Mutual diffusion coefficient and vapor-liquid equilibrium data for the system polyisobutylene+toluene

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Abstract: Vapor-liquid equilibria and mutual diffusion coefficients have been measured for polyisobutylene+toluene system from 5 ^{0}C to 65 ^{0}C by gravimetry. Empirical relations have been determined for the Flory interaction parameter and for mutual diffusion coefficients. They show a very good agreement with experimental data and can be accurately used for simulation or other purpose, as long as they are restricted to the concentration and temperature ranges covered by our study.

1 Introduction

The physico-chemical 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

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0 in the polymer concentrated domain. 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 to optimize 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 to investigate both the liquid-vapor equilibrium and the mutual diffusion coefficient for a wide range of concentration and temperature.

The system under study is polyisobutylene(1)+toluene(2) for which only 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 ($5\ ^0\mathrm{C} \leq \theta \leq 35\ ^0\mathrm{C}$, and a few values at $\theta = 65\ ^0\mathrm{C}$). 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 ^{0}C. Model and estimation method for the determination of the mutual diffusion coefficient are only briefly discussed here since they have been described in a previous publication.[1] Comparison with other data of the literature are given when possible.

2 Experimental

The experimental set-up 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 the polymer film. In this study 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 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 set-up

The gravimetric set-up 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 regulation is 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. Uncertainties on temperature measurement is ±0.1 K and 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 ^{0}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 that 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) about 10 μg.

2.2 System

The polymer+solvent solution used in this study is polyisobutylene+toluene. Polyisobutylene was supplied by Sigma-Aldrich, with $M_{\mathrm{w}} = 5 \times 10^5 \mathrm{~g} \cdot \mathrm{mol}^{-1}$ and polydispersity 2.5 for most of the experiments. A few experiments (mentioned in the text) were performed with another polyisobutylene sample, with $M_{\mathrm{w}} = 10^6 \mathrm{~g} \cdot \mathrm{mol}^{-1}$ 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 ^{0}C and 1.5 ^{0}C respectively (Sigma-Aldrich), and the 'theta' temperature is -13 ^{0}C.[2] The experimental temperature is then above the glass transition temperature, the melting temperature and the theta temperature so the system remains rubbery, amorphous and homogeneous (no demixion) all along the experiments. Films were prepared by slow drying of polyisobutylene+toluene solutions in glass dishes. The film thickness depends on the initial concentration and on the initial thickness of the solution in the dish. Drying is achieved by heating the film at 60 ^{0}C for several days. The film is then taken off from the dish and put on an aluminium substrate. A disk of diameter 20 mm is then cut with a hollow punch. The sample (polyisobutylene film + aluminium 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 experiments: The aluminium 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 solvent content is stated in solvent volume fraction, Φ_2, with $\Phi_2 = V_2/(V_2 + V_1)$ with V_2 and V_1 the solvent and polymer volumes in the solution. Mass measurements are first converted in solvent mass fraction, $w_2 = M_2/(M_2 + M_1)$, with M_2 and M_1 the solvent and polymer mass 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: $V_1^0 = 1.087 \times 10^{-3}\ \mathrm{m}^3 \cdot \mathrm{kg}^{-1}$ (Aldrich) and $V_2^0 = 1.151 \times 10^{-3}\ \mathrm{m}^3 \cdot \mathrm{kg}^{-1}$.[3]

3 Vapor/liquid equilibrium

With the assumption of thermodynamic equilibrium at the vapor/film interface and the assumption of 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 the saturated pressure vapor of the pure solvent, P the saturated pressure vapor of the solution, Φ_2 the solvent volume fraction in the solution at the interface and T 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 uniform in the film and was deduced from the mass measurement. Since there was no inert gas in the chamber $P = P_{\mathrm{V}}$, the pressure imposed by the regulation system. The saturating pressure vapor of the solvent, $P_2^0(T)$, was calculated from the Antoine formula:[4] $log(P_2^0/\mathrm{Pa}) = A - B \times (T/\mathrm{K} + C)^{-1}$, with A=9.0782, B=1343.9, 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 which 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. 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:

