1.52, and 1.01, respectively, and the experimental values are close to the theoretical value of Zimm. Considering the experimental errors in these viscoelastic parameters, we cannot discuss the difference between Zimm-like and Rouse-like behavior. Moreover, our experimental concentration range may not be appropriate to compare the observed data with these theories. However, it is to be noted that the longest relaxation process in this concentration region is not so much isolated from others as in the case of Doi–Edwards theory.

In summary, we can conclude that the weight-average relaxation time τ_w of linear polymers in semidilute solutions for η° can be well represented by the longest relaxation time τ_m, whether the entanglements are effective to J_e or not.

References and Notes

(1) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.

(2) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980; Chapters 10, 13, 17.

(3) Tobolsky, A. V.; Aklonis, J. J.; Akovali, G. *J. Phys. Chem.* **1965**, *42*, 723.

(4) Fujimoto, T.; Ozaki, N.; Nagasawa, M. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 129.

(5) Osaki, K.; Fukuda, M.; Kurata, M. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 775.

(6) Sakai, M.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1972**, *5*, 786.

(7) Takahashi, Y.; Isono, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1985**, *18*, 1002.

(8) Takahashi, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1985**, *18*, 2220.

(9) Takahashi, Y.; Umeda, M.; Noda, I. *Macromolecules* **1988**, *21*, 2257.

(10) Isono, Y.; Fujimoto, T.; Takeno, N.; Kajiura, H.; Nagasawa, M. *Macromolecules* **1978**, *11*, 888.

(11) Endo, H.; Nagasawa, M. *J. Polym. Sci., Polym. Phys. Ed.* **1970**, *8*, 371.

(12) Sakai, M.; Fukaya, H.; Nagasawa, M. *Trans. Soc. Rheol.* **1972**, *16*, 635.

(13) Kajiura, H.; Endo, H.; Nagasawa, M. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 2371.

(14) Kajiura, H.; Sakai, M.; Nagasawa, M. *Trans. Soc. Rheol.* **1974**, *18*(2), 323; **1976**, *20*(4), 575.

(15) Takahashi, Y.; Isono, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1987**, *20*, 153.

(16) Tobolsky, A. V.; Murakami, K. *J. Polym. Sci.* **1959**, *40*, 443.

(17) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, 1986; Chapter 7.

Effect of Hydrostatic Pressure on Polystyrene Diffusivity in Toluene

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ABSTRACT: The pressure dependence of the mutual diffusion coefficient of selected polystyrene-in-toluene solutions is determined by dynamic light scattering. Decreases in the observed diffusivity with pressure can be explained by changes in the polymer concentration (due to solution compression) and decreases in the solvent fluidity (due to lowering of the system free volume). Quantitative correlations of diffusivity are established for different polymer concentrations and molecular weights, and the results are compared with theoretical predictions.

Introduction

Polymer diffusion at elevated pressures is relevant to many industrial processes, including polymerization reaction engineering and enhanced oil recovery. Furthermore, determination of the mobility of macromolecules at high pressures is important to the understanding of the molecular processes governing polymer rheology and related dynamic processes. Quantitative measurements of polymer diffusion coefficients at different pressures, for example, help to establish the relative importance of system free volume (and thus fluidity) and entanglement effects influence (dictated primarily by polymer concentration and molecular weight). In this work, we determine polymer mutual diffusion coefficients in binary solutions at elevated hydrostatic pressures by dynamic light scattering, in order to isolate these two possible factors affecting macromolecular mobility.

In a binary solution the mutual diffusion coefficient is defined as the proportionality constant between the component flux and the negative of the component concentration gradient:[1]

$$J_i = -D\nabla c_i \tag{1}$$

where J_i is the component flux (in mass of component i per unit area per unit time) in the volume-fixed frame of reference and ∇c_i is the concentration gradient (in mass of component i per unit volume per unit length). Conventionally, component 1 is the solvent and component 2 is the solute. In this paper for simplicity, we delete the subscript and use c to represent the polymer concentration.

Diffusion is in fact driven by free energy gradients from the theory of irreversible thermodynamics and the fact that the chemical potential of polymer solutions can be expressed in terms of the osmotic pressure, π. One obtains

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the following result for the mutual diffusion coefficient:

$$D = \frac{(\partial\pi/\partial c)_{T,\mu_1}}{f} \tag{2}$$

where f is a friction coefficient. Kirkwood and Riseman[2] derived the following expression for the friction coefficient of a single polymer chain in the limit of infinite dilution:

$$f = 6\pi\eta_s R_H N_a/M \tag{3}$$

where η_s is the solvent viscosity, N_a is Avogadro's number, M is the molecular weight, and R_H is the hydrodynamic radius of the polymer chain, defined by

$$\frac{1}{R_H} = \frac{\int g(r)/|r|\,dr}{\int g(r)\,dr} \tag{4}$$

In eq 4, $g(r)$ is the pair correlation function for the chain, and $g(r)\,dr$ is, therefore, the probability that a chain segment is located in a small region dr around the position r, given that there is a segment of the same chain located at $r = 0$.[4] The infinite dilution gradient of the osmotic pressure with respect to the polymer concentration is[5]

$$\left(\frac{\partial\pi}{\partial c}\right)_{T,\mu_1} = \frac{RT}{M} = \frac{N_a}{M}kT \tag{5}$$

In the limit of infinite dilution, the mutual diffusion coefficient is, therefore, given by

$$D_0 = \frac{kT}{6\pi\eta_s R_H} \tag{6}$$

where the subscript zero indicates infinite dilution.

