

NOTE

Solubility of Organic Solvents at infinite dilution in Polyisobutylene

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INTRODUCTION

For many years, inverse gas chromatography (IGC) was used widely to measure partition and diffusion coefficients of solvents in polymers at the infinitely dilute solvent concentration region.^{1–4} The IGC technique is based on the distribution of solvent molecules between a mobile gas phase and a stationary polymeric phase. The measured partition coefficients for the solvent between the gas and polymer phases can be used to predict the solubility data at finite solvent concentrations in accordance with appropriate thermodynamic models.⁵

To predict the solubility data as a function of temperature, knowing the temperature dependence of the partition coefficient is very important. Recently, Vrentas and Vrentas⁶ proposed a theory that describes the temperature dependence of the partition coefficients. To test the validity of the theory, in this study, partition coefficients of several organic solvents in polyisobutylene (PIB) were measured using the IGC technique. The temperature dependence of the data was

then analyzed using the theory proposed by Vrentas and Vrentas.

BACKGROUND

Capillary Column Inverse Gas Chromatography Model

Pawlich⁷ modeled 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:

$$z(s) = \frac{\bar{C}L}{C_0v} = \exp\left(\frac{1}{2\gamma}\right) \times \exp\left(-\sqrt{\frac{1}{4\gamma^2} + \frac{S}{\gamma} + \frac{2\sqrt{s}}{\alpha\beta\gamma} \tanh(\beta\sqrt{s})}\right), \quad (1)$$

where

$$\alpha = \frac{r}{K\tau}, \quad \beta^2 = \frac{\tau^2}{D_{\text{inf}}t_c}, \quad \text{and} \quad \gamma = \frac{D_g}{vL}. \quad (2)$$

In eqs. (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

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interface, K is the dimensionless partition coefficient that represents the concentration of solvent sorbed in the polymer divided by the solvent concentration in the gas phase, 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 using the moment generating property of Laplace transforms, the following equation can be obtained:

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

where μ_1 is the first temporal moment or mean residence time. The partition coefficient K can be evaluated either by a moment analysis or a time-domain fitting analysis. In the moment analysis, μ_1 is first computed by numerical integration of the outlet peak, and the partition coefficient K is determined from eq. (3). 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 eq. (1) is inverted numerically using a fast Fourier transform algorithm with initial estimates for K and D_{inf} . The resulting theoretical profile is then compared with the experimental profile, and nonlinear least squares regression is used to obtain those values of K and D_{inf} that minimize the residual.

Determination of Polymer/Solvent Interaction Parameter

The Flory-Huggins polymer/solvent interaction parameter, χ , can be estimated, from IGC experiments, using the following equation:⁷

$$\chi = \ln \Omega_1^\infty + \ln \left(\frac{\rho_1}{\rho_2} \right) - 1, \quad (4)$$

where

$$\Omega_1^\infty = \frac{\rho_2 RT}{K P_1^0 M_1} \exp \left[\frac{P_1^0 (\bar{V}_1 - B_{11})}{RT} \right]. \quad (5)$$

In eqs. (4) and (5), Ω_1^∞ is the weight fraction activity coefficient at infinite dilution, ρ_1 and ρ_2 are the densities of the solvent and polymer, respectively, P_1^0 is the vapor pressure of the solvent, M_1 is its molecular weight, \bar{V}_1 is its molar volume, and B_{11} is its second virial coefficient.

Temperature Dependence of Partition Coefficient

Using eqs. (4) and (5) and the ideal gas law, the following equation can be obtained for the temperature dependence of K at temperatures above T_{g_2} :

$$\ln \left(\frac{T}{K} \right) = \ln \left(\frac{M_1 \hat{V}_1}{R} \right) + \ln P_1^0 + (1 + \chi), \quad (6)$$

where \hat{V}_1 is the partial specific volume of the solvent at infinite dilution. According to Vrentas and Vrentas,⁶ since the temperature dependence of \hat{V}_1 is generally small, the following expression can be derived for the temperature variation of T/K at temperatures above T_{g_2} :

$$\frac{\partial[\ln(T/K)]}{\partial(1/T)} = \frac{\partial(\ln P_1^0)}{\partial(1/T)} + \frac{\partial\chi}{\partial(1/T)}. \quad (7)$$

In general, P_1^0 can be represented by a linear function of $(1/T)^8$ and χ should be a linear function of $(1/T)$ according to Flory.⁹ Also,

$$\frac{\partial(\ln P_1^0)}{\partial(1/T)} < 0, \quad (8)$$

$$\frac{\partial\chi}{\partial(1/T)} > 0. \quad (9)$$

Since the magnitude of the first term of eq. (7) is generally greater than that of the second term,

$$\frac{\partial[\ln(T/K)]}{\partial(1/T)} < 0. \quad (10)$$

EXPERIMENTAL

The solvents used in this study were acetone, benzene, chloroform, cyclohexane, and MEK. All solvents were of HPLC grade, purchased from Aldrich Co. (Milwaukee, WI) and were used without further purification. PIB was purchased from Scientific Polymer Products, Inc. (Ontario, NY) and was characterized by the manufacturer as follows: $M_v = 4,700,000$ [GPC], density = 0.92 g/cm³, and $T_g = -64^\circ\text{C}$. The capillary column used in this study was prepared by Supelco, Inc. (Bellefonte, PA), 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 .