$\theta = 5\ ^0\mathrm{C},\ l_{dry} = (13\ \text{ and } 57)\ \mu\mathrm{m},\ a \leq 0.94,\ \Phi_2 \leq 0.36;$

$\theta = 15\ ^0\mathrm{C},\ l_{dry} = (13,\ 52\ \text{ and } 57)\ \mu\mathrm{m},\ a \leq 0.95,\ \Phi_2 \leq 0.41;$

$\theta = 25\ ^0\mathrm{C},\ l_{dry} = (9,\ 13,\ 52,\ 63,\ 67 \text{ and } 99)\ \mu\mathrm{m}$ ($M_{\mathrm{w}} = 10^6\ \mathrm{g} \cdot \mathrm{mol}^{-1}$ for the 99 μm thick film), $a \leq 0.95,\ \Phi_2 \leq 0.45;$

$\theta = 35\ ^0\mathrm{C},\ l_{dry} = (9,\ 52,\ 57\ \text{ and } 63)\ \mu\mathrm{m},\ a \leq 0.96,\ \Phi_2 \leq 0.54.$

$\theta = 65\ ^0\mathrm{C},\ l_{dry} = (67 \text{ and }\ 303)\ \mu\mathrm{m},\ a \leq 0.13,\ \Phi_2 \leq 0.03.$

The relative error on the activity is deduced from the uncertainty on the pressure and temperature measurements: $\Delta a/a = \Delta P_{\mathrm{V}}/P_{\mathrm{V}} + \Delta P_2^0/P_2^0 \leq 10^{-2}$. Relative error on the solvent mass fraction is mainly due to the error on 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 since they are small and would alter the clarity of the graphs. Data are given in Table 1 and gathered in Figures 1 ($\theta = 5\ ^0$C and 35 ^{0}C) and 2 ($\theta = 15\ ^0$C and 25 ^{0}C). As can be seen, the reproducibility for 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 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 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:

$$\chi = c_0 + c_1\,\Phi_2 + c_2\,(\theta/\,^0\mathrm{C} - 25) + c_3\,(\theta/\,^0\mathrm{C} - 25)\,\Phi_2 \tag{3}$$

The coefficients c_0, c_1, c_2 and c_3 were estimated by mean square fit on the results obtained for all the 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

$\theta = 5\ ^0\mathrm{C}$		$\theta = 15\ ^0\mathrm{C}$		$\theta = 25\ ^0\mathrm{C}$		$\theta = 35\ ^0\mathrm{C}$	
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	$\theta = 65\ ^0\mathrm{C}$	
				0.444	0.940	0.013	0.065
				0.450	0.950	0.026	0.130

Table 1: Activity as a function of the solvent volume fraction for different temperatures. (For activities differing from less than 0.002, corresponding values have been averaged).

been obtained: $c_0 = 0.757$, $c_1 = -0.261$, $c_2 = -0.0025$, $c_3 = -0.0074$. Let us underline that this relationship is empirical and then only valid in the temperature and concentration ranges spanned during the experiments.

The values of the interaction parameter χ obtained from the experiments performed at $\theta = 25\ ^0$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 ^{0}C to 0.73 at 35 ^{0}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 $\theta = 100\ ^0$C. The activity curve corresponding to eq 2 and 3 has been drawn on Figures 1 and 2 (continuous lines). A very good agreement is obtained with the experimental points.

4 Mutual diffusion coefficient

In the framework of binary systems consisting of a monodisperse polymer and a solvent, 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 of Kirkwood and al.[9] In concentrated polymer+solvent solutions self and mutual diffusion coefficients are known to decrease of several order of magnitudes when the solvent concentration decreases.[10–13] The concentration dependance of the mutual diffusion coefficient is an interplay of 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 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 that no aging effect or coupling with viscoelastic relaxation have 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 are thoroughly described in a previous paper,[1] so that we only recall 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 the solvent diffusion through the film with assumption of constant mutual diffusion coefficient during a differential step:

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

Boundary condition at the film/substrate interface is a non-permeability condition:

$$\left.\frac{\partial \Phi_2}{\partial z}\right|_{z=0} = 0 \tag{5}$$

At the film/vapor interface the boundary condition is given by eq. 1 and 2, where Φ_2 is the solvent volume fraction at the interface. Two more equations are obtained by setting the non evaporation 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}:

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

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 calculated and experimental kinetics.

