Shear Viscosity and Mass Density near the Liquid–Liquid Critical Point of Polystyrene in Diethyl Malonate

K. Gruner,[†] S. Habib,[‡] and S. C. Greer[*]

Department of Chemistry and Biochemistry, The University of Maryland at College Park, College Park, Maryland 20742.
Received April 21, 1989; Revised Manuscript Received July 10, 1989

ABSTRACT: We report new measurements of the shear viscosity and of the mass density as functions of temperature at the composition of the upper critical solution point for a mixture of polystyrene in diethyl malonate. The viscosity measurements have a precision of 0.04–0.4% and are over a temperature range of 91 K. The viscosity increases by an order of magnitude from the highest temperature to near the critical temperature. However, the analysis of the data is complicated by strong effects of shear near the critical temperature and by our lack of understanding of the behavior of the noncritical background viscosity of a polymer solution. We are unable to construct a function to describe the shear viscosity as a function of temperature. The mass density of this mixture is simply linear over the same temperature range.

Introduction

Shear Viscosity. The shear viscosity as a function of temperature of a binary liquid mixture near a liquid–liquid critical point exhibits a divergence as the critical point as approached. That divergence has been studied by theoreticians and by experimentalists for many years.[1] Theoreticians now predict that the shear viscosity at constant pressure and composition will have the functional form[2-4]

$$\eta(t) = \eta_B(t)At^{-y} \quad (1)$$

Here η is the total shear viscosity at the critical composition. $\eta_B(t)$ is the background, noncritical and nondivergent, part of the shear viscosity. The temperature dependence is indicated by t, which is the reduced temperature $(T - T_c)/T_c$, where T_c is the critical temperature.

The factor At^{-y} is the critical part of the shear viscosity, where A is the coefficient. The theoretical calculation of the critical exponent y has been controversial.[1] Calculations by both dynamic renormalization group theory and mode–mode coupling theory seem, at present, to be reconciled at $y = 0.032$.[5] In order to compare the experimental data with this prediction, corrections must be made for nonzero values of the shear[6-9] and the frequency[10] in the actual experiments. We shall discuss these corrections below.

Twenty-seven previous experimental studies of the viscosity at the liquid–liquid critical points in 12 different mixtures have been listed by Gruner.[11] Her study and that of Sengers[1] show the considerable (about 50%) scatter in the values of y reported over the last 25 years. This scatter can be attributed to uncertainties in η_B and to systematic errors due to shear and frequency effects. The most reliable experimental evidence is in the recent papers of Berg and Moldover[12] and Nieuwoudt and Sengers.[13] Berg and Moldover measured the shear viscosity in four liquid mixtures and analyzed the data to determine y, carefully correcting for shear and frequency effects and investigating the effects of the background viscosity. They concluded that $0.0404 < y < 0.0444$, which is not in agreement with the theoretical value of 0.032.[5] Nieuwoudt and Sengers reanalyzed data from the literature on seven binary liquid mixtures, with the same considerations made by Berg and Moldover, and concluded that y is close to 0.041, again differing with the theory.

Critical fluctuations in polymer solutions are larger and live longer than do fluctuations in solutions of small molecules. For example, at $t = 10^{-3}$, for polystyrene in diethyl malonate, the average size of the fluctuation is 78 nm[14] and the average lifetime is 0.1 s,[15] whereas in nitroethane + 3-methylpentane, the size is 18 nm[16] and the lifetime is 10^{-5} s.[17] These differences in the fluctuations will affect the amplitudes of phenomena near the critical point but are not expected to change the universality class, thus not changing the critical exponents. Neither Berg and Moldover nor Nieuwoudt and Sengers studied the viscosity of a mixture of a polymer in a solvent. A critical mixture of poly(dimethylsiloxane)–diethyl carbonate was studied by Hamano et al.,[18] who measured the shear viscosity in a capillary flow viscometer in the range $3.25 \times 10^{-6} < t < 4.64 \times 10^{-2}$; assuming an Arrhenius behavior for η_B and correcting for the shear, they deduced $y = 0.033 \pm 0.001$, in agreement with the theory. Izumi et al.[19] measured the shear viscosity of polystyrene–cyclohexane with a capillary viscometer; assuming a Vogel equation for η_B and correcting for the shear, they obtained $y = 0.029 \pm 0.003$, in agreement with the theory.

We report here new measurements of the shear viscosity of a critical mixture of polystyrene (of molecular weight 1.02×10^5) in diethyl malonate. These measurements are precise (0.04–0.4%) and cover the largest range in temperature ($2.18 \times 10^{-5} < t < 0.3321$) of any such measurements reported to date. The analysis of the data is very complicated. Near T_c, the effects on the viscosity due to shear are larger than ever before observed for a critical mixture. Away from T_c, the analytical "background" behavior of the viscosity cannot be described over the entire range of the data by any of the commonly used empirical functions. We have been unable to construct a function to describe the behavior of the shear viscosity of polystyrene in diethyl malonate. Consequently, we have been unable to extract a value for the critical exponent for the shear viscosity.

Mass Density. We also measured the mass density of this mixture in order to convert the measured kine-

---

[*] To whom correspondence should be addressed.

[†] Present address: Department of Physiology, The University of Maryland School of Medicine, 660 W. Redwood St., Baltimore, MD 21201.