Recently, renormalization group theories have been used to extend the expression for the mutual diffusion coefficient to finite concentrations.[6] The model treats the polymer chains as continuous curves or strings in space, while the solvent constitutes a continuum. The model imposes a balance between two competing forces: (1) an elastic (or entropic) force tending to prevent the chains from becoming too elongated and (2) an interaction force that prohibits more than one chain from occupying the same space (the excluded volume effect). With this model for the distribution of the chain segments in solution, the result from irreversible thermodynamics (eq 2), and the mode-coupling theory used by Kirkwood and Riseman to calculate the frictional resistance to the motion of segments in the solvent, one finds the following for the mutual diffusion coefficient in a good solvent:

$$\frac{D(c)}{D_0} = \frac{1}{(1+X)^{3/8}}\left[1 + \frac{1}{8}\left[9X - 2 + 2\frac{\ln(1+X)}{X}\right] \times \exp\left(\frac{1}{4}\left[\frac{1}{X} + \left(1 - \frac{1}{X^2}\right)\ln(1+X)\right]\right)\right] \tag{7}$$

where X is related to the second virial coefficient and the polymer concentration as follows:

$$X = \frac{16}{9}B_2 c \tag{8}$$

Equation 7 can be expanded in powers of X to give

$$\frac{D(c)}{D_0} = 1 + k_d c + ... \tag{9}$$

where k_d is defined by

$$k_d c = \left[e^{1/8} - \frac{3}{8}\right]X \approx 0.758X \tag{10}$$

In the experimental systems studied in this work, all of the data are in the concentration range where the linear expansion is valid.

The theory for predicting mutual diffusion coefficients as a function of molecular weight, solvent quality, and concentration can be used to formulate the pressure dependence of the diffusion coefficient. From eq 6, 7, and 8, we expect that the factors which could be pressure-sensitive and have an impact on the mutual diffusion coefficient are the solvent viscosity, η_s; the parameter X; and the chain hydrodynamic radius, R_H. The solvent viscosity will change with pressure because of the free volume loss due to compression, and the variable X may change with pressure if either the second virial coefficient or the polymer concentration changes with pressure. The polymer concentration (in kg/m^3 solution) will increase with pressure because the solvent is more compressible than the polymer. However, the hydrodynamic radius will only change if there is a change in the polymer/solvent thermodynamic interactions with pressure that affects the polymer segment pair correlation function (see eq 4).

Experimental data exist for the pressure dependence of the second virial coefficient of polystyrene in toluene. Schulz and Lechner[7] used static light scattering to measure the second virial coefficient at pressures up to 80 MPa. They found no change in the second virial coefficient with pressure at temperatures from 25 to 45 °C. McDonald and Claesson[8] have also used static light scattering to measure the second virial coefficient in the polystyrene/toluene system at pressures from atmospheric to 400 MPa. Over the range of pressures of interest to this study (0.1–100 MPa), their data show no significant change in the second virial coefficient with pressure. The lack of change of B_2 with pressure suggests that the hydrodynamic radius may be insensitive to pressure as well (since both quantities are measures of the strength of polymer/solvent interactions through the pair correlation function). Roots and Nyström[9] performed high-pressure dynamic light scattering measurements on a sample of polystyrene (MW = 110 000) dissolved in toluene. Most of their measurements were confined to dilute solution, and they found that the pressure dependence of the mutual diffusion coefficient could be described with constant values of both k_d and R_H for pressures up to 500 MPa.

The available theories and experimental data thus predict that for polystyrene in toluene the pressure dependence of the mutual diffusion coefficient is governed by the pressure dependence of the solvent viscosity and the effect of pressure on the polymer concentration.

Experimental Section

Polystyrene samples were purchased from the Toyo Soda Manufacturing Co. of Japan. All samples were of linear structure and had polydispersities (M_w/M_n) of less than 1.07. The weight-average molecular weights were 1.84 × 10^5 and 7.06 × 10^5 kg/(kg·mol) (Toyo Soda catalog numbers F20 and F80, respectively). The toluene used was HPLC grade from Aldrich Chemical Co.

The basic light scattering instrument used for this work was obtained from the Brookhaven Instruments Corporation in Holtsville, NY. A BI-200SM motorized goniometer and detection system was used to hold the sample in a temperature-controlled environment and measure the intensity of scattered light at various angles. A Lauda model number RM6 circulator was used to control the temperature in the sample cell. The temperature in the sample cell was controlled to within ±0.1 °C. A BI-2030 digital correlator with 136 data channels was used to collect the intensity autocorrelation functions in real time, analyze the correlation functions, and store the data. A

Lexel Model 95-2 argon ion laser was the light source for the experiments. The laser and goniometer were mounted on a 5 ft × 8 ft, 8 in. thick optical table supplied by Modern Optics of Pomona, CA.

The Brookhaven Instruments light scattering equipment was designed for measurements at atmospheric pressure. To make the measurements at elevated pressure, a special light scattering cell was designed and constructed. Details of this unit are documented elsewhere.[10]

The 4.88×10^{-7} m blue line of the Argon ion laser was used for the experiments. Power levels were typically in the 0.05–0.30 W range. Measurements made over a range of incident intensities showed that these laser power levels had no effect on the measured diffusion coefficients. Experiments typically lasted from 10 to 20 min, depending on the scattered light intensity. The Brookhaven Instruments light scattering detector was operated with a filter in front of the photomultiplier tube that blocked all wavelengths of light except that with a wavelength of 4.88×10^{-7} m.