Chromatograms were obtained using a Hewlett Packard 6890 gas chromatograph 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.

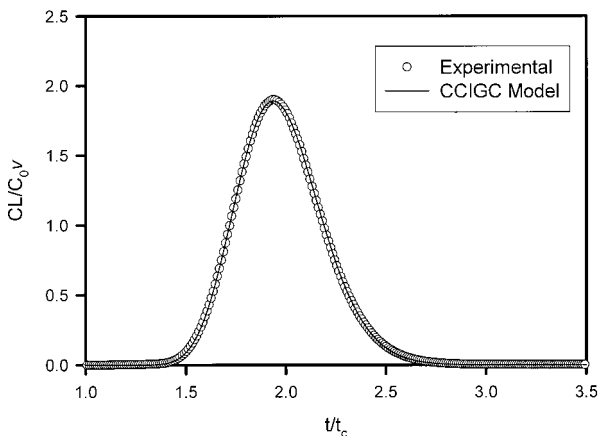
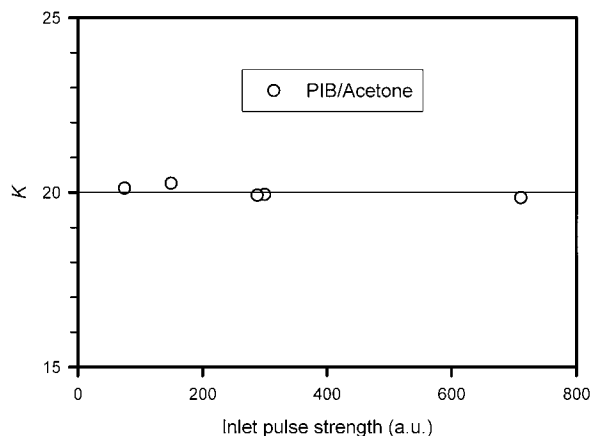


Figure 1 Comparison of experimental and theoretical elution profiles for MEK in PIB at 50°C.

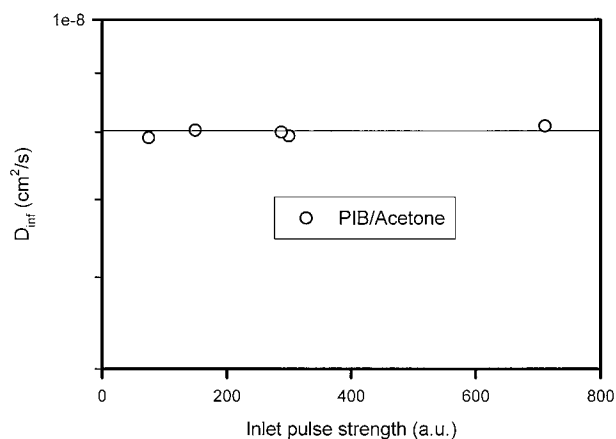
Small amounts of solvent ($<0.1 \mu\text{L}$) were injected in the column as liquids. Partition coefficients were determined using the time-domain fitting analysis described above. IGC experiments for five solvents in PIB were carried out at temperatures in the range 40–70°C. Two experiments were done at each condition and averaged. The difference between repeated experiments was less than or equal to 1%.

RESULTS AND DISCUSSION

An elution profile for MEK in PIB at 50°C is shown in Figure 1, with the regressed fit of the data indicated by the solid line. The experimental points were obtained through digitization of the chromatogram. The capillary column inverse gas chromatography (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 $0.2 \mu\text{L}$ to essentially residual vapors. Partition and diffusion coefficients for the PIB/acetone sys-



(a)



(b)

Figure 2 Dependence of (a) partition and (b) diffusion coefficients on sample amount for PIB/acetone system. The lines were drawn to guide the eye.

tem at 40°C were determined using the CCIGC model and are provided as a function of inlet pulse strength (and hence, the sample amount) in Figure 2. The results suggest that partition and diffusion coefficients are independent of the amount injected and that the

Table I Partition Coefficients and Flory–Huggins Interaction Parameters in PIB/Solvent Systems at Infinite Dilution

T (°C)	Acetone		Benzene		Chloroform		Cyclohexane		MEK	
	K	χ	K	χ	K	χ	K	χ	K	χ
40	20.0	2.42	163	0.98	160	0.42	204	0.53	60.3	1.97
50	15.4	2.32	117	0.93	114	0.41	144	0.52	44.5	1.89
60	12.3	2.22	86.2	0.89	82.5	0.40	105	0.49	33.6	1.81
70	10.2	2.10	65.5	0.84	61.1	0.40	78.6	0.47	25.8	1.73

