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Density of Polystyrene in Diethyl Malonate in the One-Phase and Two-Phase Regions Near the Critical Solution Point

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ABSTRACT: We have measured the density as a function of temperature above the critical temperature, T_c, and the densities of coexisting phases below T_c, for a sample at the critical composition of the mixture polystyrene in diethyl malonate. The polystyrene had a molecular weight of 1.07×10^5. The densities were measured to 0.01%. Above the critical temperature, in the range $1.1 \times 10^{-4} < t < 6.7 \times 10^{-2}$ (where $t = (T - T_c)/T_c$), the data showed no critical anomaly and could be fitted to a straight line. Below the critical temperature, in the range $7 \times 10^{-6} < t < 8 \times 10^{-4}$ ($t = (T_c - T)/T_c$), the difference in coexisting densities was described by Bt^{β}, with B a free parameter, T_c fixed at 280.150 K, and β fixed at 0.325.

Introduction

The modern theory of the critical solution point[1] predicts that, for a mixture at the critical composition and in the one-phase region, the leading terms in the representation of the density as a function of temperature at constant pressure near the critical temperature have the form

$$\rho = R_1 + R_2 t + R_3 t^{1-\alpha} + \ldots \qquad (1)$$

where ρ is the mass density; t is the reduced temperature, $(T - T_c)/T_c$; R_1, R_2, and R_3 are constants which depend on the particular mixture; and α is a universal critical exponent which describes the divergence of the specific heat at constant pressure and composition. Calculations by renormalization group theory find α to have the value 0.11.[2] Thus the density as a function of temperature is expected to have a weak cusp near T_c, increasing or decreasing, depending upon the sign of R_3. Equation 1 has been found to be consistent with experimental measurements for a variety of liquid mixtures.[3-7]

The theoretical prediction for the functional form of the liquid–liquid coexistence curve is[1,8,9]

$$(\rho_1 - \rho_2) = B_1 t^{\beta} + B_2 t^{\beta+\Delta} + B_3 t^{\beta+2\Delta} + \ldots \qquad (2)$$

where ρ_1 is the density of one phase; ρ_2 is the density of the other phase; B_1, B_2, and B_3 are coefficients which depend on the particular mixture; β is a universal exponent of predicted value 0.325;[2] and Δ is a universal exponent of predicted value 0.50.[2] Variables other than the density may be chosen as the "order parameter" in eq 2; the best choice is still not understood.[3,4] Equation 2 has been found to be consistent with experimental measurements.[3,4,10]

Measurements of the density[6] and of the coexistence curve[11,12] in polymer solutions showing liquid–liquid immiscibility have been reported and show that polymer solutions obey eq 1 and 2, with the exponent values given above. Thus polymers forming critical solution points with solvents are included in the critical point universality class for which the dimensionality of space is 3, the dimensionality of the order parameter is 1, and the intermolecular forces are short ranged.

We present here new measurements of the density and coexistence curve for a mixture of polystyrene (molecular weight 1.07×10^5) in diethyl malonate. An approximate coexistence curve for this mixture had been measured previously by Hamano et al.[13-15] Our results are consistent with eq 1 and 2. We hope that eventually our data will be of value in testing theoretical predictions[16] about the nonuniversal amplitudes in eq 1 and 2.

Experimental Methods

The polystyrene used for these measurements, obtained from Toyo Soda Manufacturing Co.,[17] had a molecular weight of 1.07×10^5 and a ratio of weight-average molecular weight to number-average molecular weight, M_w/M_n, of 1.01. The polystyrene was dried in a vacuum oven at 318 K for 2 weeks and then quickly transferred to a drybox.

The diethyl malonate, obtained from Aldrich Chemical Co., was specified to be at least 99% pure. Acids formed by hydrolysis of the ester were removed by extraction with 5% aqueous potassium carbonate. Then the ester was washed with deionized water to remove any potassium carbonate, shaken with sodium sulfate to remove most of the water, filtered to remove the sodium sulfate, and stored over molecular seive to dry it further. The sample was prepared in a nitrogen atmosphere drybox. All glassware and implements were carefully dried.

The critical composition for this molecular weight of polystyrene was determined by B. C. Miller and G. P. Furrow in our laboratory to be near 9.49 wt % polystyrene. Hamano et al.[14] reported a critical composition of 8.48 wt % (or 0.0837 volume fraction) for polystyrene of molecular weight 2×10^5. Studies of polystyrene in methylcyclohexane also show the critical composition decreasing as the molecular weight increases,[12] as is expected from theories of polymer solutions.[18] In the measurements reported here, we used a mixture with 9.469 wt % polystyrene; the meniscus appeared in the center of the sample, indicating nearness to the critical composition.

