J. Chem. Eng. Data **2005,** *50,* 983−988

Mutual Diffusion Coefficient and Vapor−Liquid Equilibrium Data for the System Polyisobutylene + Toluene

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Vapor−liquid equilibria and mutual diffusion coefficients have been measured for the polyisobutylene + toluene system from 5 °C to 65 °C by gravimetry. Empirical relations have been determined for the Flory interaction parameter and for mutual diffusion coefficients. They show very good agreement with experimental data and can be accurately used for simulation or other purposes as long as they are restricted to the concentration and temperature ranges covered by our study.

1. Introduction

The physicochemical properties of polymer + solvent systems such as liquid−vapor equilibria or diffusion coefficients strongly depend on the solvent concentration. For instance, the mutual diffusion coefficient varies on several orders of magnitude when the solvent volume fraction decreases from 0.3 to 0. These quantities are thus important to investigate for both fundamental and applied purposes. For example, the liquid−vapor equilibrium and the diffusion coefficient play a key role in optimizing numerous processes such as coating drying and membrane formation.

In the present work, we use measurements of the swelling and deswelling of a polymer film in a controlled solvent vapor, which is an accurate and suitable method for the investigation of both the liquid−vapor equilibrium and the mutual diffusion coefficient for wide ranges of concentration and temperature.

The system under study is polyisobutylene (1) + toluene (2) for which very few data are available in the literature. Polyisobutylene + toluene constitutes an interesting simple model system, in particular, when looking for a rubbery and amorphous system at ambient temperature. Data have been obtained for various temperatures (5 °C $\leq \theta \leq$ 35 °C and a few values at $\theta = 65$ °C). The activity has been varied from 0 to 0.95 corresponding to a solvent volume fraction Φ_2 from 0 to 0.45 at 25 °C. The model and estimation method for the determination of the mutual diffusion coefficient are only briefly discussed here because they have been described in a previous publication.[1] Comparison with other data of the literature are given when possible.

2. Experimental Section

The experimental setup consists of an accurate balance coupled with a vapor chamber whose temperature and pressure are controlled. The sample is hung in the chamber, and changing the solvent vapor pressure allows for swelling or drying of the polymer film. In this study, a series of differential steps of solvent vapor pressure were performed. The evolution of the mass of the film in response to an imposed step of the solvent vapor pressure gives access to the mutual diffusion coefficient (through a suitable model of the swelling kinetics). The asymptotic value reached at the end of the experiment gives the equilibrium solvent concentration in the film corresponding to the imposed solvent vapor pressure.

2.1. Gravimetric Setup. The gravimetric setup is a Hiden IGA system based on a precise balance. The chamber is a stainless steel cylinder with diameter 34.5 mm and height 300 mm. Temperature is regulated with a fluid circulating in the outer wall of the chamber from a thermostated bath. The temperature is measured by a platinum resistance thermometer (Pt 100) located near the sample. The uncertainty in the temperature measurement is ±0.1 K, and the temperature stability is better than ±0.05 K. The chamber is connected through various valves to a vacuum pump on one hand and to a solvent tank on the other hand, where liquid solvent is in equilibrium with its vapor at 55 °C. Pressure is regulated with a PID controller, and the pressure stability is better than 2 Pa. The solvent vapor is the only gas present in the chamber, so the total pressure and the solvent vapor pressure are the same. The pressure is measured with a manometer (relative error = 0.3%). The mass measurement noise is about 1 μg, and the reproducibility (same measurement performed at various times) is about 10 μg.

2.2. System. The polymer + solvent solution used in this study is polyisobutylene + toluene. Polyisobutylene was supplied by Sigma-Aldrich, with $M_w = 5 \times 10^5$ g·mol^{-1} and polydispersity 2.5 for most of the experiments. A few experiments (mentioned in the text) were performed with another polyisobutylene sample, with $M_w = 10^6$ g·mol^{-1} and polydispersity 1.7. Toluene was supplied by Prolabo (chromatographic use, purity 99.9%). The glass-transition temperature and the melting temperature of polyisobutylene are −76 °C and 1.5 °C, respectively (Sigma-Aldrich), and the theta temperature is −13 °C.[2] The experimental temperature is above the glass-transition temperature, the melting temperature, and the theta temperature, so the system remains rubbery, amorphous, and homogeneous (no demixing) for all of the experiments.

