Slowing Down of the Diffusion Process in Polystyrene/Cyclohexane Mixtures Approaching the Coexistence Curve and the Critical Point

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ABSTRACT: The diffusion process in solutions of polystyrene ($M_w = 2.74 \times 10^5$) in cyclohexane of noncritical composition slows down upon approaching the liquid/liquid coexistence curve from the homogeneous single fluid phase region of the phase diagram at constant temperatures below the critical temperature and along the liquid/liquid coexistence curve approaching T_c. This effect reflects the influence of the thermodynamic factor $(\partial\mu/\partial\Phi)_{T,P}$ (μ, chemical potential of polystyrene; Φ, volume fraction of polystyrene) on the diffusion coefficient D. The experimental data are discussed in terms of the Flory–Huggins theory of polymer solutions. The composition and temperature dependence of the thermodynamic factor calculated from this model leads to $D(\Phi,T)$ curves which qualitatively reflect all features of the experimental data. These findings support the assumption that a slowing down of the diffusion process upon approaching the liquid/liquid coexistence curve of binary mixtures with a miscibility gap is a system independent phenomenon.

Introduction

There are two reports of experimental data in the literature demonstrating a slowing down of the diffusion process near to as well as along the liquid/liquid coexistence curve of binary liquid mixtures of low molar mass components.[1,2] In binary polymer melts with a miscibility gap (polystyrene-*d*/polystyrene-*h*; upper critical point) a slowing down of the diffusion process in mixtures of critical and noncritical composition at temperatures above and below T_c has been observed also.[3,4]

The findings have been interpreted qualitatively[2,4] on the basis of the mean field regular solution model.[5] It was assumed that the slowing down of the diffusion processes in mixtures of noncritical composition is typical for all binary mixtures when approaching the liquid/liquid coexistence curve. It is the aim of this study to widen the experimental basis of this assumption.

The concentration and temperature dependence of the mutual diffusion coefficient is measured in solutions of a macromolecular component (polystyrene) in a low molar mass solvent (cyclohexane) at temperatures above and below the critical temperature in the homogeneous region of the phase diagram of the system approaching the liquid/liquid coexistence curve. The diffusion coefficients are determined by the dynamic light scattering technique.

Experimental Section

Materials. Polystyrene (molar mass $M_w = 2.74 \times 10^5$ g mol^{-1}, $M_w/M_n = 1.02$, density $\varrho(20\ °C) = 1.08$ g cm^{-3}) was purchased from Polymer Standards Services GmbH (D-55125 Mainz, Germany) and used without further purification. Cyclohexane (density $\varrho(20\ °C) = 0.7791$ g cm^{-3}) was purchased from Aldrich Chemical Co. (D-89555 Steinheim) and was used without further purification also. The upper critical point of the system is characterized by its visually determined critical temperature $T_c = 25.83$ °C and its critical composition $\Phi_c = 0.063$ (volume fraction of polystyrene). At the critical composition the two phases coexisting at temperatures below but close to T_c had equal volumes ("equal volume criterion"). The temperature at which the speckle pattern produced at small scattering angles by the critical opalescence changed over to a "spinodal ring" was taken as the critical temperature (uncertainty of $\delta T_c = \pm 1$ mK). The visually determined phase diagram in the vicinity of the critical point is shown in Figure 1.

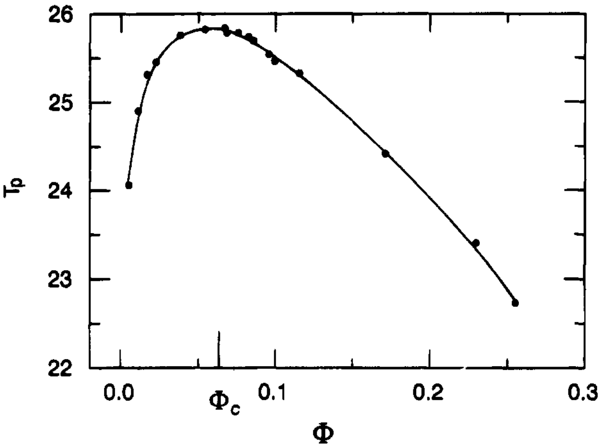

Figure 1. Experimentally determined liquid/liquid coexistence curve of the system polystyrene ($M_w = 2.74 \times 10^5$ g mol^{-1})/cyclohexane. The compositions of the samples used in this study are marked.