Data Analysis

The method of cumulants was used to analyze the light scattering data.[11] The starting point of this analysis is the following equation:[10,11]

$$\frac{\langle I(0)I(\tau)\rangle - \langle I\rangle^2}{\beta\langle I\rangle^2} = \left[\frac{\sum_{k=1}^{N} M_k c_k P_k(\theta)\exp(-\Gamma_k\tau)}{\sum_{k=1}^{N} M_k c_k P_k(\theta)}\right]^2 \quad (11)$$

where $I(0)$ and $I(\tau)$ are the scattered light intensity at angle θ at $t = 0$ and $t = \tau$, respectively; $\langle\ \rangle$ refers to a statistical ensemble average; M_k, c_k, and P_k are the molecular weight, concentration, and Debye function for species k, respectively; Γ_k is the spectral line width, which is equal to $D_k q^2$ (D_k being the diffusivity of species k and q the scattering wave vector, defined later); and β is a machine parameter to account for detection system inefficiencies and geometrical effects. The sum over all molecular weights can be converted to an integral over all possible line widths:[12]

$$\frac{\langle I(0)I(\tau)\rangle - \langle I\rangle^2}{\beta\langle I\rangle^2} = \left[\frac{\int_0^\infty f(\Gamma(M),c,\theta)\exp(-\Gamma\tau)\,\mathrm{d}\Gamma}{\int_0^\infty f(\Gamma(M),c,\theta)\,\mathrm{d}\Gamma}\right]^2 \quad (12)$$

where $f(\Gamma,c,\theta)$ is the distribution function describing the dependence of the scattered light intensity on molecular weight (implicitly through Γ), concentration, and scattering angle. To simplify this expression, we define the normalized autocorrelation function as follows:

$$Z = \frac{\langle I(0)I(\tau)\rangle - \langle I\rangle^2}{\beta\langle I\rangle^2} \quad (13)$$

Following the formalism of the method of cumulants, we expand the logarithm of Z in a power series in the delay time τ to give

$$\begin{aligned}\ln(Z(\tau)) &= \\ \ln(Z(0)) &+ \left.\frac{\partial \ln(Z)}{\partial\tau}\right|_{\tau=0}\tau + \frac{1}{2!}\left.\frac{\partial^2 \ln(Z)}{\partial\tau^2}\right|_{\tau=0}\tau^2 + \ldots \\ &= -2\langle\Gamma\rangle\tau + 2[\langle\Gamma^2\rangle - \langle\Gamma\rangle^2]\tau^2 + \ldots \quad (14)\end{aligned}$$

Experimental correlation functions were fit with a nonlinear regression algorithm to eq 14. We used second-order cumulants (keeping terms up to order τ^2) for interpreting the correlation functions. From this procedure, we obtain an estimate of the average line width, $\langle\Gamma\rangle$, and the variance about this linewidth ($\langle\Gamma^2\rangle - \langle\Gamma\rangle^2$).

Several special features of this analysis pertaining to our high-pressure systems are outlined below. From dynamic light scattering experiments we measure the average spectral line width $\langle\Gamma\rangle$, which is related to the averaged mutual diffusion coefficient $\langle D\rangle$ as follows:

$$\langle\Gamma\rangle = \langle D\rangle q^2 \quad (15)$$

As before, q is the scattered wave vector, defined by

$$q \equiv \frac{4\pi n}{\lambda_0}\sin(\theta/2) \quad (16)$$

where λ_0 is the wavelength of the incident radiation in vacuum, n is the solution refractive index, and θ is the scattering angle. Both the polymer concentration and the solution refractive index vary with pressure, and these effects must be accounted for when analyzing the data.

The polymer concentration is given by the following expression:

$$c = \frac{1}{\dfrac{\omega_1}{\rho_1(1-\omega_1)} + \bar{v}_2{}^*} \quad (17)$$

where ω_1 and ρ_1 are the solvent mass fraction and density, respectively, $\bar{v}_2{}^*$ is the apparent partial specific volume of the polymer in the solution, and c is the polymer concentration (kg/m^3 solution). Equation 17 is obtained from the following definition of the polymer apparent partial specific volume:[13]

$$v_{\mathrm{soln}} = \frac{\omega_1}{\rho_1} + (1-\omega_1)\bar{v}_2{}^* = \frac{1-\omega_1}{c} \quad (18)$$

where v_{soln} is the specific volume of the solution (m^3 of solution/kg of solution). The apparent partial specific volume is a convenient way to account for polymer solution non ideality. It is related to the partial specific volume of the polymer $\bar{v}_2$, as follows:[14]

$$\bar{v}_2 = \bar{v}_2{}^* + \omega_1\omega_2\left(\frac{\partial\bar{v}_2{}^*}{\partial\omega_2}\right)_{m_1} \quad (19)$$

where m_1 is the mass of solvent in the mixture and ω_2 is the polymer mass fraction. The apparent partial specific volume of the polymer is used in these expressions for polymer concentration because, historically, when volumetric properties of polymer solutions were measured, $\bar{v}_2{}^*$, and not $\bar{v}_2$, was the quantity calculated from the experimental data.