The critical temperature for this mixture is extremely sensitive to water as an impurity. For example, a sample prepared at the critical composition with no care taken to exclude water (i.e., using open vessels) showed a phase-separation temperature near 299 K, whereas carefully dried samples had phase-separation temperatures as low as 276 K. While the effects of impurities on critical temperatures are often dramatic, the effects on critical compositions and on critical behaviors of thermodynamic properties are small.[19,20] For the sample used in the measurements reported here, the critical temperature, determined visually as the temperature at which the meniscus appeared, was 280.150 ± 0.002 K (7.000 °C). This value for T_c was used in the data analysis: T_c was not a free parameter.

In the beginning of a run, the sample was heated into the one-phase region and mixed by shaking manually and by agitating in a sonicator. The sample was then cooled and time allowed for equilibration at each temperature step. While the temperature was stabilizing, the densimeter buoy (see below) was set into an oscillation, causing it to go up and down the cell about once per second and mix the sample. The temperature became stable in about 15 min, but total equilibration times of 1 or 2 h were allowed in the one-phase region. For temperatures above T_c, the density was measured both at the top and at the bottom of the sample in order to check for density gradients; no such density gradients were found. At 0.032 K above T_c, the sample became so turbid that the buoy could not be seen, so density measurements could not be made for $(T - T_c) < 0.032$ K. For temperatures below T_c, the density of the top phase was measured first and then that of the bottom phase was measured, after a day was allowed for

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Table I
Density, ρ, as a Function of Temperature, T, for a 9.469 wt % Solution of Polystyrene[a] in Diethyl Malonate[b]

T, K	ρ, g/cm^3	run	T, K	ρ, g/cm^3	run
285.118	1.0652	1	280.727	1.0695	2
283.830	1.0665	1	280.732	1.0696	2
283.826	1.0666	1	280.737	1.0697	2
282.591	1.0677	1	280.782	1.0697	2
282.589	1.0678	1	280.785	1.0699	2
282.584	1.0677	1	280.784	1.0697	2
281.673	1.0688	1	280.660	1.0701	2
281.675	1.0688	1	280.646	1.0698	2
280.944	1.0695	1	280.658	1.0698	2
280.939	1.0696	1	280.557	1.0698	2
280.713	1.0698	1	280.543	1.0700	2
280.711	1.0698	1	280.565	1.0699	2
280.504	1.0700	1	280.544	1.0699	2
280.500	1.0701	1	280.464	1.0700	2
280.496	1.0701	1	280.457	1.0701	2
280.502	1.0701	1	297.032	1.0527	3
280.399	1.0703	1	297.027	1.0528	3
280.391	1.0702	1	297.024	1.0529	3
280.271	1.0704	1	297.204	1.0526	3
280.277	1.0704	1	297.198	1.0526	3
280.233	1.0703	1	295.787	1.0540	3
280.227	1.0703	1	295.782	1.0540	3
280.213	1.0703	1	294.707	1.0552	3
280.207	1.0703	1	294.722	1.0552	3
280.210	1.0703	1	292.599	1.0573	3
280.200	1.0704	1	292.589	1.0573	3
280.199	1.0704	1	291.311	1.0585	3
280.198	1.0703	1	291.320	1.0586	3
280.193	1.0703	1	290.085	1.0600	3
280.196	1.0703	1	290.086	1.0600	3
280.185	1.0703	1	288.779	1.0613	3
280.185	1.0704	1	288.775	1.0614	3
280.187	1.0704	1	287.517	1.0624	3
280.185	1.0704	1	286.363	1.0639	3
282.975	1.0677	2	286.363	1.0639	3
282.973	1.0673	2	285.193	1.0650	3
282.973	1.0677	2	285.187	1.0651	3
281.972	1.0686	2	283.260	1.0671	3
282.969	1.0684	2	283.260	1.0672	3
281.971	1.0685	2	282.137	1.0682	3
281.039	1.0694	2	282.142	1.0683	3
281.039	1.0695	2	281.310	1.0691	3
281.038	1.0695	2	281.307	1.0691	3
280.842	1.0697	2	280.425	1.0701	3
280.841	1.0695	2	280.181	1.0706	3
280.840	1.0695	2	280.181	1.0706	3
280.726	1.0697	2			

[a] Molecular weight 1.07×10^5. [b] Above the critical temperature of 280.150 ± 0.002 K.

the fluid from the top phase to drain completely from the buoy. The times required for phase separation and for equilibration in the two-phase region for this mixture were very long. At least 24 h was allowed for equilibration in searching for T_c from the one-phase region and in measuring the density in all of the two-phase region.

