Coexistence Curve of a Nonpolar Binary Fluid Mixture. Perfluoroheptane–Carbon Tetrachloride

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The refractive index as a function of temperature in the one- and two-phase region near the consolute point in the nonpolar binary fluid mixture perfluoro-n-heptane–carbon tetrachloride was measured. Thirty data points over four decades in $\epsilon = (T_c - T)/T_c$, $2 \times 10^{-5} < \epsilon < 10^{-1}$, were used to determine the coexistence curve and find the critical exponent β to have a value 0.324 ± 0.005 from a properly weighted least-squares fit of the data. The uncertainty is 3 times the standard deviation. An anomaly in the rectilinear diameter was not observed, nor were any gravity effects. However, there was some evidence for the Wegner-type correction terms reported by others recently. The critical concentration was found to be 42.14 ± 0.05 vol % perfluoroheptane. The critical temperature was 330.84 ± 0.015 K.

Introduction

It has recently become important to investigate the coexistence curve of a binary fluid mixture near the consolute point in order to determine whether binary mixtures belong to the same universality class[1] as pure fluids and the Ising model, whether the rectilinear diameter of the coexistence curve has an anomaly, whether corrections to scaling as proposed by Wegner[2] are needed, and whether amplitude relations among these corrections are observed.[3] Simple scaling[4] predicts that $\Delta\phi = A'\epsilon^\beta$, where $\epsilon = (T_c - T)/T_c$, T_c is the critical consolute temperature, β is the critical exponent, and $\Delta\phi$ is the volume fraction difference between the upper and lower phases. The volume fraction would seem to be the preferred order parameter for a binary fluid mixture since it gives a coexistence curve[5-8] which approaches the completely symmetric curve predicted by the Ising model.[9]

For some time a disparity[4] existed between the critical exponent β describing the coexistence curve of pure fluids and of binary mixtures and that from the series expansion result for the Ising (lattice–gas) model. However, recent measurements on pure fluids and binary mixtures have shown that, by including gravity effects and utilizing a correct form for extended scaling, the values of β for pure fluids and binary mixtures agree with each other[4] ($\beta = 0.316-0.329$) and with recent renormalization group calculations[10] for the Ising model ($\beta = 0.323 \pm 0.003$) and are very close to the new series expansion value[11] ($\beta = 0.328 \pm 0.006$).

The coexistence curve of perfluoroheptane–carbon tetrachloride was first studied by Hildebrand, Fisher and Benesi[12] and then by Campbell and Hickman[13] and Kyle and Reed.[14] The only recent experiments on this mixture involved a single point at 25 °C by Shinoda and Hildebrand[15] and the effect of pressure on the critical temperature by Myers et al.[16] None of these authors considered the questions posed above—particularly the shape of the coexistence curve which gives the critical exponent β.

The coexistence curve of perfluoroheptane–carbon tetrachloride was determined in this experiment close to its upper consolute point by using a prism cell to measure the bulk refractive index for the 632.8-nm He–Ne laser line. That one can use the refractive index to measure the coexistence curve is now well accepted.[17] It has been shown[8] that the difference in volume fraction between the upper and lower phases is, to a good approximation, proportional to the difference in refractive index between the two phases. Thus, the data presented and fitted in this paper are the refractive index data taken in the experiment.

A nonpolar mixture was chosen since there are very few well-documented coexistence curves for nonpolar mixtures near a consolute point. The particular mixture perfluoroheptane–carbon tetrachloride was chosen to minimize gravity effects.[18] The system reported here tends to confirm that pure fluids and binary mixtures belong to the same universality class by determing $\beta = 0.324 \pm 0.005$.

It is also interesting to note that, by the method used in this work, we are able to predict the solubilities of each component in the two phases at any temperature with great precision. Thus, one could use the mutual solubility at, e.g., 298 K to determine Hildebrand's solubility parameters, δ_1 and δ_2, for this mixture.[15,19] Without knowing

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(11) Calculated from B. G. Nickel as reported in *Phys. Today*, 33, No. 11, 18 (1980), and assuming the critical exponent equality $2\beta + \gamma = d\nu$.

(12) J. H. Hildebrand, B. B. Fisher, and H. A. Benesi, *J. Am. Chem. Soc.*, 72, 4348 (1950).

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(15) K. Shinoda and J. H. Hildebrand, *J. Phys. Chem.*, 68, 3904 (1964).

(16) D. B. Myers, R. A. Smith, J. Katz, and R. L. Scott, *J. Phys. Chem.*, 70, 3341 (1966).

(17) J. M. H. Levelt Sengers in "Experimental Thermodynamics of Nonreacting Fluids", Vol. II, B. LeNeindre and B. Vodar, Eds., Butterworths, London, 1975, p 657. The refractive index itself may have an anomaly very close to T_c, but its value is typically too small to affect this data. For a discussion of this effect, see ref 8 and 22.

