

Thermal Expansion near the Upper Critical Solution Point for Polystyrene-Cyclohexane

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The density has been measured as a function of temperature in the one-phase region above the critical solution temperature of the system polystyrene-cyclohexane. The resolution of the density measurements is $\sim 2 \times 10^{-5}$ g/cm³, that of the temperature is 1-2 mK, and the range in reduced temperature $t = (T - T_c)/T_c$ is 10^{-5} - 10^{-2} . Data on two samples of different composition can be fitted to analytical functions. No critical anomaly is detected. We show this result to be consistent with the concept of two-scale-factor universality.

Introduction

The density, ρ , as a function of temperature, T , in the one-phase region near a liquid-liquid critical point is of interest because it is expected to have a critical anomaly of the form $\rho \propto t^{1-\alpha}$, $t = (T - T_c)/T_c$, sufficiently close to the critical temperature T_c .¹ Such an anomaly has been found and examined in a number of liquid mixtures.²⁻⁷ Moreover, this anomaly is important in the analysis of other properties in the liquid-liquid critical region; an anomaly in density will affect such properties as light scattering⁸ and dielectric constant.⁹

Critical phenomena in the mixture polystyrene plus cyclohexane have been studied extensively.¹⁰⁻¹² However, no measurements have been previously reported of the density in the one-phase region. We report here density measurements on two samples of different composition of polystyrene-cyclohexane. We find that both sets of data can be fitted to analytic functions, with no indication of a critical anomaly in either case. These results show that the amplitude of the critical anomaly in the thermal expansion is very small. We demonstrate that such a small amplitude is consistent with other properties of this mixture, via the relationships derived from two-scale-factor universality.¹³⁻¹⁶

Experimental Section

The polystyrene used for these measurements was obtained from the National Bureau of Standards as Standard Reference Material 1478.¹⁷ The number average molecular weight is 35 800, with a standard deviation of the mean of 0.4%.

For sample I, the cyclohexane used was freshly distilled.¹⁸ For sample II, the cyclohexane used was Malinkrodt spectrophotometric grade. Our experience has been that "pure" cyclohexane from various sources can differ in density by as much as 0.003 g/cm³. Thus the difference in the pure cyclohexane should be kept in mind in comparing data between the two samples. In addition, the difference in cyclohexane means that the transition temperatures of the two samples cannot be compared, for T_c is extremely sensitive to impurities.

Sample I was 15.42 wt % polystyrene and had a transition temperature, T_v , of 13.581 °C. Sample II was 16.29% polystyrene and had a transition temperature of 12.572 °C. Our measurements in the two-phase region¹⁹ indicated that

the critical composition of polystyrene is 16.3%, so we believe sample II to have been nearer to critical.

Both samples were contained in Pyrex screw-cap vials, sealed with Teflon cap-liners at atmospheric pressure. There was never any indication of leakage.

The density measurements were made by using the magnetic suspension densimeter described previously,²⁰ in which a magnetic buoy is levitated in the liquid of interest by using a solenoid and a servo system. The solenoid voltage is then a measure of the density. A typical buoy has been described by Greer and Hocken;⁵ the one used for the present work was made of quartz to eliminate the effect of its thermal expansion. The buoy was calibrated by suspending it in two liquids of known density. The precision of the density measurements is $\sim 2 \times 10^{-5}$ g/cm³; the accuracy is ~ 100 ppm.

The temperature of a sample in the densimeter was controlled by a circulating water bath. The temperature was measured by using an ultrastable thermistor²¹ in series with a standard resistor²² and a 1.35-V mercury battery. The ratio of the voltage across the thermistor to that across the standard resistor was measured by using a 5¹/₂ digit voltmeter and was used as the measure of temperature. The thermistor was calibrated on the International Practical Temperature Scale of 1968 to 0.01 K. The precision of the control and measurement of the temperature was 2 mK.

For each run, the sample was heated to the highest desired temperature and shaken, and then the temperature dropped incrementally. The sample was frequently searched for density gradients due to gravity²³ by moving the sample relative to the buoy. Like earlier workers,¹⁰ we found no such gradients, even at points closest to the transition temperature and for times up to 24 h. The time required to reach equilibrium after a temperature change was ~ 1 h for a change of 0.1 °C at $(T - T_v) \approx 0.1$ °C but reached 24 h for temperatures within a few millidegrees of T_v .