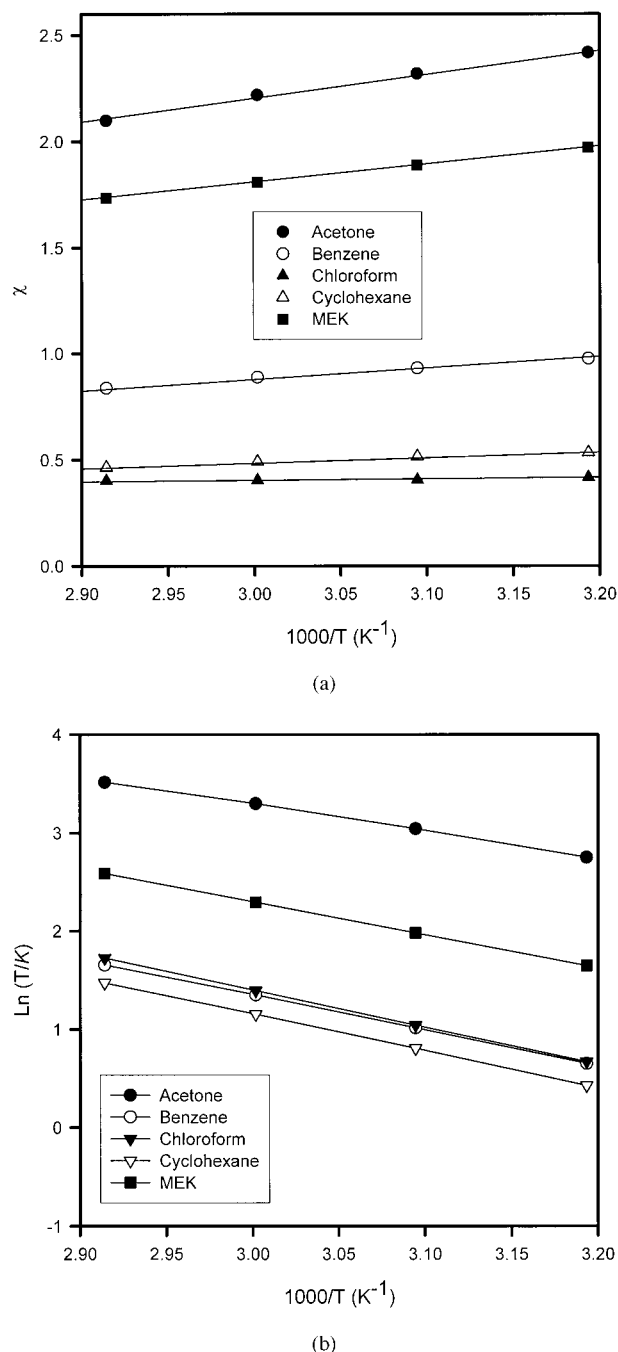


Figure 3 Temperature dependence of (a) Flory-Huggins interaction parameters and (b) partition coefficients for PIB/solvent systems. The lines represent linear regressions of the data.

IGC experiments were carried out at conditions approximating infinite dilution of the solvent in the stationary polymeric phase.

The regressed K and χ values at temperatures in the range 40–70°C for five solvents in PIB are provided in Table I. Among the solvents investigated in this study, acetone has the highest χ value in PIB at experimental temperatures, while χ value for chloroform is the lowest. Therefore, it is concluded that chloroform is the best solvent for PIB of the solvents considered. The temperature dependence of partition coefficient K is then analyzed using the theory proposed by Vrentas and Vrentas.⁶ The theory predicts a linear relationship between $\ln(T/K)$ and $(1/T)$ and a negative slope of the plot. To verify this, the temperature variations of $\ln(T/K)$ and χ were studied and shown in Figure 3. The results show that, as Flory proposed, the polymer/solvent interaction parameter has a linear relationship with inverse temperature, and the plot has a positive slope. The results also show that the plot of $\ln(T/K)$ versus $1/T$ is linear and has a negative slope owing to the greater negative slope of the $\ln P_1^0$ versus $1/T$ plot (data not shown). Because it was verified that there is a linear relationship between $\ln(T/K)$ and $1/T$, the partition coefficient K at any temperature in a certain system can be estimated when the slope and the intercept of the plot are known. Estimated K values can be used subsequently to predict the solubility data at the finite solvent concentration region in accordance with thermodynamic models, such as the perturbed soft chain theory.

REFERENCES

1. Faridi, N.; Hadj Romdhane, I.; Danner, R. P.; Duda, J. L. *Ind Eng Chem Res* 1994, 33, 2483.
2. Hadj Romdhane, I.; Danner, R. P.; Duda, J. L. *Ind Eng Chem Res* 1995, 34, 2833.
3. Faridi, N.; Duda, J. L.; Danner, R. P. *Rubber Chem Tech* 1996, 69, 234.
4. Hong, S. U.; Barbari, T. A. *Polym Int* 1999, 48, 901.
5. Hong, S. U.; Pretel, E. J. *Polym Int* 1998, 45, 55.
6. Vrentas, J. S.; Vrentas, C. M. *Macromolecules* 1998, 31, 5539.
7. Pawlish, C. A. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1985.
8. Sandler, S. I. *Chemical and Engineering Thermodynamics*; John Wiley: New York, 1977.
9. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.