(18) A. A. Fannin, Jr., and C. M. Knobler, *Chem. Phys. Lett.*, 25, 92 (1974).

(19) J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, "Regular and Related Solutions", Van Nostrand-Reinhold, New York, 1970.

precisely the refractive index at (for instance) 298 K for pure perfluoroheptane and carbon tetrachloride at 632.8 nm, and without precise density values at 298 K to determine the molal volumes, we cannot calculate the solubility parameters accurately. However, we can estimate $\delta_1 - \delta_2 = 3.05$, which agrees well with reported values.[15] These parameters could be calculated at all temperatures from the data and the fits presented here if one measures the necessary quantities described above.

Experimental Methods

Sample Preparation. The sample consisted of 41.54 vol % perfluoroheptane in carbon tetrachloride. This concentration was close to the critical composition, which was found to be 42.14%. The carbon tetrachloride was Mallinckrodt spectrophotometric-grade solvent (99.9% pure) used without further purification. Our perfluoroheptane was purchased from PCR Chemicals with mixed isomers. This perfluoroheptane was purified by washing with concentrated sulfuric acid, rinsing with distilled water, and storing over $MgSO_4$ (anhydrous). The solution was then distilled in a spinning band still with a reflux rate of about $1/_{60}$. A Hewlett-Packard gas chromatograph[20] was used to analyze the fractions; the fraction used in this experiment was found to be 99.5% pure. The fluids were placed in the cell under a dry nitrogen atmosphere.

The volume of the sample in the cell was about 7 cm³ with a small nitrogen bubble above it (<0.5 cm³). The gas bubble serves to maintain a fairly constant pressure in the cell of 1 atm.

Sample Cell and Thermostat. The sample cell and the thermostat used in this experiment were smaller versions of ones described earlier.[8] This prism cell was 1.75 in. from front to back and 2 in. high. The fluid was contained in a 0.75-in. bore and was sealed with Teflon.[8] The cell was surrounded by a separately controlled copper heat shield. The temperature-controlling circuits and thermostat were the same as described earlier.[8] The temperature-monitoring circuit was a Leeds and Northrup K-5 potentiometer with a resistance thermometer adapter allowing a precision of 10^{-7} V or 0.5 mK. We found the temperature to be stable to ± 0.001 K over 12 h. The sensor was a YSI 44004 thermistor calibrated on the International Practical Temperature Scale of 1968 to 0.01 K. Temperature gradients across the fluid were estimated to be less than 1 mK by measurements taken on matched thermistors placed above and below the fluid.

Refractive Index Measurements. The bulk refractive index was determined from measurements of the minimum deviated angle of the 632.8-nm He–Ne laser light bending through the prism-shaped sample of fluid.[8] Angles were read with a Gaertner spectrometer to a precision of 20 seconds of arc. This allowed the absolute refractive index to be determined to a precision of ± 0.0002.

Procedure. The procedure for an experimental run was to raise the temperature in steps until the critical temperature was reached, determine the transition temperature as the appearance/disappearance of the meniscus, and then lower the temperature in steps until room temperature was reached. At each step the thermostat containing the cell was shaken to assure equilibrium across the meniscus. The time from shaking the cell to taking the refractive index data depended on how close to critical the system was; this time varied from 1 h when far from T_c to several hours when close to T_c. The minimum deviated angle, ψ, was then measured for each phase (the undeviated

TABLE I: Values of the Difference in Refractive Index, Δn, and Mean Refractive Index, $\bar{n}$, below the Critical Consolute Temperature, $T_c{}^a$

$T_c - T$, K	Δn	$\bar{n}$	run
0.0063	0.0102	1.3451	1
0.010	0.0131	1.3450	3
0.018	0.0138	1.3448	2
0.021	0.0157	1.3448	1
0.021	0.0147	1.3449	3
0.034	0.0178	1.3448	2
0.044	0.0189	1.3450	3
0.045	0.0191	1.3449	2
0.045	0.0200	1.3448	1
0.059	0.0213	1.3452	3
0.093	0.0249	1.3449	1
0.101	0.0244	1.3451	3
0.113	0.0261	1.3455	2
0.223	0.0315	1.3449	1
0.320	0.0363	1.3447	1
0.427	0.0401	1.3451	1
0.536	0.0431	1.3453	1
0.630	0.0456	1.3455	1
0.806	0.0484	1.3452	1
1.040	0.0532	1.3457	1
1.087	0.0541	1.3454	2
1.601	0.0612	1.3457	2
2.075	0.0668	1.3462	1
3.152	0.0764	1.3473	3
4.181	0.0839	1.3474	2
6.158	0.0946	1.3483	1
8.255	0.1040	1.3500	3
15.210	0.1252	1.3537	3
20.168	0.1360	1.3561	3
30.538	0.1531	1.3611	3

^{a} Three different runs are reported.

angle, ψ_0, was found not to change from one data point to another but was still measured before and after each run). The standard deviation of the measured angles was typically less than their uncertainty. The refractive index (relative to air) was calculated by using

$$n = \sin\{(\psi - \psi_0 + \alpha)/2\}/\sin(\alpha/2)$$

where α is the prism angle.