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 in all the concentration range. Indeed some practical limitations impose to use various thicknesses: on one hand the diffusion characteristic time must be greater than the balance sampling time and the set-up regulation delays. On the other hand it must be "reasonable" (no longer than a few ten 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 a same differential step, the experiment has been done with various film thicknesses in order to check that the results on the diffusion coefficient are well independent of the film thickness.

The following experimental conditions have been used:

$\theta = 5\ ^0\mathrm{C},\ l_{dry} = (13 \text{ and } 57)\ \mu\mathrm{m},\ \Phi_2 \leq 0.23;$

$\theta = 15\ ^0\mathrm{C},\ l_{dry} = (13 \text{ and } 52)\ \mu\mathrm{m},\ \Phi_2 \leq 0.19;$

$\theta = 25\ ^0\mathrm{C},\ l_{dry} = (13,\ 52,\ 63,\ 99,\ 213,\ 311 \text{ and } 571)\ \mu\mathrm{m}$ ($M_\mathrm{w} = 10^6$ $\mathrm{g \cdot mol^{-1}}$ for the 99 μm thick film), $\Phi_2 \leq 0.30;$

$\theta = 35\ ^0\mathrm{C},\ l_{dry} = (52,\ 57,\ 63,\ 213 \text{ and } 311)\ \mu\mathrm{m},\ \Phi_2 \leq 0.24;$

$\theta = 65\ ^0\mathrm{C},\ l_{dry} = (67 \text{ and } 303)\ \mu\mathrm{m},\ \Phi_2 \leq 0.02.$

Figure 4 gives an example of experimental and simulated kinetics, for a sorption step and a desorption one at $\theta = 35\ ^0\mathrm{C}$ 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 model and data is very good. Sorption or desorption steps give nearly the same diffusion coefficient ($D_m = 6.2 \times 10^{-12}\ \mathrm{m^2 \cdot s^{-1}}$ for the sorption experiment and $D_m = 5.8 \times 10^{-12}\ \mathrm{m^2 \cdot s^{-1}}$ 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 the data.

4.1 Mutual diffusion coefficient at $\theta = 25\ ^0\mathrm{C}$

The variation of the mutual diffusion coefficient with the solvent volume fraction is given in Figure 5 for $\theta = 25\ ^0\mathrm{C}$. 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 on 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 of the mutual diffusion coefficient is found: about three orders of magnitude (from 7.6×10^{-11} to $1.5 \times 10^{-13}\ \mathrm{m}^2 \cdot \mathrm{s}^{-1}$) when Φ_2 goes from 0.295 to 0. This decreasing can be well fitted in the polymer concentrated domain by a polynomial relation for $log\ (D_m)$: $log\ (D_m/\mathrm{m}^2 \cdot \mathrm{s}^{-1}) = -12.96 + 15.50\ \Phi_2 - 19.45\ \Phi_2^2$.

Experimental data obtained by 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 solvent self diffusion coefficient and mutual diffusion coefficient should be the same in the limit of pure polymer ($\Phi_2 = 0$); this is not the case since the value of Bandis et al. extended to $\Phi_2 = 0$ is larger than the one we found in the same limit. However let us note that the measurement of so low diffusion coefficient is difficult using NMR technics while it corresponds to a range where gravimetric measurements are very accurate.

4.2 Mutual diffusion coefficient, $5\,^0\mathrm{C} < \theta < 65\,^0\mathrm{C}$

Results for all 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 one order of magnitude of the mutual diffusion coefficient.