[‡] Present address: Department of Physics, The University of British Columbia, 6224 Agricultural Rd., Vancouver, BC, Canada V6T2A6.

0024-9297/90/2223-0510$02.50/0

matic viscosity into the required shear viscosity. The mass density is itself expected to exhibit a critical anomaly of the form[20]

$$\rho\ (\mathrm{g/cm^3}) = R_1 + R_2 t + R_3 t^{1-\alpha} \qquad (2)$$

where the R_i are constants that depend upon the system and the critical exponent α is calculated to be 0.11.[21] We had measured the mass density previously but over a temperature range too small for present purposes.[22] We find no evidence of a critical anomaly in the density for this system within our resolution of $1/10^4$, even over the larger temperature range ($5.3 \times 10^{-4} < t < 0.287$). This confirms our earlier report[22] that the density for this system is simply linear in temperature.

Experimental Methods

Earlier Experiments. In our laboratory we have previously studied the density (in the range $1.1 \times 10^{-4} < |t| < 6.7 \times 10^{-2}$ above T_c and $7 \times 10^{-6} < |t| < 8 \times 10^{-4}$ below T_c)[22] and the dielectric constant[23] (above and below T_c) for polystyrene in diethyl malonate. Hamano et al. have used light scattering to study the osmotic compressibility and the correlation length[24-26] in this system, as have Stafford et al.[14] Fenner has studied the ultrasonic absorption[27] and the kinetics of phase separation.[28]

Sample Preparation. As discussed in our previous publications,[22,23] the critical temperature for polystyrene in diethyl malonate is extremely sensitive to water as an impurity. Thus our sample preparation involved taking care to exclude water.

Polystyrene was obtained from Toya Soda Manufacturing Co.[29] with a molecular weight of 1.02×10^5 and a ratio of weight-average to number-average molecular weight of 1.02. The polystyrene was dried in a vacuum oven at 318 K (45 °C) for 14 days.

Diethyl malonate was obtained from Aldrich Chemical Co. and was specified to be 99% pure. Additional purification to remove the acids formed by hydrolysis of the ester was done by extracting with 5% aqueous potassium hydroxide. The diethyl malonate was then extracted with distilled water to remove the potassium hydroxide, shaken with anhydrous sodium sulfate to remove most of the residual water, and filtered to remove particulates. The purified diethyl malonate was stored over molecular seive to dry it further.

The samples were prepared in a conventional drybox under a nitrogen atmosphere. All glassware and implements and the viscometer (see below) were dried in the vacuum oven at 423 K (150 °C) for 3 days before being placed in the drybox. Plastic caps, Teflon parts, and O-rings were dried in the vacuum oven for 3 days at 323 K (50 °C), then moved to the drybox. The dilatometer (see below) was heated under vacuum with a heat gun for an hour, left under vacuum for 24 h, and then placed in the drybox.

The composition of our mixture of polystyrene (molecular weight 1.02×10^5) in diethyl malonate was 9.473 wt % polystyrene. The menisci formed at the middles of our samples, indicating that they were very near the critical composition.

The same sample mixture was used to fill both the dilatometer and the viscometer. The samples in the viscometer and in the dilatometer were degassed by freezing with liquid nitrogen, pumping off residual gases, remelting, and repeating the process four times. The samples were thus sealed under their vapor pressures. The critical temperature was determined for each sample independently, because of the extreme sensitivity of T_c to trace moisture. We were not able to use the appearance of a meniscus as the indication of T_c because the phase separation times were so very long (weeks). For the dilatometer, T_c was taken as the temperature at which the sample appearance changed to "grainy"; this occurred at 277.505 ± 0.003 K (4.355 °C). For the viscometer, T_c was taken as the temperature at which inhomogeneities were visible when the sample was slightly perturbed by tilting; this occurred at 275.202 ± 0.004 K (2.052 °C). Since moisture makes the polystyrene less miscible in the diethyl malonate, the lower T_c indicates the drier sample. These values for T_c are comparable to those reported previously.[22,23] In fact, the T_c for the viscometer sample is the lowest T_c reported for this system, and therefore it is the driest sample studied. In any case, such small amounts of impurity do not affect the universal critical properties.[30,31]

Table I
Shear Viscosity, η, as a Function of Temperature, T, for 9.473 wt % Polystyrene (Molecular Weight 1.02×10^5) in Diethyl Malonate[a]