The samples used for the dynamic light scattering experiments were prepared in the following way: Polystyrene was dried for several days in a desiccator. It was dissolved in cyclohexane to form a homogeneous solution with a mass fraction of polystyrene of $y \approx 0.05$ at room temperature. The solution was filtered through a poly(tetrafluoroethylene) membrane (Sartorius, Wender Strasse, D-37073 Göttingen, Germany; type SM 118, pore size 1.2 μm). A stock solution ($y \approx$

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0.12; mass fraction of polystyrene) was prepared by removal of cyclohexane at ambient temperatures under vacuum. The samples used for the dynamic light scattering experiments had a composition in the range $5.3 \times 10^{-3} \le \Phi \le 0.255$ (Φ, volume fraction of polystyrene, 17 compositions; see Figure 1). They were prepared by introducing a known mass of the stock solution of known composition into a cylindrical quartz glass cell (internal diameter, 8 mm; thickness of the wall of the cell, 1 mm) and adding a known mass of cyclohexane. The cell contained a glass bead to facilitate a homogenization of a phase-separated sample after raising its temperature above the corresponding temperature of phase separation. The cell was closed by a screw cap with Teflon lining. The solution with concentrations of polystyrene corresponding to $y > 0.12$ were prepared by concentrating a known mass of the stock solution of known composition under vacuum. For the measurements of the diffusion coefficients the temperature of the samples was varied in the range $T_p \le T \le 36$ °C (about 20 values of each sample; T_p, temperature of phase separation).

Methods. The diffusion coefficient was obtained by photon correlation spectroscopy. The photometer consisted of a standard light scattering goniometer and a multibit, multi τ auto correlator (both from ALV, D-63225 Langen; goniometer type SP 86; correlator, ALV 3000). The correlator was operated in the single τ mode (300 channels). The temperature control of the cell containing the solution to be studied was improved by adding a thermostated shield. The short time (within 1 h) temperature fluctuations δT had a value $\delta T = \pm 20$ mK and the long time temperature fluctuation (within 24 h) had a value of $\delta T = \pm 50$ mK. The temperature was measured with a calibrated quartz thermometer (Hewlett Packard). The light source was a helium/neon laser, 20 mW; wavelength $\lambda_0 = 632.8$ nm (Spectra Physics, Siemensstrasse 2, D-64289 Darmstadt, Germany). The experiments were carried out at scattering angles in the range $30° \le \theta \le 135°$ corresponding to absolute value of the scattering vector 7.31×10^4 cm^{-1} $\le q \le 2.45 \times 10^5$ cm^{-1}. The lineup of the goniometer was checked with benzene as the scattering medium (static light scattering) and with aqueous suspensions of monodisperse polystyrene spheres (dynamic light scattering; standard Dow Latex, Serva, D-69115 Heidelberg, Germany; radii of the spheres 45.5, 99.0, 226.5, and 302.5 nm, respectively).

The calculation of the mutual diffusion coefficient D from the measured autocorrelation function of the scattered light $G^{(2)}(q,T,\tau)$ (τ, delay time) was based on eqs 1 and on the method of the cumulant expansion (see eq 2)[6]

$$g^{(2)}(q,T,\tau) = G^{(2)}(q,T,\tau)/B = 1 + A|g^{(1)}(q,T,\tau)|^2 \quad (1a)$$

with

$$g^{(1)}(\tau) = \exp\{-\Gamma(q,T)\tau\} \quad (1b)$$

A and B are constants ($B = \lim(\tau \to \infty)\, G^{(2)}(q,T,\tau)$). $\Gamma(q,T)$ is the reciprocal of the relaxation time of $g^{(1)}(\tau)$ ("line width" of scattered light). It is assumed that $g^{(1)}(\tau)$ is a single exponential.

$$\ln |g^{(1)}(\tau)| = C - \langle\Gamma\rangle\tau + 1/(2!)\hat{\mu}_2\tau^2 - \ldots \quad (2)$$

with

$$\langle\Gamma\rangle = \int_0^\infty \Gamma G(\Gamma)\, \mathrm{d}\Gamma$$

and

$$\hat{\mu}_2 = \int_0^\infty (\Gamma - \langle\Gamma\rangle)^2 G(\Gamma)\, \mathrm{d}\Gamma$$

C represents the base line. $G(\Gamma)$ describes a distribution of relaxation times. $\hat{\mu}_2$ is the second moment of the distribution $G(\Gamma)$. In the evaluation C is treated as a parameter of the fit.