The comparison with one experimental data found in the literature at $\theta = 68\,^0\mathrm{C}$ does not show a good agreement, but in the opposite sense than the previous comparison at $\theta = 25\,^0\mathrm{C}$. Indeed, while our experiments give a diffusion coefficient smaller than the values extrapolated from Bandis et al. values at $\theta = 25\,^0\mathrm{C}$, we obtain a result almost one order of magnitude greater than the gas chromatographic measurements performed by Jiang and Han[16] at $\theta = 68\,^0\mathrm{C}$: for $\Phi_2 = 0.007$ we obtain $D_m = 3.0 \times 10^{-12}\ \mathrm{m}^2 \cdot \mathrm{s}^{-1}$ at $\theta = 65\,^0\mathrm{C}$ and Jiang and Han found $D_m = 1.59 \times 10^{-13}\ \mathrm{m}^2 \cdot \mathrm{s}^{-1}$ at $\theta = 68\,^0\mathrm{C}$ for $\Phi_2 \simeq 0$. These authors used an Inverse Gas Chromatographic technique and results have only been obtained for trace amounts of toluene, so that the comparison is limited to the very small solvent content. It must be noticed that chromatography is not a direct method to get the mutual diffusion coefficient as 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 submitted 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 allows checking 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 two orders of magnitude when θ increases from 5 ^{0}C to 65 ^{0}C. Variations of the diffusion coefficient with the temperature can be described by an Arrhenius law with an apparent activation energy that depends on the concentration, especially in the polymer concentrated domain.[10,11] The mutual diffusion coefficient is expressed by: (taking $\theta = 25$ ^{0}C, i.e. $T = 298.15$ K as reference state)

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

We used a second order polynomial approximation to express the dependance of the activation energy with 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 $T = 298.15$ K. This empirical expression is displayed in Figure 7. As for other polymer+solvent systems (cf. for example polystyrene+toluene[10]), the dependance of the activation energy with the solvent concentration is important: ΔE decreases from (67 to 30) $\mathrm{kJ \cdot mol^{-1}}$ when Φ_2 increases from 0 to 0.23.

$\theta = 5\ ^{0}\mathrm{C}$		$\theta = 25\ ^{0}\mathrm{C}$		$\theta = 35\ ^{0}\mathrm{C}$	
Φ_2	$log\ (D_m/\mathrm{m}^2 \cdot \mathrm{s}^{-1})$	Φ_2	$log\ (D_m/\mathrm{m}^2 \cdot \mathrm{s}^{-1})$	Φ_2	$log\ (D_m/\mathrm{m}^2 \cdot \mathrm{s}^{-1})$
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
$\theta = 15\ ^{0}\mathrm{C}$		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	$\theta = 65\ ^{0}\mathrm{C}$	
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				

Table 2: Decimal logarithm of the mutual diffusion coefficient as a function of the solvent volume fraction for different temperatures.(For solvent volume fractions differing from less than 0.002, corresponding values have been averaged)

5 Conclusion

Gravimetric experiments have been used to obtain vapor-liquid equilibria and mutual diffusion coefficients for temperature between 5 ^{0}C and 65 ^{0}C for the system polyisobutylene+toluene. The great amount of results obtained has allowed to determine simple empirical relations that show very good agreement with experimental results and can be used for simulation or other purpose with a great accuracy, as soon as they are restricted to the concentration and temperature ranges covered by the experiments.