point	T, K	σ_T, K	η, mPa/s	run
1	366.6	0.1	5.33	1
2	363.01	0.01	5.62	1
3	362.97	0.02	5.61	1
4	358.39	0.04	6.02	1
5	358.43	0.02	6.09	1
6	353.99	0.01	6.38	1
7	347.79	0.01	7.07	1
8	347.82	0.01	7.02	1
9	343.33	0.02	7.55	1
10	343.36	0.02	7.60	1
11	338.342	0.005	8.16	1
12	338.342	0.005	8.17	1
13	333.649	0.005	8.87	1
14	328.531	0.003	9.83	1
15	323.755	0.004	10.69	1
16	318.385	0.002	11.92	1
17	313.422	0.004	13.28	1
18	308.312	0.002	15.02	1
19	303.653	0.004	16.77	1
20	298.249	0.004	19.28	1
21	293.175	0.002	22.24	1
22	288.270	0.003	26.19	1
23	283.353	0.004	31.09	1
24	278.150	0.003	38.69	1
25	277.154	0.003	40.65	1
26	276.650	0.002	41.72	1
27	276.155	0.004	43.06	1
28	275.655	0.003	44.85	1
29	275.559	0.003	45.21	1
30	275.454	0.004	45.71	1
31	275.358	0.004	46.26	1
32	275.303	0.004	46.63	1
33	275.256	0.004	47.16	1
34	281.201	0.003	33.81	2
35	279.224	0.002	36.91	2
36	277.653	0.003	39.61	2
37	277.375	0.004	40.20	2
38	276.901	0.002	41.20	2
39	276.404	0.004	42.44	2
40	276.056	0.003	43.41	2
41	275.958	0.003	43.82	2
42	275.857	0.002	44.15	2
43	275.753	0.002	44.50	2
44	275.403	0.003	46.04	2
45	275.325	0.003	46.51	2
46	275.268	0.004	47.00	2
47	275.241	0.003	47.29	2
48	275.230	0.004	47.34	2
49	275.215	0.003	47.42	2
50	275.208	0.004	47.46	2
51	275.901	0.004	43.95	3
52	275.344	0.004	46.34	3
53	275.286	0.004	46.77	3

[a] The uncertainty in T is σ_T.

Temperature Measurement and Control. The dilatometer and the viscometer were held in a stirred water bath,[32] the temperature of which was controlled by an analog controller.[33] Usually the temperature was controlled to ±0.004 K; the variations were somewhat larger for the viscosity measurements at high temperatures, as shown in Table I. The temperature was measured with a digital platinum resistance thermometer;[34] this instrument could resolve to 0.001 K and was calibrated on the International Practical Temperature Scale of 1968 to 0.01 K.

Density Measurement. To complement the kinetic viscosity measurements, we need measurements of the mass density with at least the same resolution ($1/10^4$) and over the same temperature range (from the critical temperature to about 367 K (94 °C)). We had earlier measured the density of a sample of this mixture by using a magnetic densimeter, but the temperature

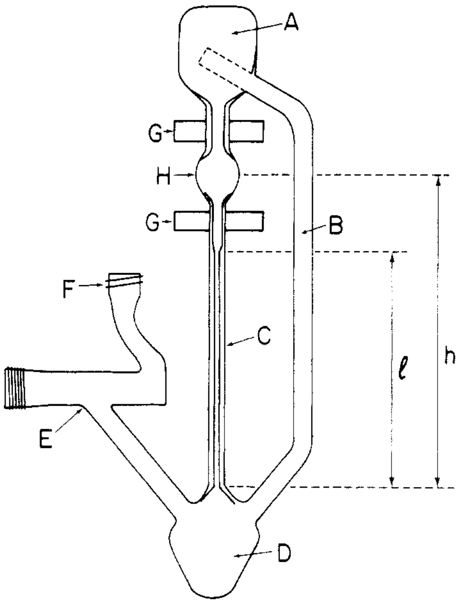

Figure 1. Viscometer. The material is quartz. The components are (A) upper reservoir, (B) side arm, (C) capillary tube (average radius = 0.0273 cm; variation at most 0.0005 cm), (D) lower reservoir, (E) seat for Teflon high-vacuum valve, (F) screw cap with Teflon-coated silicone liner, (G) meniscus sensor (see text), and (H) fiducial bulb. The length h is the average height of the sample and is 12.5 cm. The length of the capillary tube, l, is 9.75 cm.

limit of that instrument was about 333 K (60 °C). We chose to use a dilatometer to measure the mass density over a more extended range of temperature.

The dilatometer was of conventional design, with a syringe attached as an adjustable fluid reservoir. The details of its design, calibration, and filling are available in the dissertation of Gruner.[11] The final precision and accuracy of the density measurements are $1/10^4$.

Viscosity Measurement. The kinematic viscosity, ν, was measured with a capillary viscometer of the Ubbelohde type.[35] Ubbelohde viscometers have high precision and also high accuracy, since the design minimizes systematic errors due to surface tension at the ends of the capillary tube and due to changes of the sample density with temperature.[36] Our design is shown in Figure 1. Since our sample was very sensitive to moisture as an impurity, the viscometer had to be sealed completely. The valve on the viscometer allowed us to degas the sample and then to seal it tightly.

The time for the upper meniscus of the fluid to pass between the fiducial marks was measured to 0.01 s by using an automatic optoelectronic meniscus sensor developed by Habib and Gruner[37] especially for studying fluids for which the opacity changes greatly with temperature. The viscometer was calibrated over the viscosity range of our experiment by measuring the efflux times in two fluids for which the viscosities were known over a range of temperature.[38] We found from the calibration that the kinematic viscosity in the range of interest was directly proportional to the efflux time and required no kinetic energy correction,[39] within the calibration accuracy of 0.5%. Nor were any other corrections[36] made to the viscosity thus calculated, since any systematic errors are expected to be regular in nature and are thus absorbed into η_B in the data analysis.