To use eq 17 to calculate the change in polymer concentration with pressure, one needs data for the solvent density and the polymer apparent partial specific volume as functions of pressure. These data are available for the polystyrene/toluene system. Easteal and Woolf[15] measured the density of toluene as a function of temperature and pressure, and Andersson[14] measured the apparent partial specific volume of polystyrene in toluene solutions as a function of pressure at polymer concentrations of up to 2.5% by weight. Andersson found no effect of molecular weight or concentration on the apparent partial specific volume of 23 polymers in various solvents. Since the apparent partial specific volume of the polymer is independent of polymer concentration for the system under study here, eq 19 shows that the polymer partial specific volume is equal to the apparent partial specific volume.

Using literature values for the pressure dependence of the toluene density, we calculate that over the concentration range studied in our experiments the concentration of polymer can change by as much as 6.5% over the pressure range of interest. As discussed below, this magnitude of concentration change has little effect on the refractive index of the solution. It is nevertheless important because the diffusion coefficient is sensitive to concentration as shown in eq 9, and a 6.5% change in concentration can cause a discernible change in the mutual diffusion coefficient.

To calculate the scattering wave vector at high pressures (eq 16), one must know the pressure dependence of the solution refractive index. The polymer solution refractive index increases with pressure because the solvent is being compressed, which causes the solvent refractive index to rise and the polymer concentration to increase. In the concentration and pressure ranges used in this work, the change in the solution refractive index is dominated by the change in the refractive index of the solvent due to compression. We therefore use the following Taylor series expansion starting from atmospheric pressure and pure solvent to compute the solution refractive index as a function of pressure and concentration:

$$n(P,c) = n(P_a,0) + \left(\frac{\partial n}{\partial c}\right)_{P_a,0} c + [n_{solv}(P) - n_{solv}(P_a)] + O[c(P-P_a),c^2] \quad (20)$$

where n_{solv} is the solvent refractive index and P_a is atmospheric pressure (0.1 MPa). The refractive index of pure toluene as a function of pressure is available from the work of Vedam and Limsuwan.[16] As an example, eq 20 predicts a solution refractive index change of 2.6% over the pressure range studied (at a polymer concentration of 25.5 kg/m^3). Of this 2.6% change, 99.7% is due to the change in the solvent refractive index with pressure and the remaining 0.3% comes from the change in the polymer concentration.[16]

Results and Discussion

Low-Pressure Data. To confirm the validity of our experimental technique, we measured the concentration dependence of the diffusion coefficient of a polymer solution for which literature data exist. The polymer was Toyo Soda F-20 linear polystyrene with $M_w = 1.84 \times 10^5$ kg/(kg·mol) and $M_w/M_n = 1.07$. The measurements were made in toluene at 25 °C. Autocorrelation functions were determined at five different angles (from 30° to 150°) at a fixed concentration. The line widths were plotted against q^2, and the resulting slope gave the diffusion coefficient at that concentration. This procedure was repeated for several concentrations. The resulting plot of diffusion coefficient versus polymer concentration is shown in Figure 1. In agreement with theory (eq 9) and other works cited below, we find the diffusion coefficient to be a linear function of polymer concentration. Table I compares our results to the light scattering work of Han[17] and the gradient diffusion results of Meyerhoff.[18] Note that k_d should be nearly independent of temperature since toluene is a good solvent for polystyrene, but D_0 will be a function of temperature and molecular weight. If we adjust the infinite dilution values of the diffusion coefficients in Table I to the same conditions (25 °C and $M_w = 1.84 \times 10^5$ kg/(kg·mol)) in the manner suggested by eq 6, using the scaling result that $R_H \propto M_w^{0.53}$,[19] and the temperature variation of the viscosity of toluene from ref 20, we find the following: $D_0 \times 10^{11}$ (m^2/s) = 3.68 ± 0.02 (this work), 3.58 ± 0.25 (Han), and 3.38 (Meyerhoff).

At this point, we should mention that our data are likely to be affected by photomultiplier tube afterpulsing.[10] This effect can increase the diffusion coefficients obtained from the nonlinear regressions on the autocorrelation functions by as much as 5%. However, the trend is systematic throughout the data. Therefore, our D_0 values may be 5% larger than the actual values, but k_d should be unaffected. The uncertainties reported for D_0 and k_d are from the least-squares regression of the concentration dependence of the diffusion coefficient. These uncertainties do not reflect any possible systematic errors associated with afterpulsing. In the high-pressure measurements to be discussed shortly, we are concerned with ratios of diffusion coefficients at elevated pressures to those at atmospheric pressure. These ratios are, within the precision of the measurement, unaffected by the afterpulsing effect.

Atmospheric measurements of the concentration dependence of the diffusion coefficient of a higher molecular weight polymer were also made. This polymer was Toyo Soda F-80 linear polystyrene, with $M_w = 7.06 \times 10^5$ kg/(kg·mol) and $M_w/M_n = 1.05$. Figure 1 shows the concentration dependence of the diffusion coefficient at 25 °C. In accord with the results for the lower molecular weight polymer, we find a linear relationship between diffusivity and concentration over the range studied. From theory, one expects the infinite dilution diffusion coefficient to exhibit power law behavior with molecular weight.