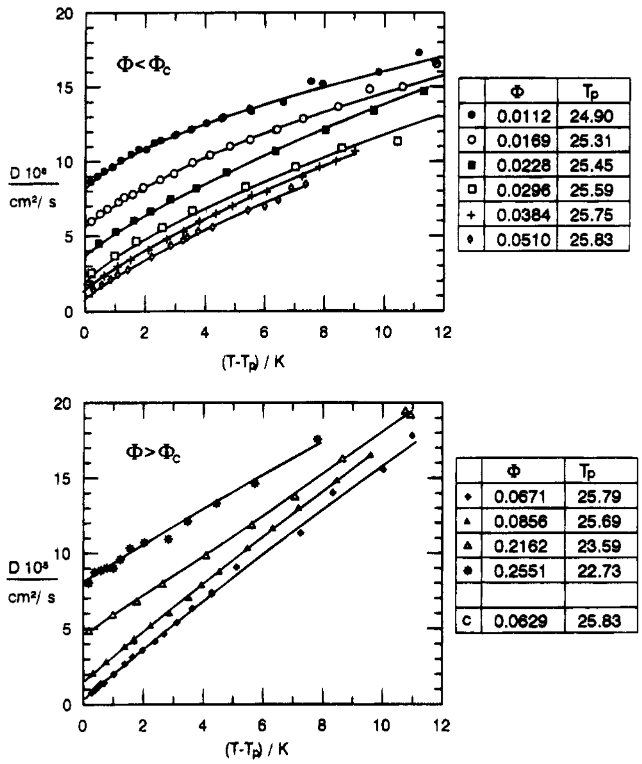

Figure 2. Plot of the mutual diffusion coefficient D of solutions of polystyrene ($M_w = 2.74 \times 10^5$ g mol^{-1}) in cyclohexane versus the temperature difference ($T - T_p$). T_P is the visually determined temperature of phase separation. The parameter is the volume fraction Φ of polystyrene. Critical concentration $\Phi_c = 0.063$; critical temperature $T_c = 25.82$ °C.

The method of the cumulant expansion is only valid for small values of τ and a sufficient narrow distribution of relaxation times.

The autocorrelation functions $g^{(1)}(q,T,\tau)$ obtained with polystyrene/cyclohexane solutions having concentrations up to a volume fraction $\Phi \cong 0.075$ were single exponentials (i.e. $\hat{\mu}_2 \cong 0$: A plot of $\log g^{(1)}$ versus τ is linear). At higher values of Φ (i.e. $0.1 \le \Phi \le 0.25$) the value of $\hat{\mu}_2$ increased but remained small ($0.04 \le \hat{\mu}_2 \le 0.16$), indicating a small contribution of a distribution of relaxation times.

The mutual diffusion coefficient D was calculated from $\Gamma(q)$ data (and $\langle\Gamma(q)\rangle$ data respectively using eq 3.

$$D = \lim(q \to 0)\, [\Gamma/q^2] \quad (3)$$

Results and Discussion

The experimentally determined temperature and composition dependence of the mutual diffusion coefficient D is shown in Figure 2. The data demonstrate that at constant composition the diffusion coefficient decreases upon approaching the liquid/liquid coexistence curve. This can be seen more clearly in Figure 3. There, the dependence of D on the composition is shown for different isotherms. The curves are constructed from the $D(T - T_p)$ curves shown in Figure 2. These curves clearly indicate that the diffusion process in the homogeneous solutions decreases upon approaching the critical point from temperatures above and below the critical temperature. At temperatures above T_c the $D(\Phi)$ curves exhibit a minimum at the critical composition. This minimum becomes more pronounced with decreasing values of ($T - T_c$). A similar observation has been reported by Rehage et al.[7] for temperatures above T_c. Figure 4a shows a double logarithmic plot of values of the diffusion coefficient $D(T_p)$ extrapolated to the temperature of phase separation T_p as a function of the temperature difference $[(T_c - T_p)/T_c]$. The data repre-