Films were prepared by the slow drying of polyisobutylene + toluene solutions in glass dishes. The film thickness depends on the initial concentration and the initial thickness of the solution in the dish. Drying is achieved by

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10.1021/je049541k CCC: $30.25

maintaining the temperature of the film at 60 °C for several days. The film is then taken off of the dish and put on an aluminum substrate. A disk of diameter 20 mm is then cut with a hollow punch. The sample (polyisobutylene film + aluminum substrate) is hung horizontally in the balance chamber and weighed to get the dry mass of the sample. The film thickness is estimated a posteriori, at the end of the experiment: The aluminum substrate is cleaned in toluene to dissolve the polyisobutylene film and weighed. The polyisobutylene mass, M_1, is then deduced by difference, and the thickness of the polyisobutylene film, l_{dry}, is estimated from its mass and from the specific volume of polyisobutylene. For the different experiments presented here, M_1 varies from 2.6 mg to 165 mg.

In the results presented in the following text, the solvent content is stated in terms of the solvent volume fraction, Φ_2, with $\Phi_2 = V_2/(V_2 + V_1)$ where V_2 and V_1 are the solvent and polymer volumes in the solution. Mass measurements are first converted into solvent mass fraction, $w_2 = M_2/(M_2 + M_1)$, with M_2 and M_1 being the solvent and polymer masses in the solution. Then, with the assumption of constant specific volumes commonly used in polymer solutions, the relation between volume and mass fractions is straightforward:

$$\Phi_2 = \frac{w_2 V_2^0/V_1^0}{1 - w_2(1 - V_2^0/V_1^0)}$$

The following values have been used for the specific volumes of pure polyisobutylene and pure toluene: $V_1^0 = 1.087 \times 10^{-3}$ m³·kg⁻¹ (Aldrich) and $V_2^0 = 1.151 \times 10^{-3}$ m³·kg⁻¹.[3]

3. Vapor/Liquid Equilibrium

With the assumption of thermodynamic equilibrium at the vapor/film interface and the assumption of an ideal gas for the solvent vapor, the equality of the solvent chemical potential leads to the following equation

$$a = \frac{P(\Phi_2, T)}{P_2^0(T)} \tag{1}$$

where a is the solvent activity, P_2^0 is the saturated vapor pressure of the pure solvent, P is the saturated vapor pressure of the solution, Φ_2 is the solvent volume fraction in the solution at the interface, and T is the temperature of the solution.

Vapor−liquid equilibrium data were obtained by setting a constant pressure in the chamber, P_V, and waiting until the film mass was constant. The solvent concentration was then assumed to be uniform in the film and was deduced from the mass measurement. Because there was no inert gas in the chamber, $P = P_V$, the pressure imposed by the regulation system. The saturating vapor pressure of the solvent, $P_2^0(T)$, was calculated from the Antoine equation[4] $\log(P_2^0/\mathrm{Pa}) = A - B \times (T/\mathrm{K} + C)^{-1}$, with $A = 9.0782$, $B = 1343.9$, and $C = -53.77$.

In the rubbery domain (temperature greater than the glass-transition temperature), the Flory−Huggins model is commonly used to express the activity versus the solvent volume fraction

$$a = \Phi_2 \exp[(1 - \Phi_2) + \chi(1 - \Phi_2)^2] \tag{2}$$

where χ is the interaction parameter that characterizes the affinity between the solvent and the polymer. In the original Flory−Huggins theory, χ was specified to be inversely proportional to the absolute temperature and independent of concentration. The original theory has been extended to account for the variation of χ with solvent concentration.[2,5]

3.1. VLE Data. For each temperature, experiments have been performed on several films with different thicknesses. (The use of different thicknesses is needed for the determination of the mutual diffusion coefficient; cf. the next section.) The solvent vapor pressure has been changed from 0 to a pressure corresponding to an activity of about 0.95. The films thicknesses, the maximal activity, and the corresponding maximal solvent volume fraction are the following:

$$\theta = 5\ ^\circ\mathrm{C},\ l_{dry} = (13 \text{ and } 57)\ \mu\mathrm{m},\ a \le 0.94,\ \Phi_2 \le 0.36$$

$$\theta = 15\ ^\circ\mathrm{C},\ l_{dry} = (13, 52, \text{ and } 57)\ \mu\mathrm{m},\ a \le 0.95,\ \Phi_2 \le 0.41$$

$$\theta = 25\ ^\circ\mathrm{C},\ l_{dry} = (9, 13, 52, 63, 67, \text{ and } 99)\ \mu\mathrm{m}\ (M_w = 10^6\ \mathrm{g{\cdot}mol^{-1}} \text{ for the 99-}\mu\text{m-thick film}),\ a \le 0.95,\ \Phi_2 \le 0.45$$

$$\theta = 35\ ^\circ\mathrm{C},\ l_{dry} = (9, 52, 57, \text{ and } 63)\ \mu\mathrm{m},\ a \le 0.96,\ \Phi_2 \le 0.54$$

$$\theta = 65\ ^\circ\mathrm{C},\ l_{dry} = (67 \text{ and } 303)\ \mu\mathrm{m},\ a \le 0.13,\ \Phi_2 \le 0.03$$