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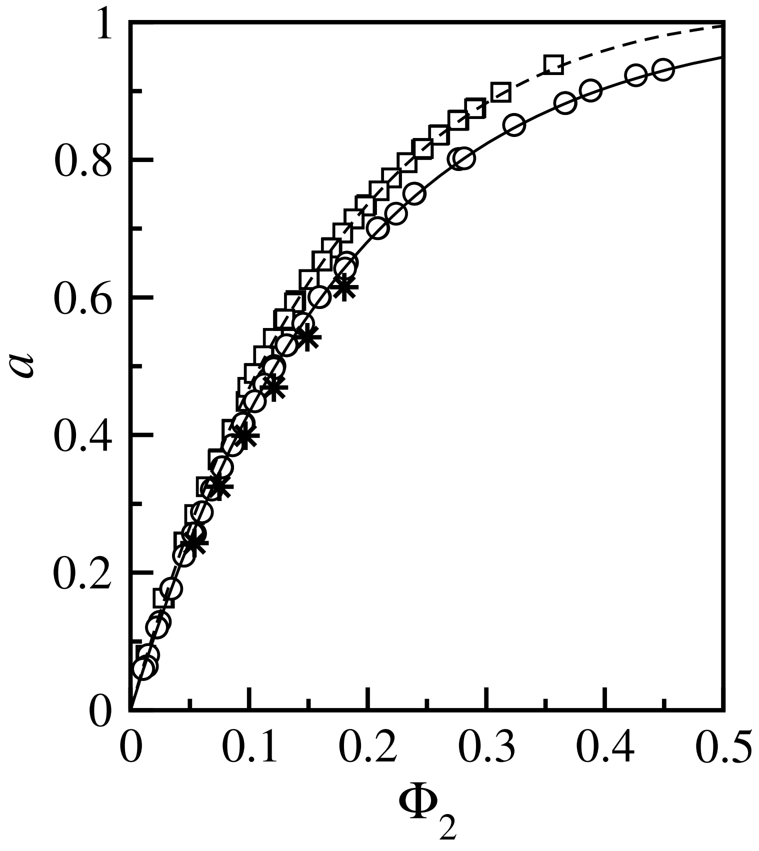

Figure 1: Activity a versus solvent volume fraction Φ_2 obtained at $\theta = 5\ ^0$C (empty squares) and $\theta = 35\ ^0$C (empty circles). The same symbols are used for all the thicknesses. Black stars are experimental data of Wibawa and coauthors[6] at $\theta = 40\ ^0$C . The sold and dashed lines correspond to the Flory-Huggins fit (eqs 2 and 3).

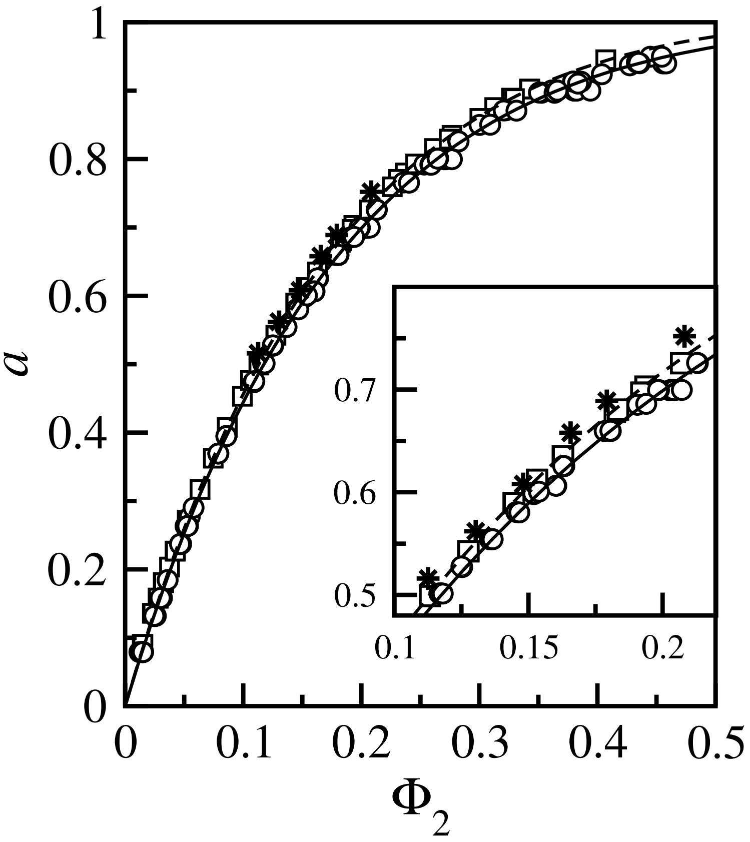

Figure 2: Activity a versus solvent volume fraction Φ_2 obtained at $\theta = 15\ ^0$C (empty squares) and $\theta = 25\ ^0$C (empty circles). The same symbols are used for all the thicknesses. Black stars are experimental data of Wibawa and coauthors[6] at $\theta = 20\ ^0$C. The solid and dashed lines correspond to the Flory-Huggins fit (eqs 2 and 3).