The density was measured with the magnetic suspension densimeter, described previously,[21] in which a magnetic buoy is levitated in the fluid by means of the magnetic field of a solenoid. A typical buoy has been described by Greer and Hocken.[22] The buoy used in this work was made of quartz to minimize the effects of its thermal expansion. The square of the current in the solenoid is then a measure of the density. The current is proportional to the voltage across a standard resistor in series with the solenoid. The density is then related to the square of that voltage: $\rho = A + BV^2$, where A and B are instrumental constants. The constants were determined by measuring the voltage required to suspend the buoy in three solutions of known densities. These calibration fluids were solutions of sucrose in water.[23] The *accuracy* of the density measurements is 0.1%. The *precision* of the density measurements is 0.01% (1 part in 10^4). The precision of the magnetic densimeter is usually about one part in 10^5. We believe that the high viscosity of the fluid mixture (45 cP at $(T - T_c) = 0.1$ K,[24] which affects the time constants of the densimeter servo system) and the high level of critical opalescence (which inhibits the sighting of the buoy) affected the precision.

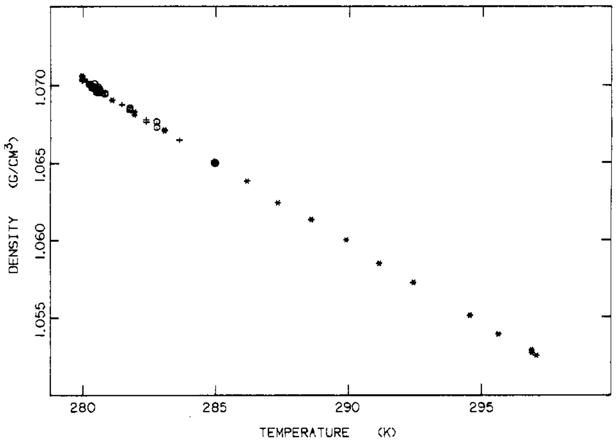

Figure 1. Density as a function of temperature above the critical temperature (280.150 K) for a critical mixture of polystyrene (molecular weight 1.07×10^5) in diethyl malonate. The data are from Table I. The symbols refer to various cooling runs: run 1 (*); run 2 (+); run 3 (○).

The temperature in the densimeter was controlled by circulating water from a water bath. The bath was controlled to 0.004 K by an analog controller.[25] The temperature in the densimeter was measured by a 2.5-kΩ ultrastable thermistor[26] in series with a 50-kΩ standard resistor[27] and a 1.35-V mercury battery. The ratio of the voltage across the thermistor to that across the standard resistor was taken as a measure of the temperature. Voltages were measured with a 5 $^1/_2$ digit digital voltmeter.[28] The thermistor was calibrated on the International Practical Temperature Scale of 1968. The *accuracy* of the temperature measurement is 0.01 K and the *precision* of the temperature measurement is 0.004 K.

Results

A. One-Phase Region. The 93 data points from three cooling runs are given in Table I and plotted in Figure 1. The temperature range is $1.1 \times 10^{-4} < t < 6.7 \times 10^{-2}$. In Table II are given the functions that were fitted to these data, using a weighted nonlinear least-squares fitting program.[29] The goodness-of-fit is essentially the same for the linear function, the quadratic function, and eq 1. Indeed, the uncertainties in A_3 for the quadratic function (fit 2) and for eq 1 (fit 3) are so large that that term is insignificant. We conclude that, within our resolution of 0.0001 g/cm^3, the density as a function of temperature above T_c

Table II
Fits of Three Functions to the Data in Table I for the Dependence of the Density, ρ (g/cm^3), of Polystyrene in Diethyl Malonate on the Reduced Temperature[a]

fit	function	$A_1 \pm \sigma$	$A_2 \pm \sigma$	$A_3 \pm \sigma$	χ_ν^2
1	$\rho = A_1 + A_2t$	1.070 38 ± 0.000 01	−0.2933 ± 0.0006		1.07
2	$\rho = A_1 + A_2t + A_3t^2$	1.070 40 ± 0.000 01	−0.298 ± 0.002	0.09 ± 0.04	1.02
3	$\rho = A_1 + A_2t + A_3t^{1-\alpha}$	1.070 41 ± 0.000 02	−0.26 ± 0.01	−0.022 ± 0.009	1.02