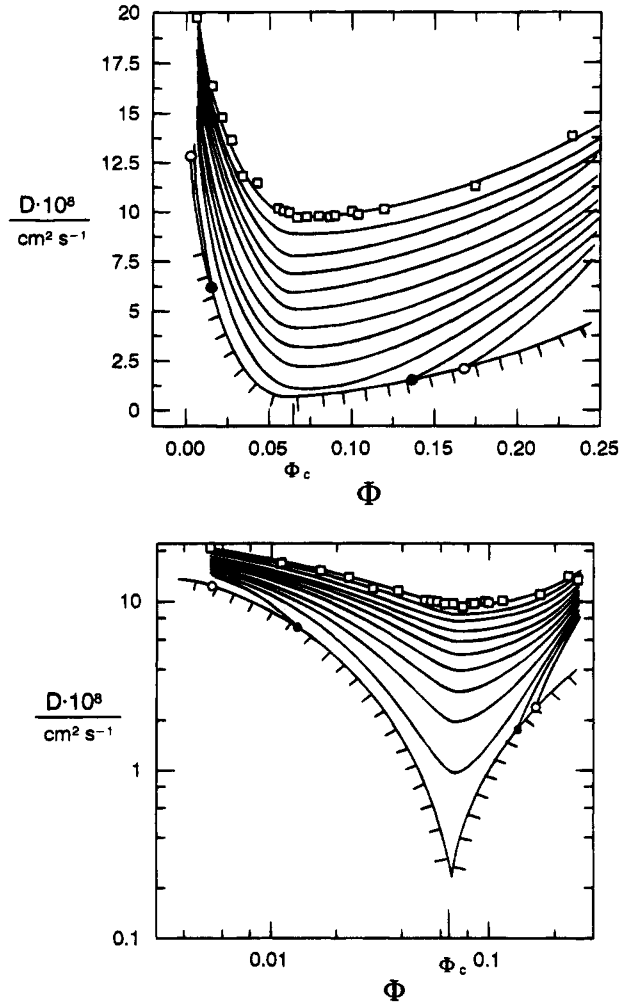

Figure 3. Temperature and composition dependence of the mutual diffusion coefficient D of solutions of polystyrene (M_w = 2.74 × 10^5 g mol^{-1}) in cyclohexane. The data are the same as those shown in Figure 2. Φ is the volume fraction of polystyrene. The hatched curves represent the liquid/liquid coexistence curve. The squares indicate the compositions of the solutions used for the measurements of $D(T - T_p)$. The most upper curve represents the data for T = 34.98 °C (i.e. $(T - T_c)$ = 9.15 K). The drawn out lines are $D(\Phi)$ isotherms for different values of $(T - T_c)$ decreasing from above to below in steps of 1 K. The circles mark values of $D(T_p)$ extrapolated to the temperature of phase separation (i.e. Figure 3a (top), linear plot; Figure 3b (bottom), double logarithmic plot). Filled circles: $(T_c - T_P) = -1.85$ K. Hollow circles: $(T_c - T_P) = -0.85$ K.

sent the change of D along the liquid/liquid coexistence curve. It is found that D converges to zero upon approaching T_c. The temperature dependence of D along this path can be represented by a power law of the form $D = D_0{}^*[(T_p - T_c)/T_c)]^{\nu_{\mathrm{eff}^*}}$ (see Figure 4a). The slope of the two branches has a similar value ($\nu^*_{\mathrm{eff}}(\Phi < \Phi_c) = \nu^*_{\mathrm{eff}}(\Phi > \Phi_c) \approx 0.62$). The viscosity of the solutions with $\Phi > \Phi_c$ is larger than that of the solutions with $\Phi > \Phi_c$. Therefore at the same temperature difference $(T_c - T_p)$ the value of $D(\Phi < \Phi_c)$ is larger than that of $D(\Phi > \Phi_c)$.

Figure 4b shows the slowing down of the diffusion process in a polystyrene/cyclohexane solution of critical composition (molar mass of the polymer, M_w = 1.35 × 10^5 g mol^{-1}) upon approaching the critical point from the homogeneous one fluid phase region of the phase diagram by lowering the temperature. The drawn out line in Figure 4b is represented by $D = D_0\ [(T - T_c(\mathrm{fit}))/T_c(\mathrm{fit})]^{\nu^*}$ with $D_0(\mathrm{fit}) = 1.058 \times 10^{-6}$ cm^2 s^{-1}. $T_c(\mathrm{fit})$ = 294.529 K and $\nu^*(\mathrm{fit}) = 0.745$. The data are taken from ref 8. The difference between the value of $\nu^*(\mathrm{fit})$ and the theoretically expected universal value of $\nu^* = 0.671$ is considered of no importance in view of the aim of this study.