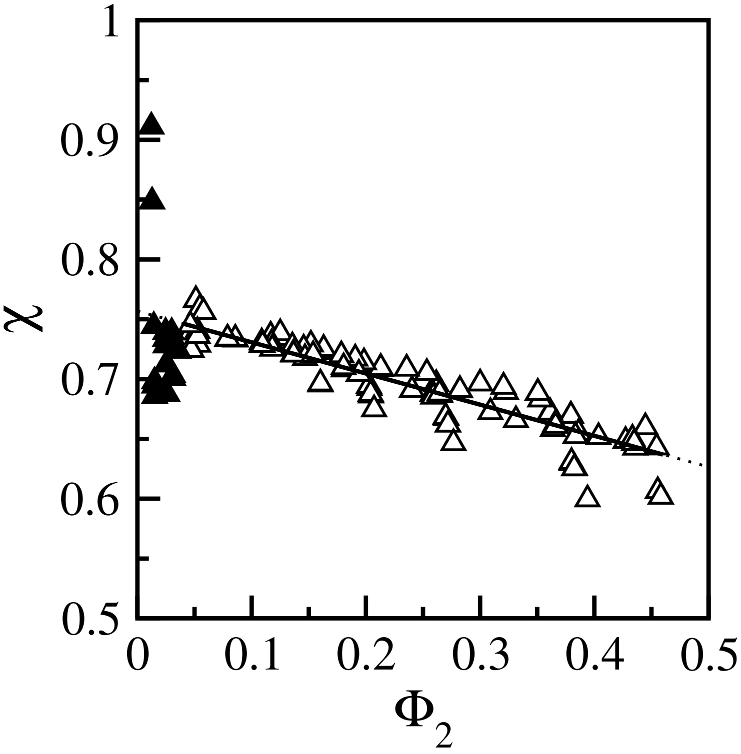

Figure 3: Flory-Huggins parameter χ versus solvent volume fraction Φ_2 deduced from eq 2 (θ = 25 ^{0}C, each triangle corresponds to a circle of Figure 2). The line corresponds to the best fit obtained from all the experimental data at different temperatures for $\Phi_2 > 0.04$ (full triangles have not been used for the fit).