Results

For sample I, 46 data points were taken on 5 different cooling runs over the range $4.9 \times 10^{-5} < t < 3.6 \times 10^{-2}$. These data are given in Table I. For sample II, 24 data points were taken on 4 different cooling runs over the range $2 \times 10^{-5} < t < 2.5 \times 10^{-2}$. These data are listed in Table II.

TABLE I: Density as a Function of Temperature for Sample I, 15.42% Polystyrene in Cyclohexane

$T, ^\circ\text{C}$	$\rho, \text{g/cm}^3$
Run 1	
23.999	0.809 14
21.578	0.811 61
19.158	0.814 06
16.740	0.816 53
14.871	0.818 43
Run 2	
21.827	0.811 33
20.725	0.812 46
18.011	0.815 23
15.586	0.817 69
14.380	0.818 92
14.356	0.818 97
14.256	0.819 08
14.163	0.819 18
14.064	0.819 26
13.968	0.819 37
13.874	0.819 45
13.777	0.819 56
13.679	0.819 65
13.652	0.819 68
13.635	0.819 70
13.617	0.819 73
13.595	0.819 75
Run 3	
21.789	0.811 39
20.445	0.812 77
19.912	0.813 30
18.477	0.814 76
17.262	0.816 02
15.695	0.817 61
14.383	0.818 94
14.205	0.819 14
14.030	0.819 31
Run 4	
16.459	0.816 84
15.325	0.818 01
14.160	0.819 17
13.826	0.819 52
13.731	0.819 62
13.682	0.819 67
13.662	0.819 68
Run 5	
16.946	0.816 29
14.007	0.819 32
13.913	0.819 42
13.821	0.819 51
13.724	0.819 60
13.682	0.819 65
13.632	0.819 73
13.597	0.819 75

The data analysis was done by means of Bevington's nonlinear least-squares fitting program CURFIT, using standard methods of propagation of errors.³⁰

In fitting the data for sample I, T_t was held fixed at 13.581 °C. The standard deviation of the temperature, σ_T , was taken to be 0.001 °C; the standard deviation of the density, σ_ρ , was taken to be 1.4×10^{-5} . The data are well fitted by a simple linear function

$$\rho = C_1 + C_2 t$$

with $C_1 = 0.819760 \pm 0.000025$ and $C_2 = -0.29258 \pm 0.00020$. The uncertainties are given as one standard deviation. The appropriateness of this function is indicated by a $\chi_r^2 = 0.91$ (see ref 30) and by the scatter of the residuals to the fit as shown in Figure 1. Functions including an anomalous $t^{1-\alpha}$ term do not improve the fit. Thus we conclude that for sample I there is no evidence of a critical anomaly in the density.

TABLE II: Density as a Function of Temperature for Sample II, 16.29% Polystyrene in Cyclohexane

$T, ^\circ\text{C}$	$\rho, \text{g/cm}^3$
Run 1	
18.845	0.816 89
16.624	0.819 15
Run 2	
19.803	0.815 88
17.405	0.818 32
13.104	0.822 67
12.920	0.822 85
12.734	0.823 00
12.712	0.822 99
12.683	0.823 04
12.616	0.823 09
12.587	0.823 12
12.591	0.823 12
Run 3	
17.202	0.818 54
13.360	0.822 36
13.830	0.821 91
13.005	0.822 74
12.633	0.823 09
12.600	0.823 12
12.578	0.823 18
Run 4	
19.349	0.816 33
16.974	0.818 78
15.147	0.820 59
16.190	0.819 55
18.043	0.817 70

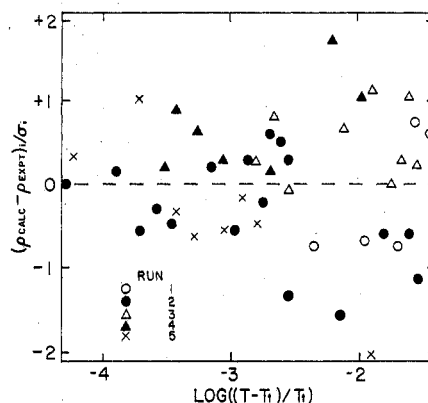


Figure 1. Residuals for the fit of the data for sample I, 15.42% polystyrene in cyclohexane, to the function $\rho = C_1 + C_2 t$, $t = (T - T_t)/T_t$. See text for constants.