We expected only very small gravity effects in this mixture.[18] Such effects should appear as a bending of the slit image near the meniscus due to the concentration gradients. We did not observe any such bending. Also we could not detect such effects in our data. The effect becomes larger as one gets closer to T_c and perhaps would be observable when within the minimum of 6 mK that we obtained for $T_c - T$.

When the mixture was within 50 mK of the transition, small bubbles were occasionally observed to form on the windows in the perfluoroheptane-rich phase that caused the slit image to be blurred. These usually disappeared when the cell was reshaken. When they did not, that data point was discarded. This effect was attributed to surface wetting as recently proposed by Cahn.[21]

Results and Analysis

Data taken on three experimental runs are listed in Table I. Data were taken at 30 temperatures in the range $2 \times 10^{-5} < (T_c - T)/T_c < 10^{-1}$. The transition temperature agreed between runs to ± 2 mK. The data agreed among runs, and whether heating or cooling.

A plot of the refractive index, n, as a function of T is shown in Figure 1 and illustrates the coexistence curve and the rectilinear diameter (mean refractive index below T_c). The average of the refractive index in the upper and lower

(21) J. J. Cahn, *J. Chem. Phys.*, **66**, 3667 (1977).

TABLE II: Summary of Parameter Values Determined by Fitting the Stated Function to the Data in Table I over the Given Region[a]

function	region, °C	T_c, °C	A_1	β	A_2	χ^2/N
$\Delta n = A_1 \Delta T^{\beta}$	$0.006 < \Delta T < 31$	57.733	0.0528 ± 0.0003	0.314 ± 0.003		3.0
	$0.006 < \Delta T < 10$	57.734	0.0526 ± 0.0003	0.324 ± 0.005		0.41
	$0.04 < \Delta T < 10$	57.732	0.0527 ± 0.0003	0.323 ± 0.003		0.47
$\Delta n = A_1 \Delta T^{\beta} + A_2 \Delta T^{\beta+1/2}$	$0.006 < \Delta T < 31$	57.737	0.0536 ± 0.0003	0.340 ± 0.005	$-1.0 \times 10^{-3} \pm 2 \times 10^{-4}$	0.37
	$0.04 < \Delta T < 31$	57.740	0.0536 ± 0.0003	0.342 ± 0.005	$-1.1 \times 10^{-3} \pm 2 \times 10^{-4}$	0.38
$\Delta n = A_1 \Delta T^{\beta} + A_2 \Delta T^{\beta+1}$	$0.006 < \Delta T < 31$	57.735	0.0527 ± 0.0002	0.329 ± 0.003	$-1.0 \times 10^{-4} \pm 2 \times 10^{-5}$	0.36

[a] ΔT is $T_c - T$. All errors are three standard deviations.
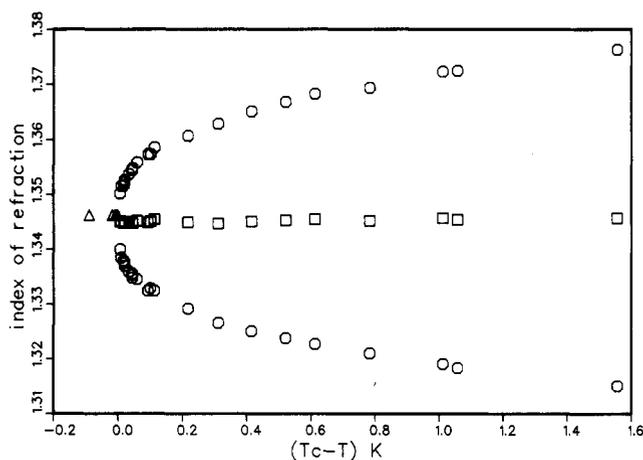

Figure 1. Coexistence curve of perfluoroheptane–carbon tetrachloride for data from Table I closest to T_c. T_c is the critical consolute temperature. The circles are the refractive index in the upper and lower phases. The squares are the mean refractive index (upper and lower phases) below T_c and the triangles are the refractive index in the one-phase region.
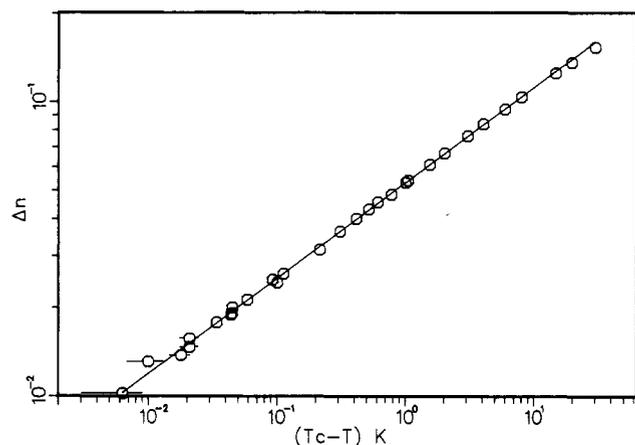

Figure 2. Shape of the coexistence curve. Δn is the difference in refractive index between the upper and lower phases. The slope of the line is β if simple scaling holds.