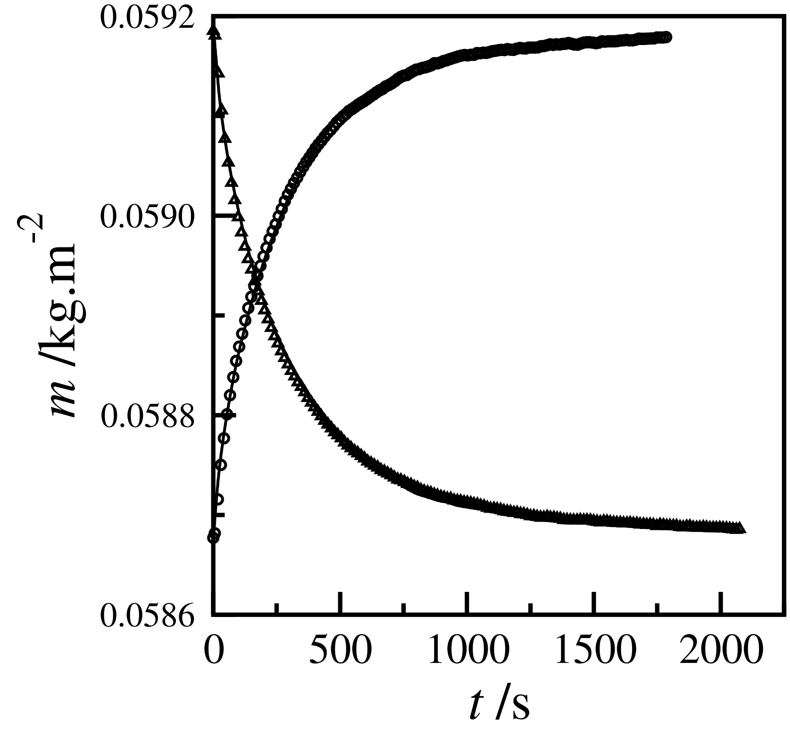

Figure 4: Film mass variation per unit area ($m = (M_1 + M_2)/S$) during a differential sorption (circles) and desorption (triangles). Continuous lines are the result of the model with the following estimation of the mutual diffusion coefficient: $D_m = 6.2 \times 10^{-12}\ \mathrm{m}^2 \cdot \mathrm{s}^{-1}$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

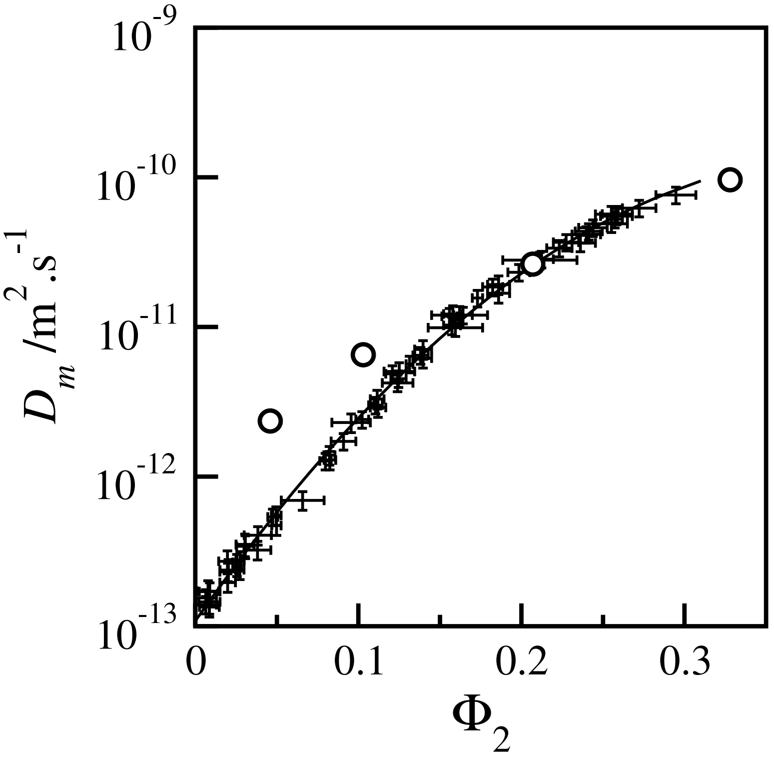

Figure 5: Mutual diffusion coefficient D_m versus solvent volume fraction at $\theta = 25$ ^{0}C. Black points and the corresponding error bars are the experimental data obtained in this study. The same symbol is used for all the thicknesses. Empty circles are experimental data of Bandis and coauthors[15] for the self-diffusion coefficient. The solid line corresponds to the polynomial fit.