To start a viscosity measurement, the viscometer was inverted so that the fluid ran into the upper reservoir through the side arm. The viscometer was righted slowly, allowing the fluid to run into the fiducial bulb with a minimum of agitation. Special care was taken to avoid trapping bubbles at the upper liquid–vapor meniscus and at the outlet of the capillary tube. The viscometer was always aligned vertically within 1° against an external mark. After the fiducial bulb was filled, the meniscus sensor was turned on and the flow time measured.

Flow times for this study varied from 250 s at the highest temperature to 3000 s at the lowest temperature. The shear viscosity, η, was calculated from the kinematic viscosity and the density: $\eta(T) = \nu(T)\rho(T)$. While the resolution in measuring the fall time was 0.01 s, the irreproducibility of the measurements from run to run was somewhat larger. We estimate the precision for η to be about 2×10^{-5} Pa s.

Procedures. The density measurements were made during three warming runs. At temperatures more than 11 K above T_c, an hour was allowed for equilibration after each temperature change. At 11 K above T_c, the fluid began to show critical opalescence. Within 11 K of T_c, 2 h were allowed for equilibration.

The viscosity measurements were made during three cooling runs. In the temperature range 275.404 K (2.253 °C) $< T <$ 281.201 K (8.051 °C), 30 min was allowed for equilibration at each temperature after the bath had stabilized before the viscosity was measured. Above 281.210 K, 15 min was allowed for equilibration. Below 275.404 K, 2 h was allowed for equilibration at each temperature. The three points in run 3 were allowed 12 h for equilibration.

Results and Analysis

Methods of Data Analysis. Various functions were tested as descriptions of the density and viscosity data by using a weighted nonlinear least-squares program.[40] The program uses the Marquardt method of optimizing the fit to the data.[41] Errors quoted include the errors due to correlations among fitted coefficients and are given as 99% confidence intervals.[41]

Mass Density. The density of the mixture was measured over the temperature range 277.653–357.270 K (4.503–84.120 °C; $5.3 \times 10^{-4} < t < 0.287$). We collected 68 points in three runs. The data lists are available.[11]

Equation 2 was fitted to the data, with and without the critical term. The entire data set could be described within an error of 0.01% by the first two terms of eq 2, which is just a straight line. There is thus no justification for a critical term. For the fitted equation for ρ in g/cm^3, $R_1 = 1.073\,67 + 0.000\,04$ and $R_2 = -0.2933 \pm 0.0006$.

This result is in excellent agreement with our earlier measurements of the density of this mixture over a smaller temperature range of only 17 K.[22] In that work, we found $R_1 = 1.070\,38 \pm 0.000\,03$ and $R_2 = -0.2933 \pm 0.0018$, for a sample of slightly different molecular weight polystyrene (1.07×10^6) and slightly different composition (9.469 wt % polystyrene).

Shear Viscosity. The kinematic viscosity of the mixture was measured in three runs over the temperature range 275.208–366.6 K (2.058–93.5 °C; $2.18 \times 10^{-5} < t <$ 0.3321). The conversion $\eta(T) = \rho(T)\nu(T)$ requires an extrapolation of the density equation for 9 K beyond the density measurements; this does not seem problematical, since the density is linear in temperature. The original kinematic viscosity measurements are available.[11]

The shear viscosity data are given in Table I. Figure 2a shows the shear viscosity as a function of temperature over the entire range of the data. The viscosity increases by an order of magnitude as T_c is approached from higher temperatures. By comparison, the increases seen in mixtures of small molecules are 10–50%. The analysis of these data in terms of eq 1 is not simple. There is a special problem near T_c, and there are other problems away from T_c.

The problem near T_c is that of the effect of the shear rate on the critical fluctuations. Early work on this issue was done by Botch and Fixman,[42] Sallavanti and Fixman,[43] and Oxtoby,[6] who pointed out that the shear would lead to a rounding off of the critical anomaly in the viscosity. Such a rounding off is easy to see for polystyrene + diethyl malonate in Figure 2b, where the data near T_c are plotted. Oxtoby[6] used a mode–mode coupling theory to correct the measured viscosity for the shear effect.

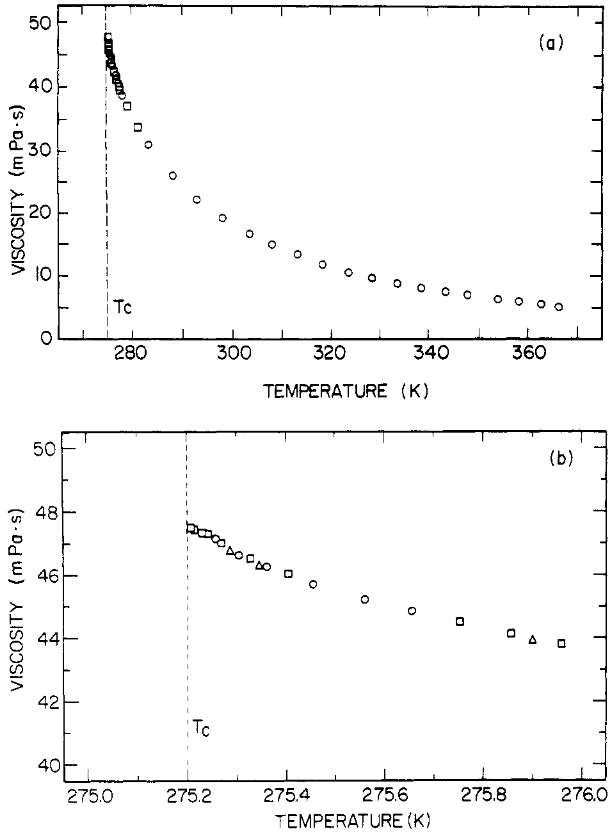

Figure 2. Shear viscosity of 9.473 wt % polystyrene (molecular weight 1.02×10^5) in diethyl malonate as a function of temperature: (a) the entire data set from Table I; (b) the data near the critical temperature, T_c. The three runs are indicated by ○ for run 1, □ for run 2, and △ for run 3.