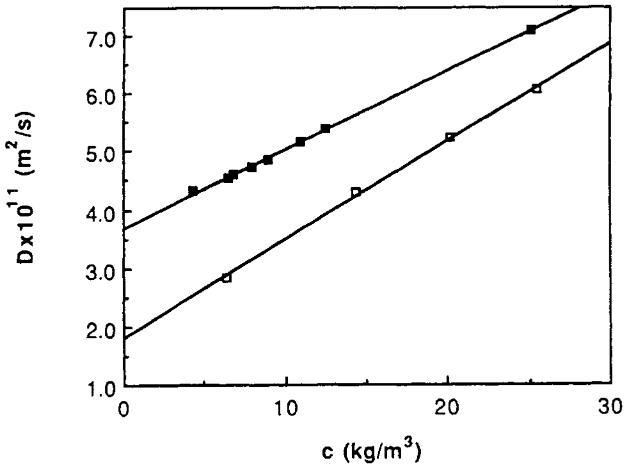

Figure 1. Concentration dependence of mutual diffusion coefficient at atmospheric pressure for polystyrene in toluene (T = 25 °C). Filled symbols represent data of $M_w = 1.84 \times 10^5$ kg/(kg·mol), while open symbols represent data of $M_w = 7.06 \times 10^5$ kg/(kg·mol).

Table I
Low-Pressure Data Comparison

	this study	Han	Meyerhoff
$10^{-5}M_w$, kg/(kg·mol)	1.84	1.79	1.40
T, °C	25	23	20
$10^{11}D_0$, m^2/s	3.68 ± 0.02	3.59 ± 0.25	3.69
10^3k_d, m^3/kg	36.7 ± 0.8	24 ± 21	29

Table II
Literature Values for Power Law Exponent Relating Infinite Dilution Mutual Diffusion Coefficient to Weight-Average Molecular Weight of Linear Polystyrene Dissolved in Good Solvents

exponent	group
0.53 ± 0.03	this study
0.53 ± 0.02	Wiltzius et al.[19]
0.55 ± 0.02	Adam and Delsanti[21]
0.55 ± 0.02	Weill and desCloizeaux[22]
0.54	Mukherjea and Rempp (gradient technique)[23]
0.564 ± 0.004	Mandema and Zeldenrust (polystyrene in tetrahydrofuran)[24]

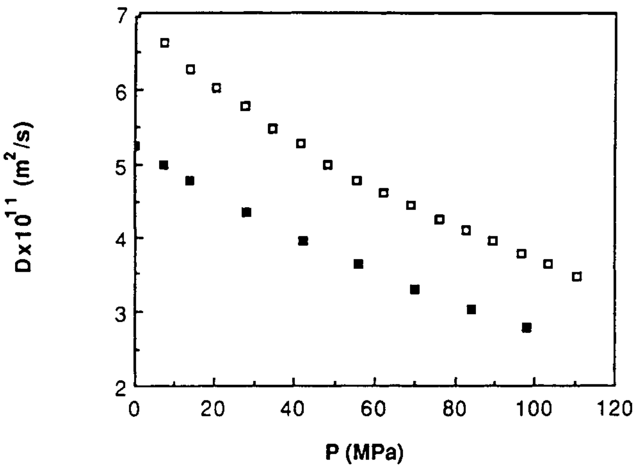

Figure 2. Pressure dependence of mutual diffusion coefficient for polystyrene in toluene (M_w = 1.84 × 10^5 kg/(kg·mol); T = 25 °C). Filled and open symbols represent data at polymer concentrations of 12.0 and 25.2 kg/m^3, respectively.

The theoretical power law exponent is −0.55. The slope of −0.53 ± 0.03 based on our two samples agrees with the theoretical result and also compares favorably with the results of other researchers, as shown in Table II.

Wiltzius et al.[19] also give results for the change in k_d with molecular weight. They find power law behavior, with a power law exponent of 0.99 ± 0.05. Our data give a slope of 0.70 ± 0.07. The source of the discrepancy is unknown. Berry[25] has measured the second virial coefficient for a series of linear polystyrenes of different molecular weight in solution in toluene, and his data show a power law dependence between the second virial coefficient and M_w with an exponent of 0.75 ± 0.03. From eq 7 and 9 of the theory of Oono,[6] one expects the second virial coefficient to be equal to approximately $0.74k_d$ in a good solvent. If there is a power law dependence between the second virial coefficient and molecular weight, one would therefore expect that the same power law exponent applies to the molecular weight dependence of k_d. From scaling[19] and renormalization group theory,[26] one expects the second osmotic virial coefficient to be proportional to $M_w^{0.80}$ and $M_w^{0.65}$, respectively, in a good solvent. In this sense, our measured slope of 0.70 ± 0.07 is in good agreement with the results of Berry and in accord with the theory. However, comparing our results for k_d with B_2 by Berry, we find that $B_2 \approx 2k_d$.

High-Pressure Data. Mutual diffusion coefficients were measured as a function of pressure and concentration. Figure 2 shows the pressure dependence of the diffusion coefficient of the lower molecular weight polymer at two concentrations.