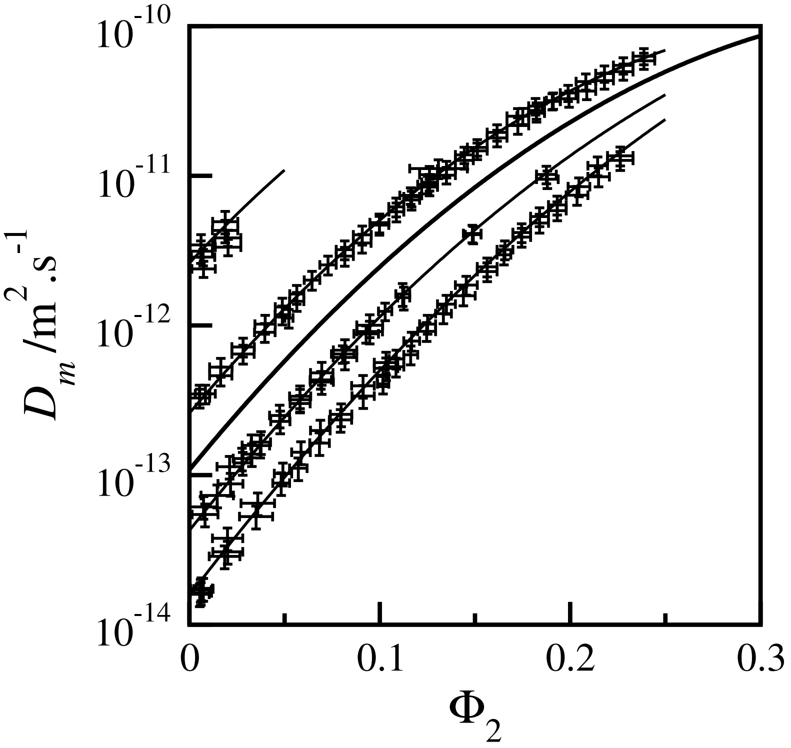

Figure 6: Mutual diffusion coefficient D_m versus solvent volume fraction at different temperatures. From bottom to top: $\theta = 5\ ^0$C, $15\ ^0$C, $25\ ^0$C, $35\ ^0$C and $\theta = 65\ ^0$C. The solid lines correspond to the empirical relations (polynomial fit of $log(D_m)$ at $\theta = 25\ ^0$C + polynomial fit of the activation energy). For clarity experimental points are not drawn for $\theta = 25\ ^0$C.

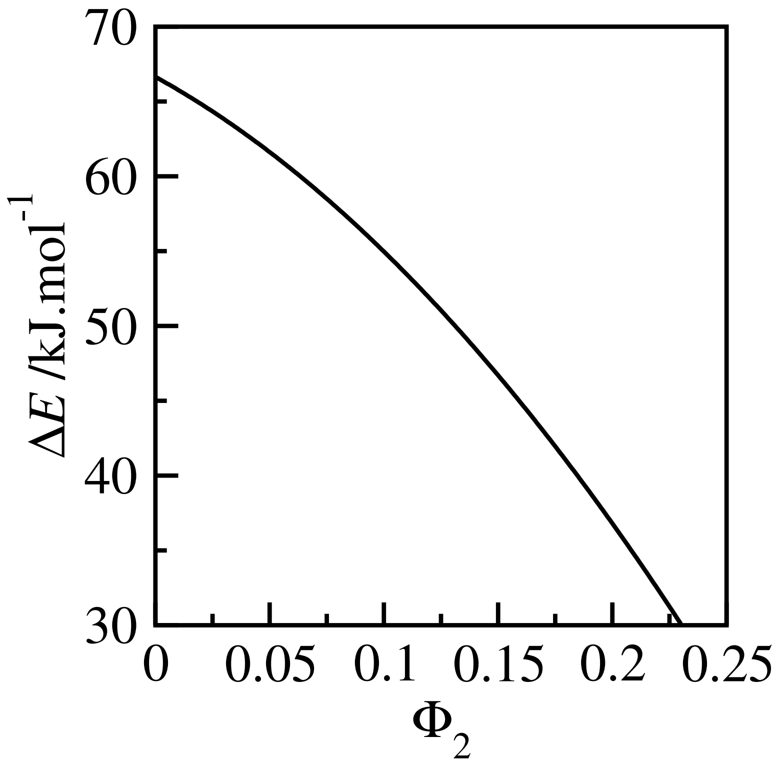

Figure 7: Polynomial fit of the activation energy ΔE versus solvent volume fraction Φ_2.