of $\tilde{V}_1^0(0)$ even for solvents moving as single units. This kind of

Table 2. Free-volume parameters used to correlate the diffusion coefficients for solvents in polyisobutylene at infinite dilution

Solvent	$\hat{V}_2*$	K_{12}/γ_2 $(cm^3 g^{-1} K^{-1})$	$K_{22}-T_{g_2}$ (K)	ξ	$D_{01} \times 10^2$ $(cm^2 s^{-1})$
Acetone	1.004	2.51×10^{-4}	-100.6	0.817	3.72
Benzene	1.004	2.51×10^{-4}	-100.6	0.910	11.7
Chloroform	1.004	2.51×10^{-4}	-100.6	0.836	1.16
Cyclohexane	1.004	2.51×10^{-4}	-100.6	0.961	9.01
MEK	1.004	2.51×10^{-4}	-100.6	0.885	9.91

behaviour was previously reported for natural rubber and polybutadiene.[19] The non-linearity for these polymers was explained by the importance of energy term E for the diffusion of small molecules at temperatures far above T_{g2}. The results also suggested that it was reasonable to expect that the energy effect would become less significant as solvent size increased. In that paper,[19] the values of $\tilde{V}_{2j}^*$ for several polymers were correlated with their glass transition temperatures, and a linear regression of the data yielded

$$\tilde{V}_{2j}^*(cm^3\,mol^{-1}) = 0.0925 \times T_{g2}\,(K) + 69.47 \quad (9)$$

Because the glass transition temperature of PIB used in this study was 209 K, $\tilde{V}_{2j}^*$ of PIB was determined as $89\,cm^3\,mol^{-1}$ from eqn (9). Therefore, a slope of the $\tilde{V}_1^0\,(0)$ versus ξ plot, for solvents moving as single units in PIB, can be calculated and is shown as a dotted line in Fig 4. Although the ξ value for cyclohexane was determined without considering the energy effect, the point was on the dotted line. Therefore, cyclohexane can be assumed to be free from the energy effect. If the diffusivity data at finite concentrations are available as a function of temperature, ξ values for the solvents can be re-evaluated using eqn (5) which includes the energy term E. The re-evaluated ξ values should be smaller than those determined in this study and may be located on the dotted line. In a previous paper,[7] the diffusion coefficients for the PIB/MEK system were measured at various solvent concentrations and temperatures (Fig 2), and the ξ value was determined as 0.657 using eqn (5). Although MEK is assumed not to move as a single unit, this ξ value is smaller than the one determined in this study.
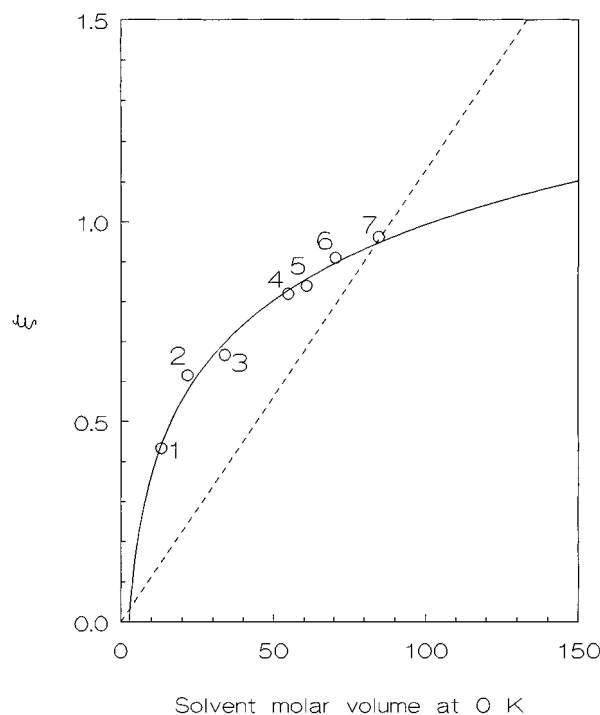
In a previous study,[8] the diffusion behaviour of MEK/toluene vapour mixtures in PIB at 50 °C was investigated at finite concentrations from FTIR-ATR spectroscopy. The results suggested that the addition

of the toluene to the PIB/MEK system simply reduced the activity of the system and might not affect the diffusion behaviour of the MEK under certain experimental conditions. In other words, if the MEK activities, and hence the MEK concentrations in PIB, are identical, the diffusion coefficients of MEK should be the same regardless of the mixture composition. At infinite dilution, therefore, diffusion coefficients of MEK for MEK/toluene mixtures should be identical to the one determined from pure MEK transport data.