The relative error in the activity is deduced from the uncertainty in the pressure and temperature measurements: $\Delta a/a = \Delta P_V/P_V + \Delta P_2^0/P_2^0 \le 10^{-2}$. The relative error in the solvent mass fraction is mainly due to the error in the estimation of the polymer mass, M_1: $\Delta w_2/w_2 \simeq \Delta M_1/M_1$, with $\Delta M_1 \simeq 0.1$ mg. Error bars are not reported on the graphs because they are small and would alter the clarity of the graphs. Data are given in Table 1 and gathered in Figures 1 ($\theta = 5$ °C and 35 °C) and 2 ($\theta = 15$ °C and 25 °C). As can be seen, the reproducibility of the experiments performed in this study is good, and the results for the different thicknesses all gather on the same curve for a given temperature.

The observed behavior is typical of polymer solutions: the activity is greater than 0.9 for a solvent volume fraction greater than 0.31 to 0.39, depending on the temperature. The influence of the temperature on the activity is small as expected for polymer + solvent solutions. For comparison, results obtained by Wibawa et al.[6] are reported on the same graphs. These values were also obtained by gravimetry (with a piezoelectric−quartz microbalance) and are very close to our results.

3.2. Interaction Parameter χ. For each measurement (i.e., one pressure and one temperature), the value of the interaction parameter χ was deduced by a simple inversion of eq 2. A polynomial expression giving the variation of the interaction parameter with the solvent volume fraction and temperature has then been deduced from these values:

$$\chi = c_0 + c_1\Phi_2 + c_2(\theta/^\circ\mathrm{C} - 25) + c_3(\theta/^\circ\mathrm{C} - 25)\,\Phi_2 \tag{3}$$

Coefficients c_0, c_1, c_2, and c_3 were estimated by mean square fit of the results obtained for all concentrations and temperatures (except for $\Phi_2 < 0.04$: indeed, at very small solvent concentration a and Φ_2 are both very small so that the inversion of eq 2 is meaningless). The following values have been obtained: $c_0 = 0.757$, $c_1 = -0.261$, $c_2 = -0.0025$, and $c_3 = -0.0074$. Let us emphasize that this relationship

Table 1. Activity as a Function of the Solvent Volume Fraction for Different Temperatures[a].

$\theta = 5$ °C		$\theta = 15$ °C		$\theta = 25$ °C		$\theta = 35$ °C	
Φ_2	a	Φ_2	a	Φ_2	a	Φ_2	a
0.013	0.080	0.015	0.090	0.014	0.079	0.011	0.060
0.028	0.163	0.023	0.136	0.025	0.132	0.014	0.064
0.045	0.245	0.028	0.158	0.031	0.158	0.015	0.080
0.054	0.284	0.032	0.181	0.036	0.184	0.022	0.120
0.064	0.325	0.038	0.203	0.047	0.237	0.025	0.128
0.074	0.365	0.042	0.227	0.052	0.263	0.034	0.176
0.086	0.408	0.053	0.272	0.055	0.277	0.045	0.225
0.097	0.449	0.063	0.317	0.058	0.290	0.053	0.257
0.099	0.469	0.075	0.363	0.079	0.369	0.060	0.288
0.106	0.489	0.086	0.408	0.086	0.395	0.069	0.321
0.112	0.515	0.099	0.453	0.109	0.474	0.077	0.353
0.120	0.540	0.106	0.476	0.117	0.501	0.086	0.385
0.129	0.566	0.113	0.499	0.125	0.527	0.095	0.417
0.130	0.569	0.128	0.543	0.136	0.554	0.105	0.449
0.138	0.592	0.145	0.589	0.146	0.581	0.113	0.473
0.139	0.595	0.153	0.612	0.152	0.599	0.116	0.481
0.151	0.626	0.163	0.635	0.154	0.601	0.121	0.497
0.161	0.653	0.182	0.679	0.160	0.606	0.121	0.500
0.170	0.672	0.183	0.681	0.163	0.626	0.132	0.530
0.179	0.694	0.192	0.697	0.180	0.660	0.146	0.562
0.188	0.714	0.194	0.703	0.192	0.686	0.159	0.600
0.198	0.734	0.207	0.726	0.203	0.700	0.181	0.642
0.210	0.755	0.226	0.759	0.213	0.726	0.182	0.650
0.220	0.774	0.231	0.770	0.238	0.766	0.209	0.701
0.233	0.796	0.237	0.780	0.257	0.792	0.224	0.722
0.246	0.816	0.246	0.793	0.268	0.800	0.239	0.751
0.260	0.836	0.262	0.815	0.282	0.826	0.278	0.801
0.276	0.857	0.274	0.829	0.305	0.850	0.324	0.851
0.291	0.875	0.277	0.835	0.325	0.871	0.367	0.882
0.312	0.898	0.300	0.859	0.356	0.897	0.388	0.901
0.357	0.938	0.313	0.875	0.373	0.900	0.426	0.923
		0.328	0.889	0.384	0.910	0.449	0.931
		0.343	0.902	0.382	0.913	0.541	0.963
		0.407	0.945	0.404	0.924		
				0.427	0.937	$\theta = 65$ °C	
				0.444	0.940	0.013	0.065
				0.450	0.950	0.026	0.130