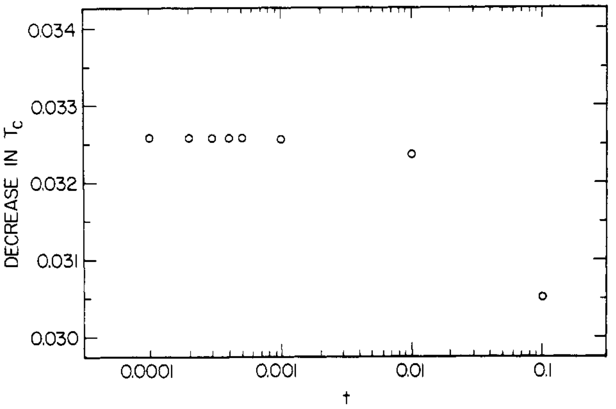

Figure 3. Calculated decrease in the critical temperature, T_c, in kelvin, for the data in Table I due to the effect of the shear on the critical fluctuations. The abscissa is log t, where $t = (T - T_c)/T_c$. The effect is calculated by the method of ref 7-9. Details are in the text.

Lee and Purvis[44] provided an algebraic equation for Oxtoby's correction. Onuki and collaborators[7-9] have made a renormalization group calculation of the shear effect. Onuki et al. point out that the shear elongates the fluctuations, thereby lowering T_c for an upper critical solution point; the suppression of the fluctuations leads to mean-field behavior and a rounding off of the viscosity anomaly. More recently, Hashimoto et al.[45] report that the shear effect will be different for a polymer mixture, but they have not yet published details of that theory that would be helpful in analyzing our data.

Both Oxtoby[6] and Onuki et al.[9] give criteria for the reduced temperature at which the onset of the shear effect occurs. For polystyrene in diethyl malonate in our viscometer, we calculated that shear effects will become important at $t = 3 \times 10^{-4}$ by Oxtoby's criterion and at $t = 8 \times 10^{-4}$ by Onuki's criterion. We used for these calculations Oxtoby's equation for the effective shear rate in a capillary viscometer, the dimensions of the viscometer as given in Figure 1, our own equation for $\rho(t)$, and the results of Stafford et al.[14] for the correlation length. As an example of the magnitude of the effective shear rate in our experiment, we calculate a value of 15 s^{-1} at $t = 2.18 \times 10^{-5}$. We also calculated the effect of the shear on T_c using the equation of Onuki et al.[9] The decrease in T_c due to the effect of shear on the fluctuations is shown in Figure 3. Thus our data on polystyrene in diethyl malonate are strongly affected by the shear, showing a rounding of the critical anomaly, an onset of rounding at nearly $t = 10^{-3}$, and a shift in T_c of nearly 33 mK.

The first problem for the data away from T_c is that we do not know the functional form of the background viscosity, η_B. Semiempirical functions such as the Arrhenius equation

$$\eta = b_1 \exp(b_2/T) \qquad (3)$$

or the Vogel–Fulcher equation

$$\eta = b_1 \exp(b_2/(T + b_3)) \qquad (4)$$

describe experimental data only over limited temperature ranges.[46,47] There seems to be no theoretically based function for the viscosity as a function of temperature for a simple fluid or mixture of simple fluids, much less for a polymer solution.

The second problem for the data away from T_c is that eq 1 applies only "asymptotically close" to the critical point. The nature of the full function, including the crossover to nonsingular behavior, has not been determined for a liquid–liquid critical point, although progress has been made for the liquid–gas critical point.[48] If we write the function as a series, a reasonable first guess for the next terms in this series is[12,13]

$$\eta = \eta_B A t^{-y}[1 + b_1 t^{\Delta} + b_2 t^{2\Delta} + ...] \qquad (5)$$

where $\Delta = 0.5$.[21] For the critical behavior of thermodynamic properties near liquid–liquid critical points, the inclusion of these higher order terms is necessary to obtain agreement between experiment and theory for the values of the exponents when t is greater than about 10^{-2}.[49] We can expect these higher order terms to be important for transport properties as well.

We have tried three approaches to analyzing the viscosity data. First,[11] we fitted various empirical equations for η_B to as much of the data away from T_c as would fit the particular function; then we fitted the function $\eta/\eta_B = At^{-y}$ to the remaining data near T_C. We tried both excluding the data affected by the shear and correcting the viscosity and T_c for the effect of the shear. The value of y obtained was extremely sensitive to the range of the data and to the choice of η_B, varying from 0.015 to 0.060.