To test this hypothesis, diffusion coefficients for MEK/toluene mixtures in PIB were measured at 50 °C using the CCIGC method. Because solvent concentration in the polymer is assumed to be infinitely dilute in IGC experiments, the diffusion coefficients for MEK and toluene should be independent of solvent inlet composition. Elution profiles of MEK and toluene for an MEK/toluene 1:2 mixture with an MEK mole fraction x_1 of 0.641 in polyisobutylene (PIB) at 50 °C are shown in Fig 5. Because the two elution curves are well separated, partition and

Table 3. Free-volume parameters for polyisobutylene/solvent systems

Solvent	$\tilde{V}_1^0\,(0)$	ξ	Ref
Hydrogen	13.2	0.423	18
Oxygen	21.8	0.616	
Carbon dioxide	33.9	0.667	
Acetone	54.8	0.817	This work
Chloroform	60.9	0.836	
Benzene	70.5	0.910	
Cyclohexane	84.8	0.961	

Figure 4. Variation of ξ with solvent molar volume at 0 K for polyisobutylene/solvent systems: (1) hydrogen; (2) oxygen, (3) carbon dioxide; (4) acetone; (5) chloroform; (6) benzene; (7) cyclohexane. A solid line is drawn to guide the eye, while a dotted line is based on eqn (9).
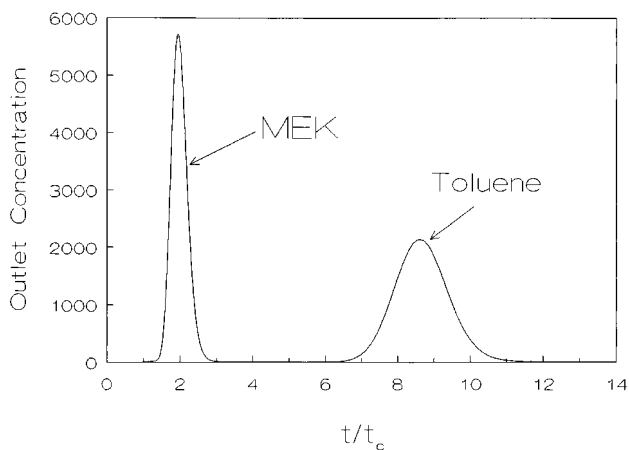
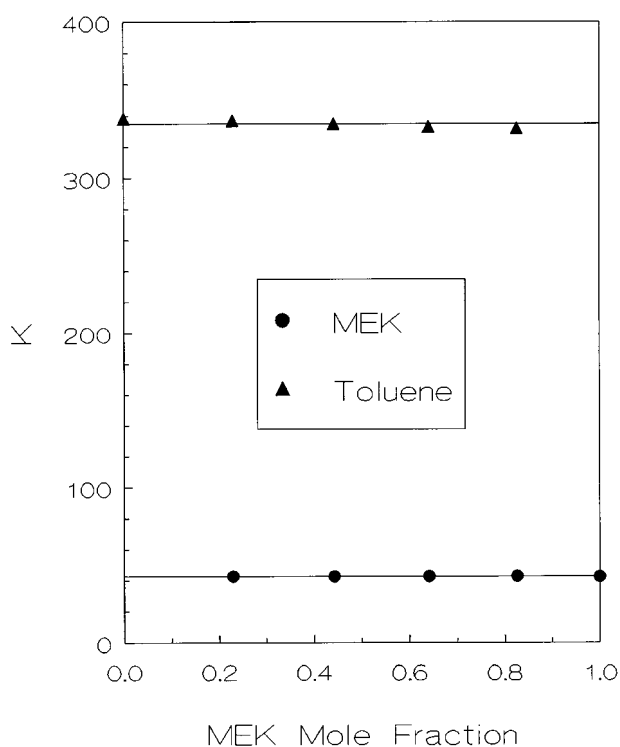**Figure 5.** An IGC elution profile for the PIB/MEK/toluene system with $x_1 = 0.641$ at 50 °C.

Figure 6. Dependence of partition coefficients on MEK/toluene mixture composition for MEK and toluene in PIB. The lines are to guide the eye.