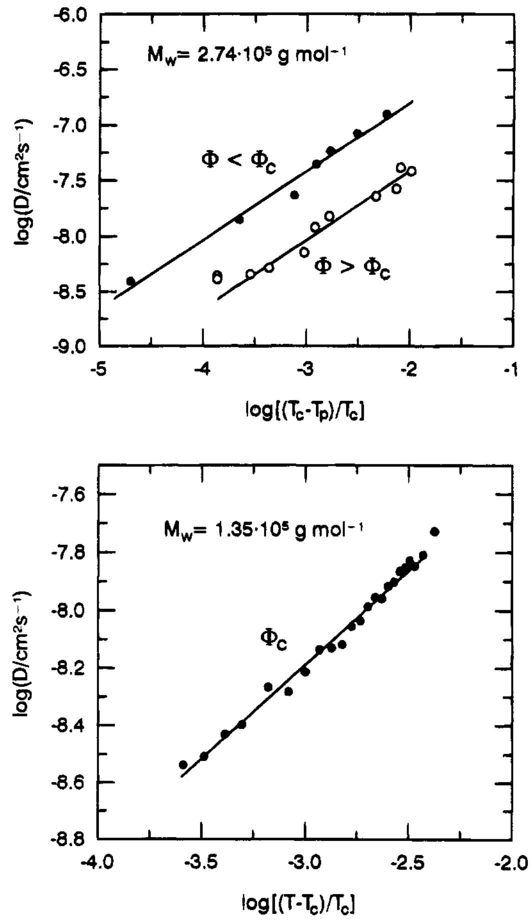

Figure 4. (a, top) Double logarithmic plot of the mutual different coefficient $D(T_p)$ of solutions of polystyrene (M_w = 2.74 × 10^5 g mol^{-1}) in cyclohexane extrapolated to the temperature of phase separation T_p of the solutions as a function of the reduced temperature difference $(T_c - T_P)/T_c$. For details see text. (b, bottom) Temperature dependence of the mutual diffusion coefficient $D(T - T_c)$ of a polystyrene (M_w = 1.35 × 10^5 g mol^{-1})/cyclohexane solution of critical composition (Φ_c = 0.0783; T_c(visual) = 294.498 K). For details see text.

Plots of ln D versus $1/T$ in the temperature range $(T - T_p) \lesssim 10$ K are curved upon approaching T_p (see Figure 5a). The slope of the curves at temperatures away from T_p in which the ln D versus $1/T$ curves are linear (see Figure 5a, upper drawn out line) corresponds to an apparent activation energy of about E_A = 19.8 kJ mol^{-1}. This value contains contributions from the temperature dependence of composition fluctuations. The curvature of the ln D versus $1/T$ plot near T_p will be discussed below.

From a thermodynamic point of view the temperature and composition dependence of D at temperatures above as well below the critical temperature can be understood qualitatively by assuming that it is mainly determined by the temperature and composition dependence of the thermodynamic factor $(\partial\mu_i/\partial p_i)_{T,P}$ (μ_i, chemical potential of component i; p_i order parameter of component i). The appropriate order parameter of a polymer solution is the volume fraction Φ_i. The relation between the mutual diffusion coefficient D defined by Fick's law (vanishing mean volume velocity) and the thermody-