[a] For activities differing from less than 0.002, corresponding values have been averaged.

is empirical and valid only in the temperature and concentration ranges spanned during the experiments.

The values of the interaction parameter χ obtained from the experiments performed at $\theta = 25$ °C and the empirical expression are given in Figure 3. χ increases when the polymer concentration increases, which is often observed for poor solvents.[2] χ decreases when the temperature increases. For example, at $\Phi_2 \simeq 0$, χ decreases from 0.81 at 5 °C to 0.73 at 35 °C, which is consistent with the value reported by Du et al.[7] for the system polyisobutylene + toluene at infinite solvent dilution ($\chi = 0.603$ for $\theta = 100$ °C). The activity curve corresponding to eqs 2 and 3 has been drawn in Figures 1 and 2 (continuous lines). Very good agreement is obtained with the experimental points.

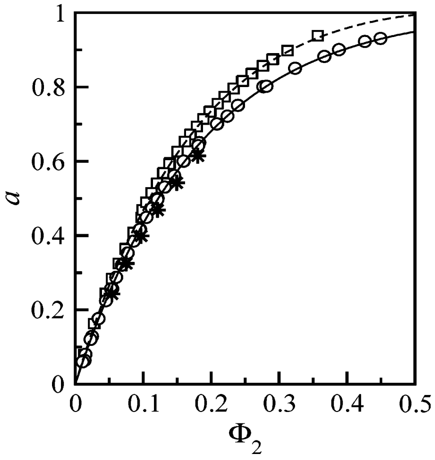

Figure 1. Activity a vs solvent volume fraction Φ_2 obtained at $\theta = 5$ °C (open squares) and $\theta = 35$ °C (open circles). The same symbols are used for all thicknesses. Black stars are the experimental data of Wibawa and coauthors[6] at $\theta = 40$ °C. The solid and dashed lines correspond to the Flory−Huggins fit (eqs 2 and 3).

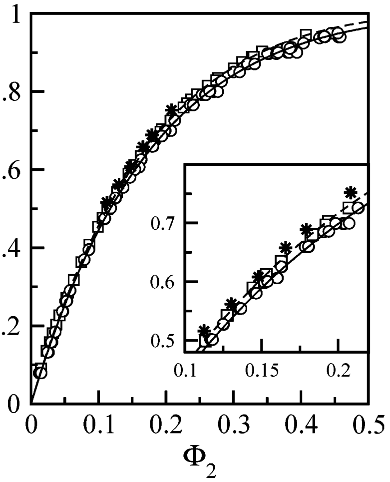

Figure 2. Activity a vs solvent volume fraction Φ_2 obtained at $\theta = 15$ °C (open squares) and $\theta = 25$ °C (open circles). The same symbols are used for all the thicknesses. Black stars are experimental data of Wibawa and coauthors[6] at $\theta = 20$ °C. The solid and dashed lines correspond to the Flory−Huggins fit (eqs 2 and 3).

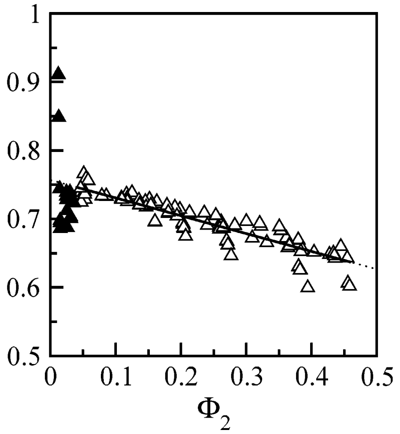

Figure 3. Flory−Huggins parameter χ vs solvent volume fraction Φ_2 deduced from eq 2 ($\theta = 25$ °C, each triangle corresponds to a circle of Figure 2). The line corresponds to the best fit obtained from all of the experimental data at different temperatures for $\Phi_2 > 0.04$ (full triangles have not been used for the fit).