The earlier theoretical discussion indicated that the system thermodynamics do not change appreciably with pressure; i.e., B_2 and k_d are independent of pressure (see eq 8 and 10). Therefore, the mutual diffusion coefficient should depend on hydrostatic pressure through the change in D_0 and polymer concentration with pressure by

$$D(c(P),P) = D_0(P)[1 + k_d c(P)] \qquad (21)$$

To interpret the high-pressure diffusion coefficient measurements, it is convenient to work with the ratio of the diffusivity at pressure P to that at atmospheric pressure P_a

$$\frac{D(c(P),P)}{D(c(P_a),P_a)} = \frac{D_0(P)}{D_0(P_a)}\,\frac{[1 + k_d c(P)]}{[1 + k_d c(P_a)]} \qquad (22)$$

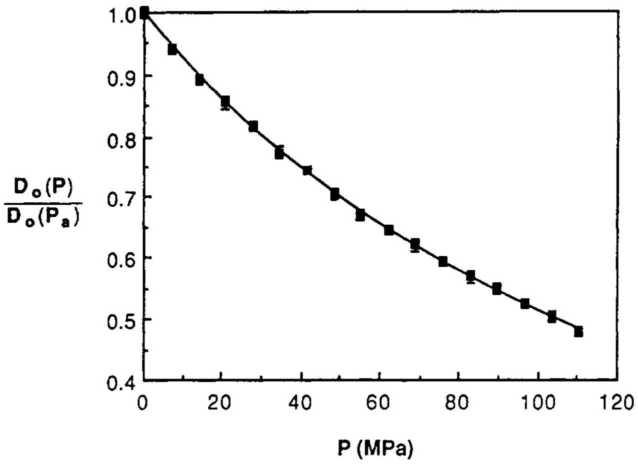

Figure 3. Comparison of relative diffusion coefficient to solvent fluidity. Solid curve is relative fluidity of toluene from Kashiwagi and Makita.[27] Points are experimental results for M_w = 1.84 × 10^5 kg/(kg·mol), T = 25 °C, and concentration = 25.2 kg/m^3.

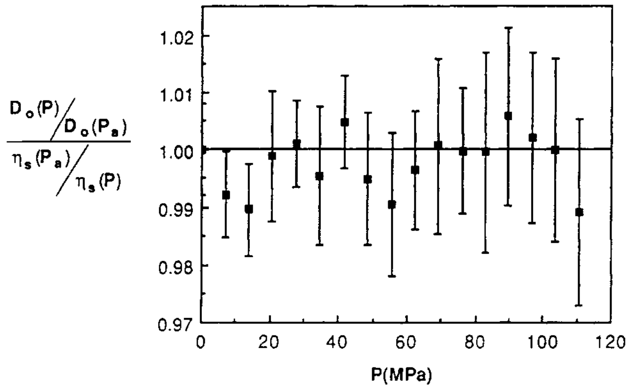

Figure 4. Deviation of relative infinite dilution diffusion coefficient from toluene fluidity for polystyrene in toluene (M_w = 1.84 × 10^5 kg/(kg·mol); T = 25 °C; concentration = 25.2 kg/m^3).

which can be rearranged to give

$$\frac{D(c(P),P)}{D(c(P_a),P_a)}\,\frac{[1 + k_d c(P_a)]}{[1 + k_d c(P)]} = \frac{D_0(P)}{D_0(P_a)} = \frac{\eta_s(P_a)}{\eta_s(P)} \qquad (23)$$

If the theory and its extension to high pressure are correct, then a plot of the left-hand side of eq 23 against pressure should coincide with the curve of the relative solvent fluidity, $\eta_s(P_a)/\eta_s(P)$, versus pressure. Figure 3 shows a set of data plotted in this manner, where the solid curve is the relative fluidity of toluene. To show the comparison quantitatively, Figure 4 gives the deviation of the ratio of the infinite dilution diffusion coefficients from the relative fluidity. Measurements on the same polymer at half the concentration reveal the same effect. Since the error bars on the relative diffusivities are about 1%, there is no significant change in $D(P)$ beyond the concentration and fluidity effects. This result is in agreement with current theory and with the results of Roots and Nyström[9] on the same system.

The above conclusion is significant in view of the vast amount of literature data required to reach it. We repeat here the information needed to convert the measured line widths as functions of angle, concentration, and pressure into mutual diffusion coefficients. The pressure dependences of the toluene fluidity and refractive index are from Kashiwagi and Makita[27] and Vedam et al.,[16] respectively. The refractive index increment of polystyrene in toluene is available from Hadjichristidis and

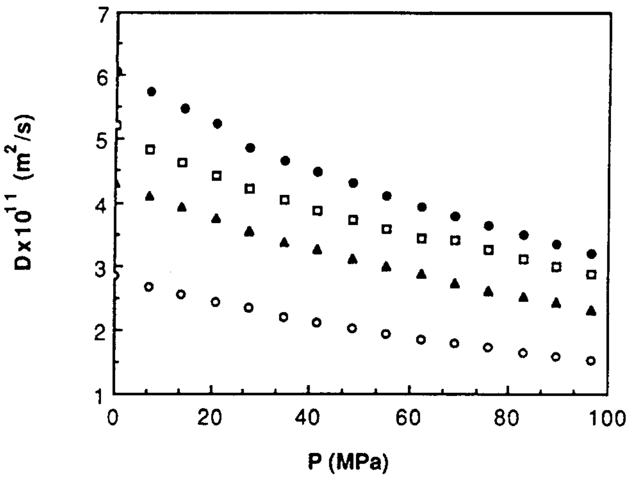

Figure 5. Pressure dependence of mutual diffusion coefficient for polystyrene in toluene at four concentrations (M_w = 7.06 × 10^5 kg/(kg·mol); T = 25 °C): ●, 25; □, 20.2; ▲, 14.4; ○, 6.4 (units are kg of polymer/m^3).