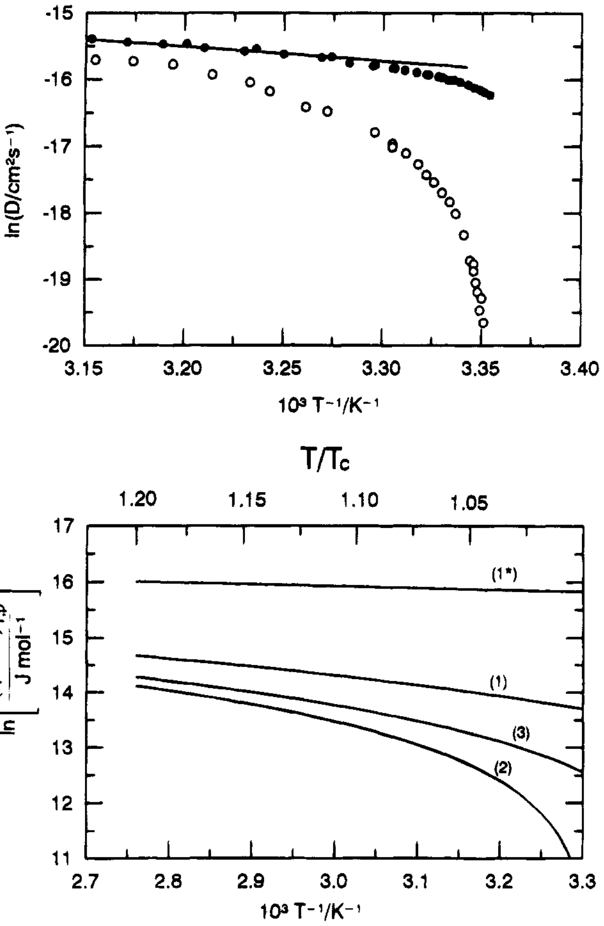

Figure 5. (a, top) Temperature dependence of the mutual diffusion coefficient of two polystyrene ($M_w = 2.74 \times 10^5$ g mol^{-1})/cyclohexane mixtures of noncritical compositions: plot of ln D versus $1/T$. The data marked by filled circles refer to a composition $\Phi = 0.011$ ($T_P = 24.90$ °C), and the data marked by hollow circles refer to a composition $\Phi = 0.067$ ($T_P = 25.79$ °C). The critical data are $\Phi_c = 0.063$, $T_P = 25.79$ °C. The slope of the drawn out line corresponds to an apparent activation energy of the diffusion coefficient of $E_a \approx 23$ kJ mol^{-1} (temperature range used for the determination of E_a: $1.025 \le T/T_c < 1.05$; $T_P = 24.90$ °C). The slope of a curve through the hollow circles in the temperature range $1.025 \le (T/T_c) \le 1.05$ corresponds to $E_a \approx 77$ kJ mol^{-1}. (b, bottom) Temperature dependence of the thermodynamic factor $(\partial\mu/\partial\Phi)_{T,P}$ calculated on the basis of the Flory–Huggins theory of polymer solutions using eq 5 with $N = 2.6 \times 10^3$. For the calculations the following approximation is used: $\Phi_c = N^{-1/2}$, i.e. $\Phi_c = 0.0193$; $T_c = 298.8$ K. Plot of $\ln[(\partial\mu/\partial\Phi)_{T,P}]$ versus $(1/T)$. For details see text.

namic factor $(\partial\mu/\partial\Phi)_{T,P}$ (μ and Φ refer to polystyrene) is given by eq 4.[9] Λ is a phenomenological transport

$$D = \Lambda V_m/(1 - \Phi)\cdot(\partial\mu/\partial\Phi)_{T,P} \qquad (4)$$

coefficient (mobility). At constant pressure, Λ is a function of temperature and mean composition. V_m is the molar volume of polystyrene. In deriving eq 4 it is assumed that the partial molar volume of polystyrene and the molar volume of polystyrene have the same value.

The Flory–Huggins model of a polymer solution in its simplest form is used to describe qualitatively the composition dependence of the chemical potential μ of polystyrene in cyclohexane (see eq 5, where N is the number of structural units in a given polymer molecule).[10]

In eq 5 it is assumed that the number of structural units in a given polymer molecule is large compared

$$(\mu - \mu^0) = RT[\ln \Phi - N(1 - \Phi) + 0.5(T_c/T)N(1 - \Phi)^2] \qquad (5)$$

with 1 (i.e. $N \gg 1$) and that the Flory–Huggins interaction energy parameter χ is only a function of temperature. The temperature dependence of χ is expressed by $\chi(T) = \chi_c(T_c)/T$ with $\chi_c = 0.5$ (for $N \gg 1$). Differentiation of eq 2 with respect to Φ leads to eq 6. Combination of eqs 5 and 6 leads to eq 7. $D(T,\chi=0)$ is

$$(\partial\mu/\partial\Phi)_{T,P} = RT_c[(T/T_c)\{(1/\Phi) + N\} - N(1 - \Phi)] \qquad (6)$$

$$[D(T)/D(T,\chi=0)] = 1 - (T_c/T)[\{N\Phi(1 - \Phi)\}/(1 + N\Phi)\} \qquad (7)$$

with

$$D(T,\chi=0) = \Lambda RTV_m/(1 - \Phi)\cdot[(1/\Phi) + N] \qquad (8)$$

the mutual diffusion coefficient of the polystyrene/cyclohexane solution in a hypothetical state in which the Flory–Huggins interaction parameter is zero ("ideal polymer solution"). It is introduced to bring out more clearly the influence of the interaction parameter χ on the diffusion process and to eliminate the factor $[\Lambda RTV_m/(1 - \Phi)]$. It is assumed that at constant temperature and composition the value of Λ in the ideal polymer solution and that in the real polymer solution have the same value.