4. Mutual Diffusion Coefficient

In the framework of binary systems consisting of a monodisperse polymer and a solvent, the transport of solvent (or polymer) caused by the gradient of its chemical potential can be described in terms of a single parameter D_m, the mutual diffusion coefficient.[8] D_m is expressed in the volume-fixed frame of reference. Relations between the diffusion coefficients expressed in different frames of reference are detailed in the paper by Kirkwood and al..[9] In concentrated polymer + solvent solutions, self and mutual diffusion coefficients are known to decrease by several orders of magnitude when the solvent concentration decreases.[10−13] The concentration dependence of the mutual diffusion coefficient is an interplay between a hydrodynamic factor (friction) and a thermodynamic factor (variation of the osmotic pressure with the concentration).[8]

In the experiments presented here, the mutual diffusion coefficient was derived from the analysis of the kinetics of drying or swelling of the sample following a step change in the solvent vapor pressure. During a swelling experiment, if the vapor pressure variation is small enough, the solvent content variation in the solution is small, and the diffusion coefficient can be assumed to be constant during the experiment. In that case, sorption and desorption steps give the same kinetics. By performing differential vapor pressure steps at various pressures, it is then possible to estimate the mutual diffusion coefficient for various solvent contents. Let us recall that the system studied is rubbery, so no aging effect or coupling with viscoelastic relaxation has to be taken into account when modeling the swelling kinetics. The system behavior does not depend on its thermal or swelling "history".[14]

The model and numerical procedure used to analyze the data have been thoroughly described in a previous paper,[1] so we recall only the main features. External inputs are the chamber temperature $T_a(t)$ and the solvent vapor pressure $P_V(t)$ imposed by the regulation systems. Unknown variables are the film temperature $T(t)$, the local solvent volume fraction $\Phi_2(z, t)$, and the film thickness $l\ (t)$.

The Fick law is used to describe solvent diffusion through the film with the assumption of a constant mutual diffusion coefficient during a differential step:

$$\frac{\partial \Phi_2(z, t)}{\partial t} = D_m \frac{\partial^2 \Phi_2(z, t)}{\partial z^2} \qquad 0 < z < l \tag{4}$$

The boundary condition at the film/substrate interface is a nonpermeability condition:

$$\frac{\partial \Phi_2}{\partial z}\Big|_{z=0} = 0 \tag{5}$$

At the film/vapor interface, the boundary condition is given by eqs 1 and 2, where Φ_2 is the solvent volume fraction at the interface. Two more equations are obtained by setting the nonevaporation of the polymer and the heat balance. Heat balance takes into account the energy needed to vaporize the solvent (or brought by the condensation when considering a desorption step), the variation of the internal energy of the sample, and the exchange with the environment at temperature T_a:

$$\mathcal{C}\frac{dT}{dt} = h_{th}(T_a - T) + \frac{L}{V_2^0}\frac{d(l\Phi_2)}{dt} \tag{6}$$

where L is the solution latent heat, h_{th} is the global heat transfer coefficient between the sample and the chamber, and $\mathcal{C}$ is the heat capacity of the sample.

The evolution of the film mass derived from the above model depends on the mutual diffusion coefficient, and a classical minimization procedure is used to get the mutual diffusion coefficient that minimizes the distance between the calculated and experimental kinetics.

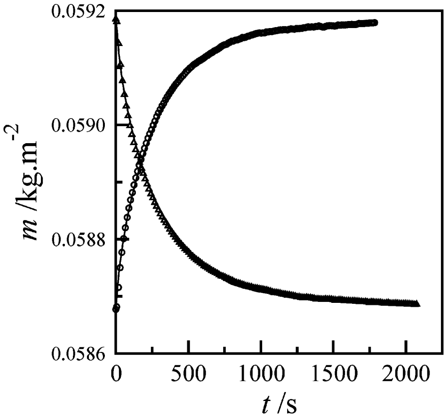

Figure 4. Film mass variation per unit area ($m = (M_1 + M_2)/S$) during a differential sorption (circles) and desorption (triangles). Continuous lines are the result of the model with the following estimation of the mutual diffusion coefficient: $D_m = 6.2 \times 10^{-12}$ m^2·s^{-1} (sorption) and $D_m = 5.8 \times 10^{-12}$ m^2·s^{-1} (desorption).