Figure 7. Dependence of infinite dilution coefficients on MEK/toluene mixture composition for/MEK and toluene in PIB. The lines are to guide the eye.

Figure 8. Comparison of mutual diffusion coefficients for MEK in the PIB/MEK/toluene system measured at 50 °C from IGC and FTIR-ATR[8] experiments. The line represents the linear regression of the diffusivity data from FTIR-ATR experiments, while the points at infinite dilution indicate the diffusion coefficients determined from IGC experiments.

diffusion coefficients for each solvent were determined individually using the CCIGC model for binary systems, and are shown as a function of inlet mixture composition in Figs 6 and 7, respectively. The results suggest that partition and diffusion coefficients are independent of mixture composition for both solvents. Mutual diffusion coefficients for MEK in a PIB/MEK/toluene system at 50 °C measured using IGC are then compared with those determined previously from vapour sorption FTIR-ATR spectroscopy[8] in Fig 8 in which the line represents the linear regression of the diffusivity data from FTIR-ATR experiments. Diffusion coefficients of pure MEK in PIB are also provided for comparison.[7] The points at infinite dilution
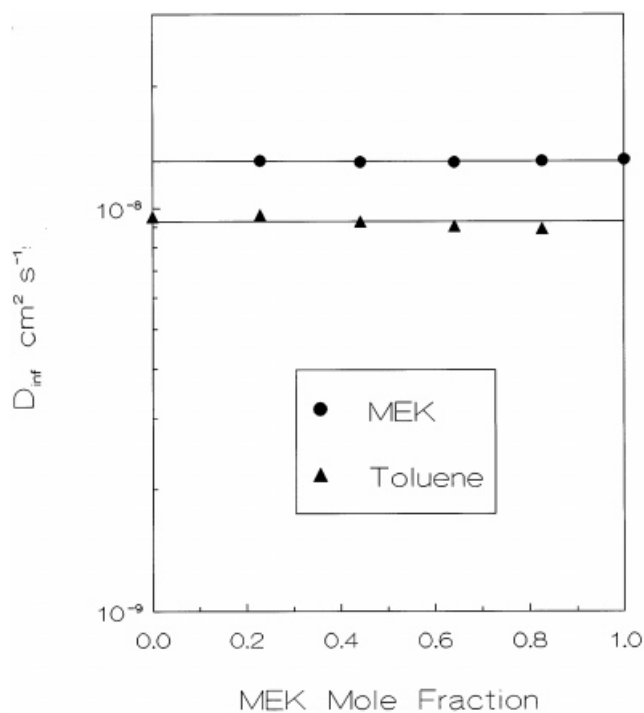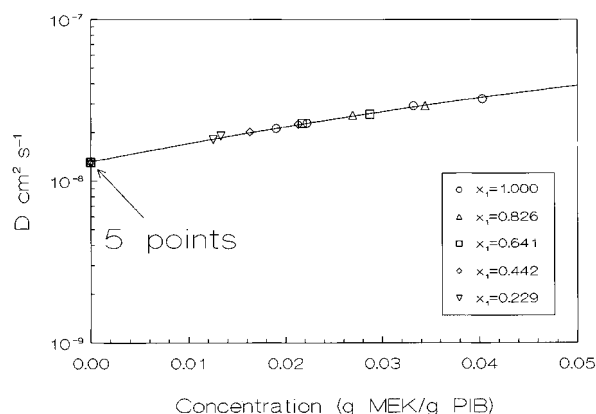
indicate the diffusion coefficients of pure MEK and MEK for MEK/toluene mixtures in PIB determined from the IGC experiments. The results indicate that the multicomponent diffusion coefficients determined by IGC agree very well with the one determined from FTIR-ATR experiments when extrapolated to infinite dilution.