Then we tried omitting the data near T_c ($T < 275.4$ K; $t < 7 \times 10^{-4}$) and fitting eq 1 in its entirety to the remaining data, thus fitting the equation to the background viscosity and the critical viscosity simultaneously. For the form of η_B, we tried the simple Arrhenius equation (eq 3), the Arrhenius equation with a higher order term ($\ln \eta_B = b_1 + b_2/T + b_3/T^2$), the Vogel–Fulcher equation (eq 4), the Vogel–Fulcher equation with a higher power ($\eta = b_1 \exp(b_2/(T + b_3)) \exp(b_4/(T + b_3)^2)$), and a simple power series ($\eta_B = b_1 + b_2T + b_3T^2$

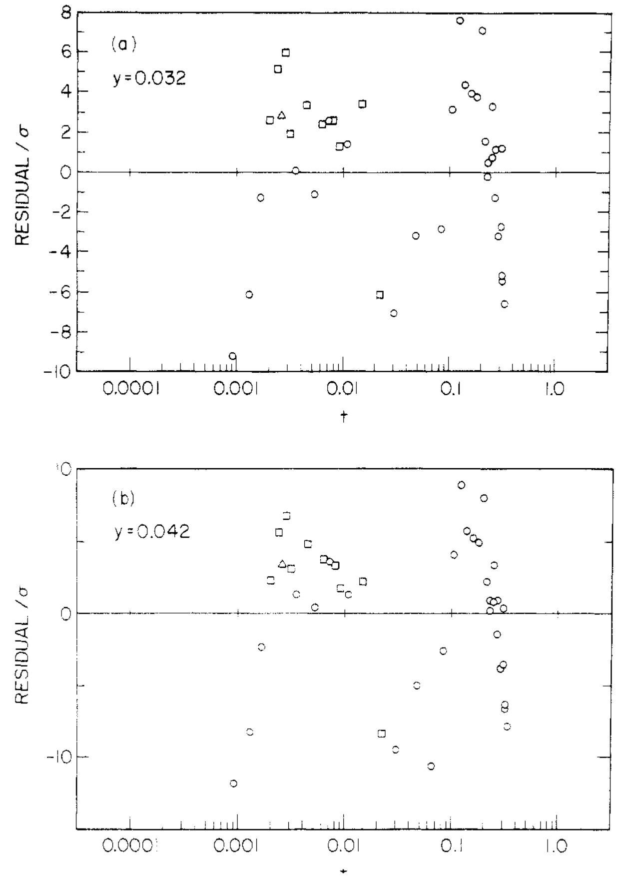

Figure 4. Residuals for two fits to eq 5, using the Volger–Fulcher equation (eq 4) for η_B and using only one correction term, b_1t^{Δ}: (a) y fixed at 0.032; (b) y fixed at 0.042. The different symbols indicate the different experimental runs, as described in the caption for Figure 1. See the text for more details.

+ b_4T^3). In no case did we obtain a good fit, with random residuals. The Vogel–Fulcher equation seemed to be the most promising, so we tried using that form of η_B in eq 5, which includes higher order critical terms; with two critical correction terms, the reduced χ^2 was 6, but the resulting value of y of 0.01 was not reasonable. Eliminating the data for which $t > 0.02$ did not improve the fit. The fits were not very sensitive to a change of T_c from 275.202 to 275.172 K, the shift expected from the shear effect. As examples, we show in Figure 4 the residual plots for two such fits, both using the Vogel–Fulcher equation for η_B in eq 5 with one correction term; y was fixed either at the theoretical value of 0.032 or at the experimental value in nonpolymer solutions of 0.042, so that four parameters were free. The residuals in Figure 4 are clearly systematic, as were those for all the other fits attempted for the data outside the shear-affected region. Thus we were unable to find a function to fit simultaneously all the data outside the shear-affected region.

As a last resort, we tried fitting just the data for $t < 0.02$, the temperature range of the systems considered by Berg and Moldover[12] and Nieuwoudt and Sengers.[13] This approach required correcting the viscosity data for the shear[44] and using the effective T_c for each datum. As discussed above, the correction for shear may not be accurate for polymer systems.[45] The parameters we used for the corrections are given in the discussion above. We fitted eq 1 with η_B from the Arrhenius function, but without the critical correction terms, to the 29 data points near T_c; the preferred value of y was 0.040 ± 0.002, but the reduced χ^2 was 28 and the residuals were not random. We fitted eq 1 with η_B from the Vogel–Fulcher equation to the same data; the preferred value of y was 0.0398 ± 0.0004, but the reduced χ^2 was 29 and the residuals were not random. We tried adding one correction term (eq 5) while using the Vogel–Fulcher equation for η_B; the reduced χ^2 was 16, the residuals were systematic, and y was 0.058 ± 0.002. We were thus unable to fit a function to the data near T_c, within the error of the data and with random residuals.

In summary, we have no function to describe our data.