The diffusion characteristic time is l^2/D_m, where l is the film thickness. Given the large variations of D_m, it is not possible to use a unique sample over the entire concentration range. Indeed, some practical limitations require us to use various thicknesses: On one hand, the diffusion characteristic time must be greater than the balance sampling time and the setup regulation delays. On the other hand, it must be "reasonable" (no longer than a few tens of hours). Other side effects due to the coupling between temperature and mass evolution may also limit the suitable thickness domain.[1] That is why thicknesses between 13 μm and 571 μm have been used. When possible, for the same differential step, the experiment has been done with various film thicknesses to verify if the results for the diffusion coefficient are independent of the film thickness.

The following experimental conditions have been used:

$$\theta = 5\ °\text{C},\ l_{dry} = (13 \text{ and } 57)\ \mu\text{m},\ \Phi_2 \le 0.23$$

$$\theta = 15\ °\text{C},\ l_{dry} = (13 \text{ and } 52)\ \mu\text{m},\ \Phi_2 \le 0.19$$

$$\theta = 25\ °\text{C},\ l_{dry} = (13, 52, 63, 99, 213, 311, \text{ and } 571)\ \mu\text{m}$$
$$(M_w = 10^6\ \text{g·mol}^{-1} \text{ for the 99-}\mu\text{m-thick film}),\ \Phi_2 \le 0.30$$

$$\theta = 35\ °\text{C},$$
$$l_{dry} = (52, 57, 63, 213, \text{ and } 311)\ \mu\text{m},\ \Phi_2 \le 0.24$$

$$\theta = 65\ °\text{C},\ l_{dry} = (67 \text{ and } 303)\ \mu\text{m},\ \Phi_2 \le 0.02$$

Figure 4 gives an example of the experimental and simulated kinetics for a sorption step and a desorption step at $\theta = 35$ °C for a 57-μm-thick film (dry film thickness). The activity was changed from 0.45 to 0.47 (sorption) and from 0.47 to 0.45 (desorption). The solvent volume fraction varies from 0.105 to 0.113 during the experiment. As can be seen, the agreement between the model and data is very good. Sorption or desorption steps give nearly the same diffusion coefficient ($D_m = 6.2 \times 10^{-12}$ m^2·s^{-1} for the sorption experiment and $D_m = 5.8 \times 10^{-12}$ m^2·s^{-1} for the desorption experiment), confirming that the assumption of a constant D_m during a step is valid. Nearly as good agreement was obtained for all of the data.

4.1. Mutual Diffusion Coefficient at $\theta = 25$ °C. The variation of the mutual diffusion coefficient with the solvent volume fraction is given in Figure 5 for $\theta = 25$ °C. The horizontal error bar corresponds to the solvent volume fraction interval covered during the sorption or desorption step. The vertical error bar that corresponds to the estimation of D_m is mainly due to the error in the thickness of the dry film: $\Delta D_m/D_m = 2\Delta l_{dry}/l_{dry}$, with $\Delta l_{dry}/l_{dry} = \Delta V_2^0/V_2^0 + \Delta S/S + \Delta M_1/M_1 = 6 \times 10^{-2} + \Delta M_1/M_1$ ($\Delta M_1 \simeq 0.1$ mg), where S is the sample surface.

A strong decrease in the mutual diffusion coefficient is found: about 3 orders of magnitude (from 7.6×10^{-11} to 1.5×10^{-13} m^2·s^{-1}) when Φ_2 goes from 0.295 to 0. This

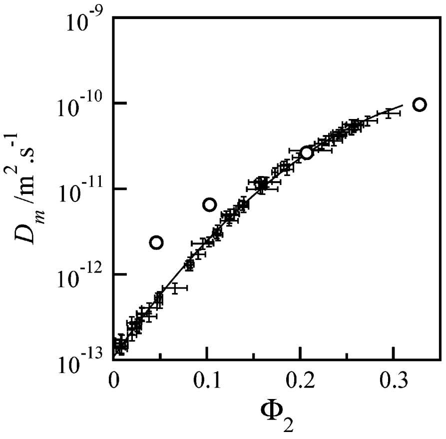

Figure 5. Mutual diffusion coefficient D_m versus solvent volume fraction at $\theta = 25$ °C. Black points and the corresponding error bars are the experimental data obtained in this study. The same symbol is used for all thicknesses. Open circles are the experimental data of Bandis and coauthors[15] for the self-diffusion coefficient. The solid line corresponds to the polynomial fit.

decrease can be well fitted in the domain of high concentration of polymer by a polynomial relation for $\log(D_m)$: $\log(D_m/\mathrm{m^2{\cdot}s^{-1}}) = -12.96 + 15.50\Phi_2 - 19.45\Phi_2^2$.