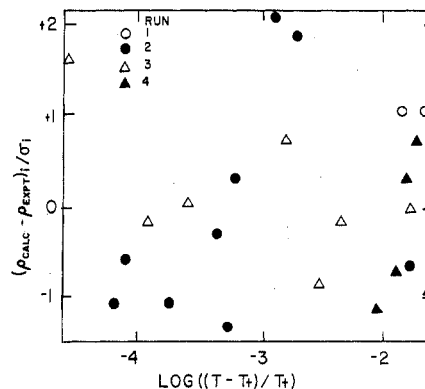


Figure 2. Residuals for the fit of the data for Sample II, 16.29% polystyrene in cyclohexane, to the function $\rho = C_1 + C_2 t + C_3 t^2$, $t = (T - T_t)/T_t$. See text for constants.

In fitting the data for sample II, T_t was held fixed at 12.572 °C, σ_T was 0.002 °C, and σ_ρ was 2×10^{-5} . The data are best fitted by a function including a quadratic term

$$\rho = C_1 + C_2 t + C_3 t^2$$

with $C_1 = 0.823\,153 \pm 0.000\,006$, $C_2 = -0.2795 \pm 0.0019$, and $C_3 = -0.306 \pm 0.085$; for this function $\chi_\nu^2 = 1.1$ and the residuals are scattered as shown in Figure 2. Thus for sample II also, $\rho(t)$ can be fitted to an analytical function, and there is no improvement in the fit if an anomalous term is used.

Discussion

It was postulated by Stauffer et al.¹³ and later confirmed by renormalization group calculations¹⁴⁻¹⁵ that the amplitude of the divergence of the correlation length near a critical point is related to the amplitudes of divergence of the thermodynamic properties. These relationships, called "two-scale-factor universality", were initially difficult to confirm because of lack of experimental precision;²⁴⁻²⁵ but recent work seems to confirm the expected relationships for both pure fluids²⁶ and liquid mixtures.²⁷⁻²⁸

If we assume the predictions of two-scale-factor universality to be valid, we can use them to estimate²⁵ the size of the anomaly in the thermal expansion in polystyrene-cyclohexane from the coefficient of the divergence of the correlation length in the same system. The correlation length ξ^+ in the one-phase region is described by

$$\xi^+ = \xi_0^+ t^{-\nu}$$

and the heat capacity per unit volume at constant pressure and composition in the one-phase region by

$$C_{px} = (A/\alpha)t^{-\alpha}$$

Then from the concept of two-scale-factor universality,¹³⁻¹⁶ there is a universal dimensionless parameter denoted by X (ref 13) or by R_ξ^+ (ref 14-16) such that

$$X = (R_\xi^+)^3/k_B = A\xi_0^3/k_B$$

where k_B is Boltzmann's constant. X or R_ξ^+ can be calculated from renormalization group theory.¹⁴⁻¹⁶ We can now relate ξ_0 to the thermal expansion α_{px} at constant pressure and composition in the one-phase region, where

$$\alpha_{px} = \frac{-1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_{px} = \frac{B}{\alpha} t^{-\alpha}$$

by using the relationship¹

$$C_{px}/(\alpha_{px}T_c) = dP/dT_c$$

between C_{px} , α_{px} , and the change of critical temperature with pressure P . Thus a knowledge of ξ_0 and X allows A to be calculated, which, with the measured value of dP/dT_c , allows the calculation of B , the coefficient of the anomaly in the thermal expansion. We use the following parameters: $\xi_0 = 5.8 \text{ \AA}$ (ref 29); $X = 0.017$ (ref 13-16); $dT_c/dP = 3.14 \text{ mK/atm}$ (ref 11).

The calculation gives $B = 1.3 \times 10^{-7} \text{ K}^{-1}$ for polystyrene-cyclohexane. Comparing B as measured for other systems (nitroethane-3-methylpentane,^{5,25} $6 \times 10^{-6} \text{ K}^{-1}$; isobutyric acid-water,⁴ $-1.3 \times 10^{-5} \text{ K}^{-1}$; methanol-cyclohexane,⁶ $2.5 \times 10^{-5} \text{ K}^{-1}$) indicates that the anomaly in polystyrene-cyclohexane will be relatively small. From our measurements, the background α_{px} will be $\sim 10^3$ times the critical α_{px} at $T - T_c = 10 \text{ mK}$. Thus our measurements are quite consistent with other thermodynamic data on

polystyrene-cyclohexane in indicating a very small critical thermal expansion anomaly.

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