To investigate the diffusion behaviour of solvent mixtures which are capable of intersolute solvation through hydrogen bonding in the polymer at infinite dilution, diffusion coefficients for MEK/ethanol mixtures in PIB were also measured at 50 °C. Recent
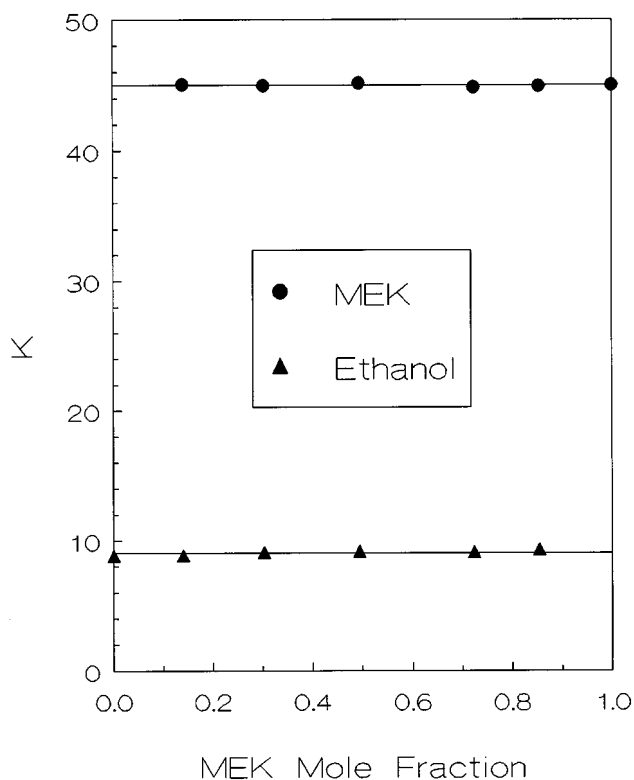
Figure 9. Dependence of partition coefficients on MEK/ethanol mixture composition for MEK and ethanol in PIB. The lines are to guide the eye.

transport data for the polypropylene/MEK/ethanol system obtained by FTIR-ATR spectroscopy, showed that MEK was solvated with ethanol through hydro-
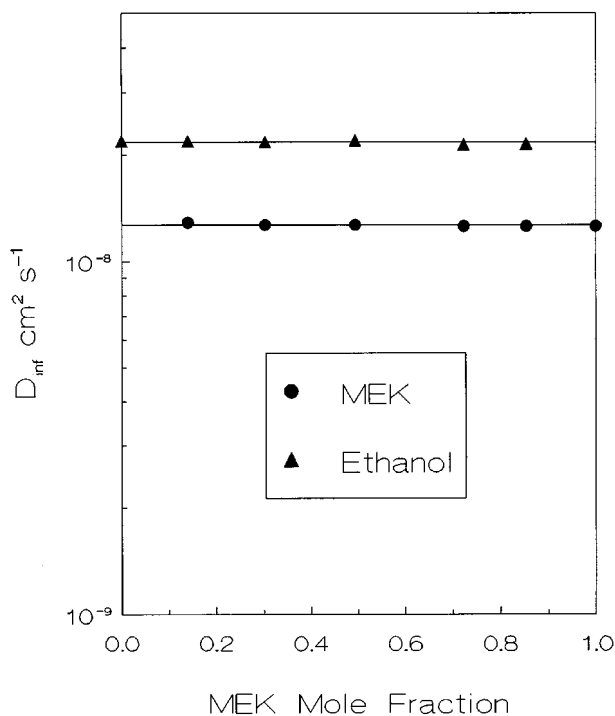
gen bonding and the transport of MEK in polymer was slowed in the presence of ethanol.[20] Partition and diffusion coefficients for MEK and ethanol in PIB at 50 °C are shown for several inlet mixture compositions in Figs 9 and 10, respectively. The results indicate that the partition and diffusion coefficients for MEK and ethanol at infinite dilution also are independent of mixture composition, even though the two solvents interact strongly at finite concentrations. This suggests that hydrogen bonding in the vapour phase between MEK and ethanol is negligible at infinite dilution.

CONCLUSIONS

The results presented in this study demonstrate that diffusion coefficients measured using capillary column inverse gas chromatography (CCIGC) agree very well with those determined gravimetrically and spectroscopically. In addition, the multicomponent diffusion behaviour in polymers at infinite dilution for each solvent concentration can successfully be studied using the CCIGC technique. The results also demonstrate that the diffusion coefficient of one solvent is not affected by the presence of a second solvent at infinite dilution, even if the second solvent is capable of intersoluble solvation through hydrogen bonding. Further studies are necessary with other systems to elucidate the conditions over which these results can be applied generally.

Figure 10. Dependence of infinite dilution coefficients on MEK/ethanol mixture composition for MEK and ethanol in PIB. The lines are to guide the eye.

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