Experimental data obtained from NMR by Bandis et al.[15] for the solvent self-diffusion coefficient have been reported on the same graph. Some discrepancies between the results are obtained: Indeed, the solvent self-diffusion coefficient and mutual diffusion coefficient should be the same in the limit of pure polymer ($\Phi_2 = 0$), but this is not the case because the value of Bandis et al. extended to $\Phi_2 = 0$ is larger than the value that we found in the same limit. However, let us note that the measurement of such a small diffusion coefficient is difficult using NMR techniques although it corresponds to a range where gravimetric measurements are very accurate.

4.2. Mutual Diffusion Coefficient, 5 °C < θ < 65 °C. Results for all of the temperatures are gathered in Table 2 and in Figure 6. Here again a change of 0.1 in solvent volume fraction corresponds to a variation of more than 1 order of magnitude of the mutual diffusion coefficient.

The comparison with one experimental data point found in the literature at $\theta = 68$ °C does not show good agreement, but in the opposite sense from the previous comparison at $\theta = 25$ °C. Indeed, although our experiments give a diffusion coefficient smaller than the values extrapolated from Bandis et al. values at $\theta = 25$ °C, we obtain a result 1 order of magnitude greater than the gas chromatographic measurements performed by Jiang and Han[16] at $\theta = 68$ °C: for $\Phi_2 = 0.007$ we obtain $D_m = 3.0 \times 10^{-12}$ $\mathrm{m^2{\cdot}s^{-1}}$ at $\theta = 65$ °C, and Jiang and Han found $D_m = 1.59 \times 10^{-13}$ $\mathrm{m^2{\cdot}s^{-1}}$ at $\theta = 68$ °C for $\Phi_2 \simeq 0$. These authors used an inverse gas chromatographic technique, and results

Table 2. Decimal Logarithm of the Mutual Diffusion Coefficient as a Function of the Solvent Volume Fraction for Different Temperatures[a]

$\theta = 5$ °C		$\theta = 25$ °C		$\theta = 35$ °C	
Φ_2	$\log(D_m/\mathrm{m^2{\cdot}s^{-1}})$	Φ_2	$\log(D_m/\mathrm{m^2{\cdot}s^{-1}})$	Φ_2	$\log(D_m/\mathrm{m^2{\cdot}s^{-1}})$
0.006	−13.77	0.008	−12.82	0.005	−12.47
0.020	−13.49	0.020	−12.63	0.008	−12.46
0.035	−13.23	0.026	−12.59	0.016	−12.31
0.049	−13.02	0.031	−12.46	0.028	−12.17
0.058	−12.90	0.038	−12.44	0.040	−12.02
0.069	−12.74	0.049	−12.29	0.049	−11.90
0.080	−12.61	0.066	−12.16	0.052	−11.95
0.091	−12.44	0.080	−11.90	0.056	−11.81
0.102	−12.32	0.082	−11.87	0.064	−11.70
0.109	−12.25	0.091	−11.76	0.073	−11.60
0.116	−12.15	0.096	−11.64	0.082	−11.51
0.125	−12.02	0.102	−11.62	0.091	−11.42
0.134	−11.89	0.111	−11.51	0.100	−11.32
0.145	−11.77	0.121	−11.31	0.109	−11.22
0.156	−11.62	0.125	−11.34	0.117	−11.14
0.165	−11.51	0.131	−11.25	0.126	−11.04
0.175	−11.39	0.139	−11.18	0.131	−10.95
0.184	−11.29	0.157	−10.96	0.135	−10.98
0.193	−11.21	0.159	−10.96	0.144	−10.88
0.204	−11.10	0.163	−10.92	0.151	−10.82
0.215	−10.97	0.173	−10.81	0.162	−10.73
0.226	−10.88	0.182	−10.73	0.172	−10.63
		0.186	−10.75	0.175	−10.60
$\theta = 15$ °C		0.198	−10.63	0.182	−10.56
0.008	−13.24	0.212	−10.55	0.191	−10.50
0.015	−13.14	0.223	−10.47	0.199	−10.47
0.021	−13.00	0.227	−10.43	0.208	−10.40
0.028	−12.90	0.236	−10.44	0.218	−10.34
0.033	−12.83	0.240	−10.37	0.228	−10.28
0.037	−12.79	0.244	−10.34	0.239	−10.22
0.048	−12.62	0.255	−10.28		
0.058	−12.50	0.258	−10.26	$\theta = 65$ °C	
0.069	−12.35	0.272	−10.21	0.007	−11.53
0.081	−12.19	0.295	−10.12	0.020	−11.39
0.094	−12.03				
0.103	−11.91				
0.112	−11.80				
0.149	−11.39				
0.188	−11.01				

[a] For solvent volume fractions differing from less than 0.002, corresponding values have been averaged.