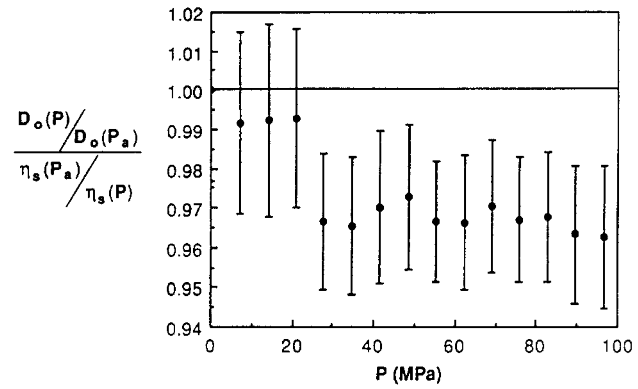

Figure 6. Deviation of relative infinite dilution diffusion coefficients from toluene fluidity. System studied is polystyrene in toluene (M_w = 7.06 × 10^5 kg/(kg·mol); T = 25 °C; concentration = 25.5 kg/m^3).

Fetters,[28] Candau and Benoit,[29] and Binboga and Kisakürek;[30] the variation in the refractive index of toluene with wavelength is from Johnson and Smith;[21] the effect of pressure on toluene density is from Easteal and Woolf;[15] and the effect of pressure on the partial specific volume of polystyrene is from Andersson.[14] After all of this information is adopted to convert the measurements into a form which can be compared to theory, we are pleased to find that the experimental results are in very close agreement with the current theory. This discussion, however, points out a weakness of the light scattering technique for mobility determination at high pressures: a large amount of physical property data are needed to interpret the results.

High-pressure measurements were also made on the 7.06 × 10^5 M_w polystyrene (Toyo Soda F-80). Figure 5 shows the pressure dependence of the mutual diffusion coefficient for several concentrations. As with the lower molecular weight sample, there is a difference in the change of the diffusion coefficient with pressure at the different concentrations, which is again caused by the stronger dependence of the concentration on pressure at higher concentrations. Careful analysis following the procedure illustrated by Figures 3 and 4 reveals an interesting feature. The lower concentration data at 6.4 and 14.4 kg/m^3 track the solvent fluidity, as in the case of the lower molecular weight experiments. At higher concentrations, however, a systematic deviation from the postulated correspondence of pressure dependence of the mutual diffusion coefficient with solvent fluidity appears. This behavior is illustrated in Figure 6. At the higher concentrations and pressures for this polymer, the data show a clear deviation which is in the same direction for both concentrations (one not shown): the infinite dilution diffusion coefficient changes more rapidly with pressure than would be predicted on the basis of the solvent fluidity and concentration variation alone. The source of this discrepancy is unclear, but the trend is in the same direction as that observed for the pressure dependence of the polymer solution viscosity. Geerissen et al.[32] and Claesson et al.[33] both observed, in a wide variety of different polymers and solvents, that the polymer solution viscosity increased more with pressure than the solvent viscosity. In addition, Claesson et al. observed that, in the case of polystyrene in toluene, the polymer solution viscosity changed more rapidly with pressure as the polymer concentration increased. The solution viscosity change, however, is much greater than that observed for the mutual diffusivity.

Conclusions

Mutual diffusion coefficients for the system polystyrene in toluene were measured by means of dynamic light scattering as a function of applied hydrostatic pressure. For low concentrations and low molecular weight, the pressure dependence of the mutual diffusion coefficient mirrors that of the solvent fluidity once the effect of concentration change with pressure is accounted for. This result is in agreement with recent polymer diffusion theory and available experimental data. At higher concentrations and molecular weights, a small systematic deviation of the mutual diffusion coefficient from the solvent fluidity is observed. When these discrepancies occur, the diffusion coefficient always changes faster with pressure than the solvent fluidity. This result is not predicted by the current theories; the direction of the deviation of the diffusion coefficient with pressure is consistent, however, with that observed in the polymer solution fluidity.

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Registry No. Polystyrene, 9003-53-6; toluene, 108-88-3.

References and Notes

(1) Bearman, R. J. *J. Chem. Phys.* **1960**, *32*(5), 1308.
(2) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.
(3) deGennes, P. G. In *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1976; p 175.
(4) deGennes, P. G. In *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1976; p 36.
(5) Flory, P. In *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(6) Oono, Y.; Baldwin, P. R.; Ohta, T. *Phys. Rev. Lett.* **1984**, *53*(22), 2149.
(7) Schulz, G. V.; Lechner, M. Influence of Pressure and Temperature. In *Light Scattering From Polymer Solutions*; Huglin, M. B., Ed.; Academic Press: New York, 1972; p 503.
(8) McDonald, C. J.; Claesson, S. *Chem. Scr.* **1976**, *9*, 36.
(9) Roots, J.; Nyström, B. *Macromolecules* **1982**, *15*, 553.
(10) Freeman, B. D. Ph.D. Thesis, University of California, Berkeley, Dec 1987.
(11) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*(11), 4814.
(12) Caroline, D. *Polymer* **1981**, *23*, 492.