Conclusions

Mass Density. The absence of a measurable critical anomaly in the mass density as a function of temperature for polystyrene in diethyl malonate is not surprising, since the same is true for polystyrene in cyclohexane.[50] The amplitude of the anomaly in the density (R_3 in eq 2) can be estimated from[51,52]

$$R_3 = [-C\rho_c^2(\mathrm{d}T_c/\mathrm{d}P)]/(1-\alpha) \qquad (6)$$

where C is the amplitude of the critical anomaly in the heat capacity per unit mass, $\mathrm{d}T_c/\mathrm{d}P$ is the change of the critical temperature with pressure, and ρ_c is the mass density at the critical point. The amplitude C and the derivative $\mathrm{d}T_c/\mathrm{d}P$ have not been measured for this mixture. However, C can be calculated, by the hypothesis of two-scale factor universality, from the amplitude of the correlation length of the critical fluctuations, ξ_0:[53]

$$C = \alpha k_B X/\xi_0^3$$

where k_B is Boltzmann's constant and X is a universal constant. Thus

$$\begin{aligned} R_3 &= [-\alpha k_B X\rho_c^2(\mathrm{d}T_c/\mathrm{d}P)]/\xi_0^3(1-\alpha) \\ &= [-K\rho_c^2(\mathrm{d}T_c/\mathrm{d}P)]/\xi_0^3 \qquad (7) \end{aligned}$$

where all the universal constants are collected into K in the second line. Let us assume that $\mathrm{d}T_c/\mathrm{d}P$ is about the same for polystyrene in diethyl malonate as it is for polystyrene in cyclohexane (which may or may not be true). The mass densities ρ_c are 0.820 and 1.07 g/cm^3 for polystyrene in cyclohexane[50] and in diethyl malonate, respectively. The amplitudes ξ_0 are 0.58 nm for polystyrene in cyclohexane[54] and 1.01 nm for polystyrene in diethyl malonate.[14] Then from eq 7 we calculate the ratio of R_3 for polystyrene in diethyl malonate to R_3 for polystyrene in cyclohexane to be 0.3. The critical anomaly in the mass density is expected to be three times smaller if the polystyrene is in diethyl malonate than if the solvent is cyclohexane.

Shear Viscosity. We have been unable to find a function to describe the viscosity as a function of temperature at the critical composition of polystyrene in diethyl malonate. We have no adequate theoretical description of the effect of shear on the critical fluctuations of a polymer solution. We have no adequate theoretical description of the background analytical temperature dependence of the viscosity of such a solution.

Acknowledgment. We are grateful to J. C. Nieuwoudt, J. V. Sengers, and F. A. Goncalves for many helpful discussions. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research. This work was also supported by the National Science Foundation under Grants CHE-8413404 and CHE-8708426.

Registry No. Polystyrene, 9003-53-6; diethyl malonate, 105-53-3.