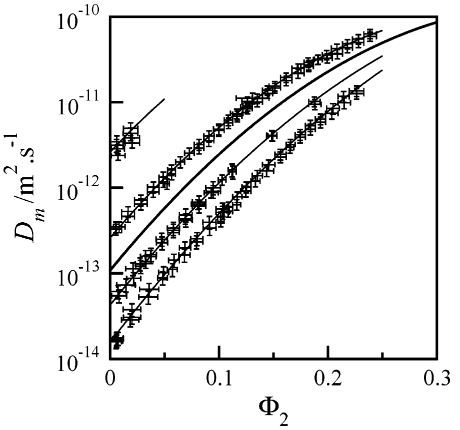

Figure 6. Mutual diffusion coefficient D_m versus solvent volume fraction Φ_2 at different temperatures. From bottom to top: $\theta = 5$ °C, 15 °C, 25 °C, 35 °C, and 65 °C. The solid lines correspond to the empirical relations (polynomial fit of $\log(D_m)$ at $\theta = 25$ °C + polynomial fit of the activation energy). For clarity, the experimental points are not drawn for $\theta = 25$ °C.

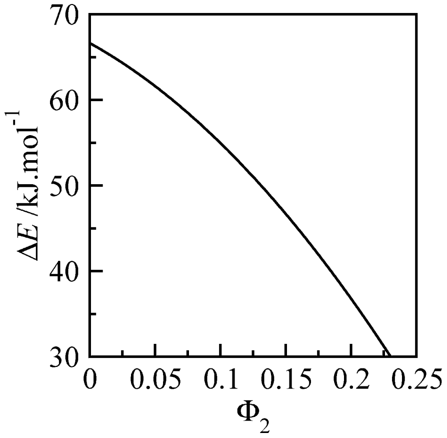

Figure 7. Polynomial fit of activation energy ΔE versus solvent volume fraction Φ_2.

have only been obtained for trace amounts of toluene so the comparison is limited to the very small solvent content. It must be noticed that chromatography is not a direct method of obtaining the mutual diffusion coefficient because it is deduced from a set of equations describing the behavior in the whole column. On the contrary, in our experiments, the whole surface of the sample is subjected at the same time to the increase (or decrease) of the solvent vapor pressure. Moreover, the superposition of the kinetics obtained with various sample thicknesses when the time is scaled by l^2/D_m allow us to check the pertinence of the results.

For a given solvent concentration, the diffusion coefficient is very sensitive to the temperature. For example, for $\Phi_2 = 0$, the variation of D_m is larger than 2 orders of magnitude when θ increases from 5 °C to 65 °C. Variations of the diffusion coefficient with temperature can be described by an Arrhenius law with an apparent activation energy that depends on the concentration, especially in the polymer concentration domain.[10,11] The mutual diffusion coefficient is expressed by (taking $\theta = 25$ °C, i.e., $T = 298.15$ K, as a reference state)

$$D_m(\Phi_2, T) = D_m^0(\Phi_2) \exp\left[\frac{-\Delta E(\Phi_2)}{R}\left(\frac{1}{T/\mathrm{K}} - \frac{1}{298.15/\mathrm{K}}\right)\right] \quad (7)$$

We used a second-order polynomial approximation to express the dependence of the activation energy on the solvent concentration:

$$\Delta E/\mathrm{kJ{\cdot}mol^{-1}} = 66.65 - 84.24\Phi_2 - 324.9{\Phi_2}^2$$

The coefficients of the polynomial were estimated by a mean square fit for $\Phi_2 \leq 0.23$ using the experimental values at the different temperatures and the logarithmic fit of D_m at the reference temperature of $T = 298.15$ K. This empirical expression is displayed in Figure 7. As for other polymer + solvent systems (cf., for example, polystyrene + toluene[10]), the dependence of the activation energy on the solvent concentration is important: ΔE decreases from (67 to 30) kJ·mol^{-1} when Φ_2 increases from 0 to 0.23.

5. Conclusions

Gravimetric experiments have been used to obtain vapor−liquid equilibria and mutual diffusion coefficients for temperature between 5 °C and 65 °C for the system polyisobutylene + toluene. The great number of results obtained has allowed us to determine simple empirical relations that show very good agreement with experimental results and can be used for simulation or other purposes with great accuracy, as long as they are restricted to the concentration and temperature ranges covered by the experiments.

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Received for review December 23, 2004. Accepted March 28, 2005. Financial support from the ACI Physicochimie de la Matière Complexe (French research ministry) is acknowledged.

JE049541K