Figure 6 shows two different graphical representations of eq 7 with $N = 2.6 \times 10^3$ (N, number of monomer units per macromolecule used in this study). The calculated curves reflect all the characteristic features of the experimentally observed composition and temperature dependence of the mutual diffusion coefficient of the system polystyrene/cyclohexane:

(a) For a mixture of critical composition (i.e. $\Phi = \Phi_c$) at temperatures $T > T_c$ the ratio $[D(T)/D(T,\chi = 0)]$ decreases upon approaching T_c and reaches the value $[D(T)/D(T,\chi = 0)] = 0$ at T_c (see Figure 6b). This is in agreement with experimental data (i.e. lim $T \to T_c$, $D \to 0$; see Figure 4b).

(b) For constant values of (T_c/T) (i.e. $T > T_c$) the $[D(T)/D(T,\chi = 0)]$ versus Φ curves have a minimum at the critical composition (see Figure 6a). This is in agreement with the experimentally observed minimum of the $D(\Phi)$ curves shown in Figure 3. The experimental fact that the minimum of the $D(\Phi)$ curves become more pronounced approaching $(T_c/T) = 1$ is reproduced by eq 7 also.

(c) For mixtures of noncritical composition at temperatures below the critical temperature the ratio $[D(T)/D(T,\chi = 0)]$ decreases with decreasing values of $|\Phi - \Phi_c|$ (see Figure 6a). This is in agreement with the experimental results (see Figures 2 and 3): D decreases upon approaching the coexistence curve.

(d) The value of $[D(T_p)/D(T,\chi = 0)]$ decreases upon approaching the critical point along the coexistence curve with decreasing values of $(T_c - T_p)$ (see Figures 6a and 6b). This is in agreement with the experimental results (see Figure 4a).

It is assumed that the curvature of the log D versus $1/T$ curve approaching T_c reflects the temperature dependence of the thermodynamic factor $(\partial\mu/\partial\Phi)_{P,T}$.[5]

If the temperature dependence of the phenomenological transport coefficient Λ can be represented by a function of the form $\Lambda = \Lambda_0 \exp\{-E_\Lambda/RT\}$ the tempera-

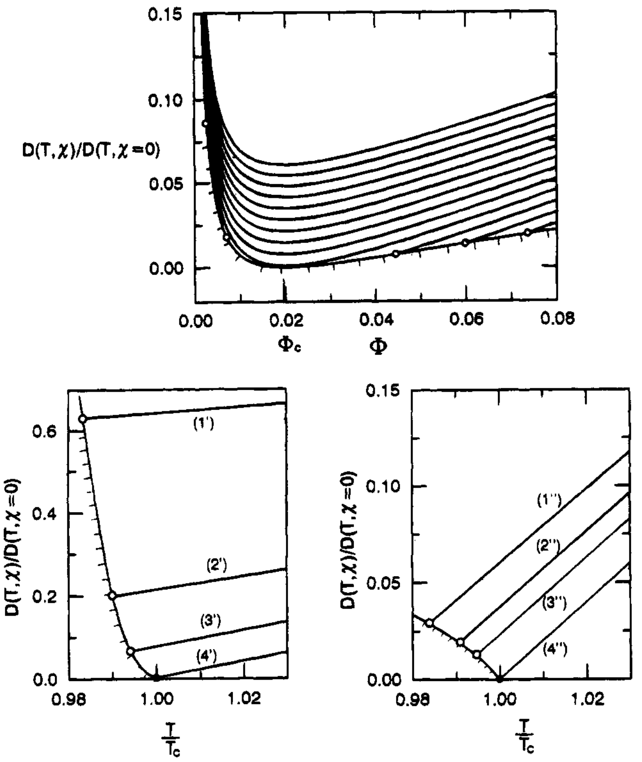

Figure 6. Graphical representation of eq 7. $(D(T)/D(T,\chi{=}0)$ is the ratio of the mutual diffusion coefficient of the polymer mixture at temperature T divided by the corresponding hypothetical value in an "ideal polymer mixture" (i.e. $\chi = 0$). Φ is the volume fraction of polystyrene. The critical temperature used for the calculations has a value of $T_c = 298.8$ K. In Figure 6a (top), the parameter is the temperature difference $(T - T_c)$ (9.15 K $\leq (T - T_c) \leq -3.85$ K in steps of $\delta(T - T_c) = 1$ K). In Figures 6b and 6c, (bottom left and right) the parameter is the volume fraction Φ of the polymer. Figure 6b refers to compositions $\Phi' < \Phi_c$, and Figure 6c, to compositions $\Phi'' > \Phi_c$. The parameter values of Φ in Figure 6b and in Figure 6c represent mixtures with compositions which coexist along the binodal curve. Curve 1': $\Phi' = 2.0 \times 10^{-4}$. Curve 1'': $\Phi'' = 0.0929$. Curve 2': $\Phi' = 0.0012$. Curve 2'': $\Phi'' = 0.0696$. Curve 3': $\Phi' = 0.0031$. Curve 3'', $\Phi'' = 0.0542$. Curve 4' = curve 4'': $\Phi_c = 0.0196$. Φ_c (theoretical)$(=N^{-1/2}) = 0.0196$ for $N = 2.6 \times 10^3$.