(13) Ende, H. A. Sedimentation Constants, Diffusion Constants, Partial Specific Volumes, Frictional Ratios and Second Virial Coefficients of Polymers in Solution. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1966; p IV-78.
(14) Andersson, G. R. *Ark. Kemi* **1963**, *20*(39), 513.
(15) Easteal, A. J.; Woolf, L. A. *Int. J. Thermophys.* **1985**, *6*(4), 331.
(16) Vedam, K.; Limsuwan, P. *J. Chem. Phys.* **1978**, *69*(11), 4762.
(17) Han, C. C.; Akcasu, A. Z. *Polymer* **1981**, *22*, 1165.
(18) Meyerhoff, G.; Nachtigall, K. *J. Polym. Sci.* **1962**, *57*, 227.
(19) Wiltzius, P.; Haller, H. R.; Cannell, D. S. *Phys. Rev. Lett.* **1984**, *53*(8), 834.
(20) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, 1979; p F-57.
(21) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*(6), 1229.
(22) Weill, G.; desCloizeaux, J. *J. Phys. (Les Ulis, Fr.)* **1979**, *40*, 99.
(23) Kuherjea, R. N.; Rempp, P. *J. Chim. Phys. Phys.-Chim. Biol.* **1959**, *56*, 94.
(24) Mandema, W.; Zeldenrust, H. *Polymer* **1977**, *18*, 835.
(25) Berry, G. C. *J. Chem. Phys.* **1966**, *44*(12), 4550.
(26) Oono, Y.; Freed, K. F. *J. Phys. A: Math. Gen.* **1982**, *15*, 1931.
(27) Kashiwagi, H.; Makita, T. *Int. J. Thermophys.* **1982**, *3*(4), 289.
(28) Hadjichristidis, N.; Fetters, L. J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2163.
(29) Candau, F.; François, J.; Benoit, H. *Polymer* **1974**, *15*, 626.
(30) Binboga, N.; Kisakürek, D. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 925.
(31) Johnson, B. L.; Smith, J. Refractive Indices and Densities of Some Common Polymer Solvents. In *Light Scattering From Polymer Solutions*; Huglin, M. B., Ed.; Academic Press: New York, 1972; p 27.
(32) Geerissen, H.; Schmidt, J. R.; Wolf, B. A. *J. Appl. Polym. Sci.* **1982**, *27*, 1277.
(33) Claesson, S.; McAtee, J. L., Jr.; Ali, S. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1873.

Hydrophobic Microphase Formation in Surfactant Solutions Containing an Amphiphilic Graft Copolymer

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ABSTRACT: Strong association between the hydrophobic side chains on water-insoluble C$_{12}$-grafted hydroxyethyl cellulose and sodium dodecyl sulfate in aqueous solution is reported. This association gives rise to viscoelastic solutions and hydrogels with dispersed hydrophobic microdomains, indicating that intermolecular surfactant bridges are linking alkyl chains from more than one macromolecule. The solutions were characterized using conductivity, viscosity, and pyrene fluorescence measurements.

Introduction

Considerable effort has been devoted toward understanding the bulk and microscopic properties of aqueous solutions containing surfactants and water-soluble polymers. This work has made use of a variety of experimental techniques including neutron scattering,[1] NMR,[2] fluorescence spectroscopy,[3-5] dye solubilization,[5,6] viscosity,[6,7] and ESR spin probe techniques[8] and has focused on determining the types of structures that form as a result of interactions between the polymer segments and the surfactant molecules. Both polymer/surfactant interactions and self-aggregation of surface-active copolymers have been studied.

Results on water-soluble homopolymers like poly(ethylene oxide)[1-4] and poly(vinylpyrrolidone)[3,9-12] in sodium dodecyl sulfate (SDS) indicate that initially surfactant molecules prefer to adsorb onto the polymer chain rather than aggregate into micelles. These interactions occur on uniform hydrophilic polymer backbones where there is no preferred site for adsorption. The adsorbed surfactant aggregates have aggregation numbers reported to be 30–50% lower than pure surfactant micelles,[4] but which in fact increase with increasing total surfactant concentration. Beyond a certain concentration of the surfactant that is higher than the critical micelle concentration (cmc), the system favors aggregation of any additional surfactant molecules into free micelles. This transition occurs because Coulombic repulsion among the adsorbed surfactant aggregates precludes any additional adsorption on the polymer.[1]

With water-soluble surface-active copolymers in pure water, self-aggregation has been observed that is reminiscent of the process of micellization in monomeric surfactants. The formation of these aggregates depends on the free energies of the hydrophilic and hydrophobic groups in water. Self-aggregation has been demonstrated using water-soluble copolymers composed of long chain alkenes alternating with maleic anhydride (poly(1-alkene-*co*-(maleic anhydride))).[13-16] They form structures described as polymeric micelles, with "aggregation numbers" comparable to those of surfactants with the same alkyl groups in certain concentration regimes. These polymeric aggregates may form either intra- or intermolecularly depending on the length of the hydrophobic side chains and the flexibility of the polymer, as governed in this case by the charge density of its backbone. Also, the shape of the resulting aggregates has been shown to vary with side chain length.[15]

The present study is an investigation of the properties of water-insoluble surface-active copolymers in aqueous surfactant solutions. We have investigated the properties of a hydrophobically modified water-soluble polymer to determine the effects of alkyl grafts on the asso-

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