[a] $t = (T - T_c)/T_c$, where T is the temperature and T_c is the critical temperature; T_c was fixed at 280.150 K and the exponent α at 0.11. The standard deviation in T was taken to be 0.004 K and that in ρ was taken to be 0.0001 g/cm^3. The uncertainty, σ, given for each parameter is its standard deviation. The measure of goodness-of-fit is χ_ν^2 (see ref 29).

Table III
Densities of Coexisting Phases of Polystyrene[a] in Diethyl Malonate[b]

T, K	ρ_u, g/cm³	ρ_l, g/cm³	run
280.148	1.0702	1.0707	2
280.131	1.0701	1.0708	2
280.114	1.0702	1.0710	2
280.098	1.0701	1.0709	2
280.091	1.0702	1.0711	2
280.141	1.0701	1.0709	2
280.131	1.0701	1.0708	2
280.102	1.0700	1.0708	2
280.101	1.0700	1.0709	2
280.085	1.0701	1.0710	2
280.075	1.0701	1.0710	2
280.058	1.0701	1.0710	2
280.059	1.0701	1.0712	2
280.036	1.0702	1.0714	2
280.021	1.0702	1.0714	2
280.005	1.0702	1.0714	2
279.986	1.0701	1.0713	2
279.967	1.0701	1.0713	2
280.049	1.0702	1.0712	1

[a] Molecular weight 1.07×10^5. [b] The density of the upper phase is ρ_u and that of the lower phase is ρ_l.

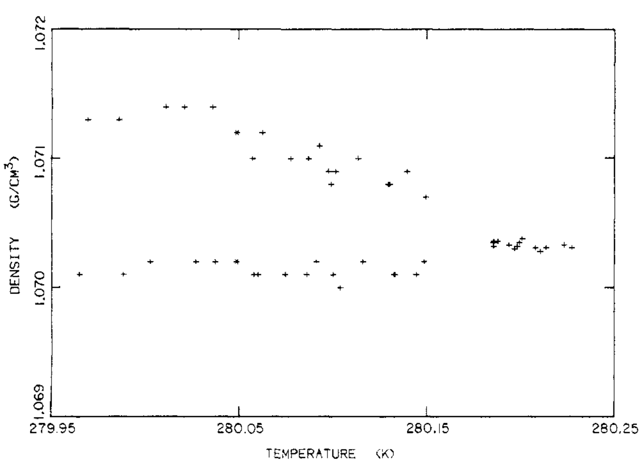

Figure 2. Densities of coexisting phases below the critical temperature (280.150 K) for a critical mixture of polystyrene (molecular weight 1.07×10^5) in diethyl malonate. The data are from Table III. The symbols refer to two cooling runs: run 1 (*); run 2 (+). Also shown are a few of the measurements of the density near the critical temperature in the one-phase region (see Table I).

can be fitted by a straight line and shows no critical anomaly.

B. Two-Phase Region. The densities of the coexisting phases in the reduced temperature range $7 \times 10^{-6} < t < 8 \times 10^{-4}$ are given in Table III and plotted in Figure 2. There are 19 data pairs from two cooling runs. The difference in density is very small over this range, at most 0.001 g/cm³. Equation 2, with only one term and with β fixed at 0.325 and T_c fixed at 280.150, described the data within the precision. For this fit, the free parameter, B, was found to be 0.0141 ± 0.0003 g/cm³.

Conclusions

We have found no critical anomaly in the density of polystyrene in diethyl malonate as a function of temperature above T_c, in the range $1.1 \times 10^{-4} < t < 6.7 \times 10^{-2}$ and within our experimental standard deviation of 0.01%. It is not uncommon for this anomaly to be small. For example, it is about 0.001% in the similar mixture of polystyrene in cyclohexane.[6] The amplitude of the anomaly can be estimated[6] from the amplitude of the derivative of the critical temperature with pressure and the amplitude of either the anomalous heat capacity or of the correlation length; this information is not available for this mixture.[30]

The shape of the coexistence curve is consistent with theoretical predictions for the range $7 \times 10^{-6} < t < 8 \times 10^{-4}$ and for a resolution of 0.01%.

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

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