ture dependence of D is expected to be represented by eq 9 which follows from eqs 4 and 6

$$\ln D = -E_\Lambda/RT + \ln[(\partial\mu/\partial\Phi)_{P,T}] + \text{constant} \quad (9)$$

The differential coefficient $(\partial\mu/\partial\Phi)_{P,T}$ is a function of temperature and composition. In Figure 5b plots of $\ln[(\partial\mu/\partial\Phi)_{P,T}]$ as function of $(1/T)$ calculated from the Flory–Huggins model (see eq 5) for mixtures of different compositions are shown (curve 2: critical composition, $\chi = 0.5(T_c/T)$; $(\partial\mu/\partial\Phi)_{P,T} = RT[(N - 1)/\Phi_c - (T_c/T)N(1 - \Phi_c)]$; $\Phi_c = 0.0193$, $1.07 \leq (T/T_c) \leq 1.20$, $E_a \approx 25$ kJ mol^{-1}; $1.025 \leq (T/T_c) \leq 1.05$, $E_a \approx 70$ kJ mol^{-1}. Curve 1*: "ideal solution", $\chi = 0$, $(\partial\mu/\partial\Phi)_{P,T} = RTN/\Phi$; $\Phi = 0.003$, $1.025 \leq (T/T_c) \leq 1.20$, $E_{app} \approx 3$ kJ mol^{-1}. Curve 1: noncritical composition, $(\partial\mu/\partial\Phi)_{P,T} = RT[(N - 1)/\Phi - (T_c/T)(1 - \Phi)N]$; $\Phi = 0.003$, $1.07 \leq (T/T)_c \leq 1.20$, $E_{app} \approx 12$ kJ mol^{-1}; $1.025 \leq (T/T_c) \leq 1.05$, $E_a \approx 17$ kJ mol^{-1}; curve 3: noncritical composition, $\Phi = 0.007$, $1.07 \leq T/T_c \leq 1.20$, $E_{app} \approx 16$ kJ mol^{-1}; $1.025 \leq (T/T_c) \leq 1.05$, $E_a \approx 35$ kJ mol^{-1}). The shape of these curves is in qualitative agreement with the experimental data (see Figure 5a).

Conclusions

The diffusion process in solutions of polystyrene in cyclohexane slows down along different paths in the isobaric phase diagram of the system approaching T_c:

(a) At constant temperatures above the critical temperature the $D(\Phi)$ curves exhibit a minimum at the critical composition Φ_c. Approaching the critical temperature the minimum of the $D(\Phi)$ curve becomes more pronounced.

(b) At constant temperatures below the critical temperature the $D(|\Phi - \Phi_c|)$ curves decrease upon approaching the liquid/liquid coexistence curve from the homogeneous single fluid phase region.

(c) Approaching the critical point along the liquid/liquid coexistence curve the values of $D(T_p')$ and $D(T_p'')$ decrease along this path (T_p', temperature of phase separation along the liquid/liquid coexistence curve with $\Phi \leq \Phi_c$; T_p'', temperature of phase separation along the coexistence curve with $\Phi \geq \Phi_c$). They converge to zero at T_c.

(d) The slowing down of the diffusion process along these paths is dominated by the temperature and composition dependence of the thermodynamic factor $(\partial\mu/\partial\Phi)_{T,P}$ (μ, chemical potential of polystyrene; Φ, volume fraction of polystyrene) which appears in the relation connecting the mutual diffusion coefficient D with the thermodynamic factor and the phenomenological transport coefficient Λ. The predictions of the temperature and composition dependence of D based on the Flory–Huggins theory in its simplest form are in qualitative agreement with the experimental data.

(e) These findings together with the data given in refs 2 and 4 give support to the assumption that a slowing down of the diffusion process approaching the liquid/liquid coexistence curve in binary mixtures with a miscibility gap is a system independent phenomenon.

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