Macromolecules **1990,** *23,* 515–520

References and Notes

(1) For a review, see: Sengers, J. V. *Int. J. Thermophys.* **1985,** *6,* 203.
(2) Ohta, T. *J. Phys. C* **1977,** *10,* 791.
(3) Oxtoby, D. W.; Gelbart, W. M. *J. Chem. Phys.* **1974,** *61,* 2957.
(4) Bhattacherjee, J. K.; Ferrell, R. A.; Basu, R. S.; Sengers, J. V. *Phys. Rev. A* **1981,** *24,* 1469.
(5) Bhattacharjee, J. K.; Ferrell, R. A. *Phys. Rev. A* **1983,** *28,* 2363.
(6) Oxtoby, D. W. *Phys. Lett.* **1975,** *50A,* 459; *J. Chem. Phys.* **1975,** *62,* 1463.
(7) Onuki, A. *Phys. Lett.* **1979,** *70,* 31.
(8) Onuki, A.; Kawasaki, K. *Ann. Phys.* **1979,** *121,* 456.
(9) Onuki, A.; Yamazaki, K.; Kawasaki, K. *Ann. Phys.* **1981,** *131,* 217.
(10) Bhattacharjee, J. K.; Ferrell, R. A. *Phys. Rev. A* **1983,** *27,* 1544.
(11) Gruner, K. Ph.D. Dissertation, Department of Chemistry and Biochemistry, The University of Maryland at College Park, College Park, MD, 1988.
(12) Berg, R. F.; Moldover, M. R. *J. Chem. Phys.* **1988,** *89,* 3694.
(13) Nieuwoudt, J. C.; Sengers, J. V. *J. Chem. Phys.* **1989,** *90,* 457.
(14) Stafford, S. G.; Ploplis, A. G.; Jacobs, D. T. *Macromolecules,* submitted for publication.
(15) Kawasaki, K. *Ann. Phys.* (*New York*) **1970,** *61,* 1.
(16) Chang, R. F.; Burstyn, H.; Sengers, J. V. *Phys. Rev. A* **1979,** *19,* 866.
(17) The viscosity value needed for this calculation (see ref 15) was obtained from: Pegg, I. L.; McLure, I. A. *Mol. Phys.* **1984,** *53,* 897.
(18) Hamano, K.; Nomura, T.; Kawazura, T.; Kuwahara, N. *Phys. Rev. A* **1982,** *26,* 1153.
(19) Izumi, Y.; Sawano, H.; Miyake, Y. *Phys. Rev. A* **1984,** *29,* 826.
(20) Sengers, J. V.; Bedeaux, D.; Mazur, P.; Greer, S. C. *Physica* (*Utrecht*) **1980,** *104,* 473.
(21) Le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. B* **1980,** *21,* 3976; *J. Phys. Lett.* **1985,** *46,* L137.
(22) Gruner, K.; Greer, S. C. Macromolecules **1987,** *20,* 2238.
(23) Tveekrem, J. L.; Greer, S. C.; Jacobs, D. T. *Macromolecules* **1988,** *21,* 147.
(24) Hamano, K.; Kuwahara, N.; Nakata, M.; Kaneko, M. *Phys. Lett.* **1977,** *63A,* 121.
(25) Hamano, K.; Kuwahara, N.; Kaneko, M. *Phys. Rev. A* **1979,** *20,* 1135.
(26) Hamano, K.; Kuwahara, N.; Kaneko, M. *Phys. Rev. A* **1980,** *21,* 1312.
(27) Fenner, D. B. *J. Chem. Phys.* **1987,** *87,* 2377.
(28) Fenner, D. B. *J. Chem. Phys.* **1988,** *88,* 2021.
(29) The distributor in the United States is the Varian Instrument Co., Sunnyvale, CA.
(30) Tveekrem, J. L.; Jacobs, D. T. *Phys. Rev. A* **1983,** *27,* 2773.
(31) Cohn, R. H.; Jacobs, D. T. *J. Chem. Phys.* **1984,** *80,* 856.
(32) Greer, S. C. In *Building Scientific Apparatus,* 2nd ed.; Moore, J. H., Davis, C. C.; Coplan, M. A., Eds.; Addison-Wesley: Reading, MA, 1989.
(33) Tronac, Inc., Orem, UT, Model PTC-41.
(34) Guildline Instruments, Inc., Orlando, FL, Model 9540.
(35) Ubbelohde, L. *Ind. Eng. Chem., Anal. Ed.* **1937,** *9,* 85.
(36) Hardy, R. C. *NBS Viscometer Calibrating Liquids and Capillary Tube Viscometers*; U. S. National Bureau of Standards Monograph 55; U. S. Government Printing Office: Washington, DC, 1962.
(37) Habib, S.; Gruner, K. *Rev. Sci. Instrum.* **1988,** *59,* 2290.
(38) Standards S20 and S6 from the Cannon Instrument Co., State College, PA.
(39) Cannon, M. R.; Manning, R. E.; Bell, J. D. *Anal. Chem.* **1960,** *32,* 355.
(40) Andrews, K. P.; Jacobs, D. T., submitted for publication in Physics Academic Software.
(41) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes*; Cambridge: New York, 1986.
(42) Botch, W.; Fixman, M. *J. Chem. Phys.* **1962,** *36,* 3100.
(43) Sallavanti, R.; Fixman, M. *J. Chem. Phys.* **1968,** *48,* 5326.
(44) Lee, S. P.; Purvis, A. *J. Chem. Phys.* **1977,** *24,* 191.
(45) Hashimoto, T.; Takeba, T.; Suehiro, S. *J. Chem. Phys.* **1988,** *88,* 5874.
(46) Tager, A. *Physical Chemistry of Polymers,* 2nd ed.; Mir Publishers: Moscow, 1978. The Vogel–Fulcher equation is equivalent to the Doolittle equation or the Williams–Landel–Ferry equation.
(47) Bohdanecky, M.; Kovar, J. *Viscosity of Polymer Solutions*; Elsevier: New York, 1982.
(48) Olchowy, G. A.; Sengers, J. V. *Phys. Rev. Lett.* **1988,** *61,* 15.
(49) See, for example: Greer, S. C. *Phys. Rev. A* **1976,** *14,* 1770.
(50) Greer, S. C.; Jacobs, D. T. *J. Phys. Chem.* **1980,** *84,* 2888.
(51) Griffiths, R. B.; Wheeler, J. C. *Phys. Rev. A* **1970,** *2,* 1047.
(52) Morrison, G.; Knobler, C. M. *J. Chem. Phys.* **1976,** *65,* 5507.
(53) Stauffer, D.; Ferer, M.; Wortis, M. *Phys. Rev. Lett.* **1972,** *29,* 345.
(54) Kuwuhara, N.; Kojima, J.; Kaneko, M. *Phys. Rev. A* **1975,** *12,* 2606.

Solvent Effect on the Complexation between Poly(ethylene oxide) and Alkali-Metal Ions

Hisashi Honda,* Katsumichi Ono, and Kenkichi Murakami

Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira, Sendai 980, Japan.

Received February 22, 1989; Revised Manuscript Received June 1, 1989

ABSTRACT: Solvent effect on the complexation between poly(ethylene oxide) and alkali-metal ions in organic solvent was correlated with the dielectric constant, ϵ, and the donor number, DN, of the solvent. The binding constant of the cation to the polymer, K_0, was determined by the method based on the one-dimensional lattice model. For the purpose to separate these two solvent effects, solvent mixtures with isodielectric constant and isodonicity were investigated. A linear relationship between log K_0 and ϵ^{-1} was found. This was explained by the contribution of ϵ to the electrostatic interaction energy. A linear relationship was also shown to hold between log K_0 and DN, which could be accounted for the model base on the preferential solvation to the ion. It was concluded that the strength of the complexation was mainly governed by DN.

Introduction

The solvent effect on the complexation between metal ions and macromolecular ligand has not so far been investigated quantitatively, while a great number of experimental data have been accumulated for low molecular weight ligands. This is due to the difficulty in determining the intrinsic formation constant for the polymer, since the binding metal ions on a polymer chain strongly interact with each other. In our previous report, we have devel-

0024-9297/90/2223-0515$02.50/0