Figure 3. (A) Deviation (in units of σ = standard deviation) between the data and the values determined by fitting the equation $\Delta n = A_1(T_c - T)^{\beta}$ to all 30 data points. Δn is the difference in the refractive index between the upper and lower phases, $A_1 = 0.0528$, and $\beta = 0.314$. The systematic deviations indicate that additional terms are necessary. (B) Deviation between the data and the values determined by fitting the equation $\Delta n = A_1(T_c - T)^{\beta}$ to the 27 data points closest to T_c. $A_1 = 0.0526$ and $\beta = 0.324$ in this fit. The lack of systematic deviations indicates that a correction-to-scaling term is needed to fit all of the data. (Note the different vertical scale from Figure 3A.)

phases as a function of temperature was well determined (reduced χ^2 of 0.4) by a straight line of slope $(-5.5 \pm 0.1) \times 10^{-5}$ and intercept 1.3767 ± 0.0006. Thus, no observable anomaly close to T_c was observed in the diameter of the coexistence curve. Small anomalies have been reported by others.[22] The critical temperature was found to be 57.734 ± 0.015 °C (a value slightly lower than reported elsewhere[13,14,16,23]), where the uncertainty is due to calibration error (10 mK), reproducibility (2 mK), and a discrepancy between the transition temperature observed
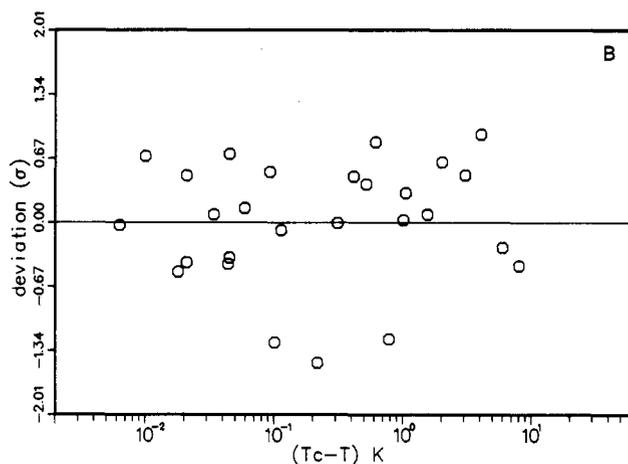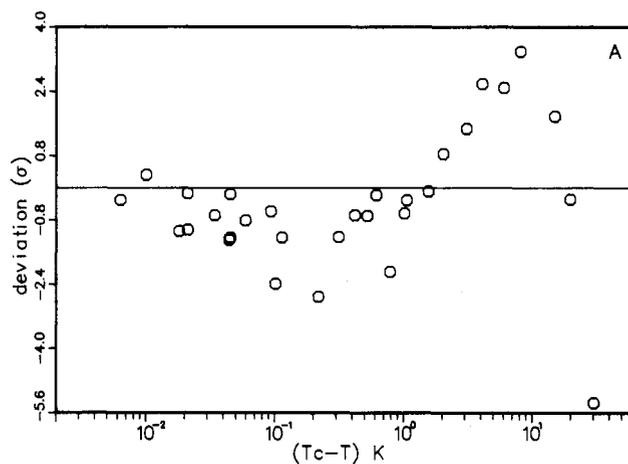
and the fitted critical temperature (3 mK; see below). By noting the difference between the refractive index above T_c and the value extrapolated from the rectilinear diameter below T_c, the critical composition could be determined[8] to be 42.14 ± 0.05 vol % perfluoroheptane.

To determine the shape of the coexistence curve and the value of the critical exponent β, a properly weighted[17] least-squares fit[24] was done on the data in Table I by varying the parameters until a minimum in the reduced χ^2 (ref 24) was found. If simple scaling holds, then $\Delta \phi \propto \Delta n = A_1(T_c - T)^{\beta}$ and a log–log plot of $\Delta n \equiv n_u - n_l$ vs. T_c

(22) See S. C. Greer and M. R. Moldover, *Annu. Rev. Phys. Chem.*, **32**, 233 (1981).
(23) C. P. Hicks et al., *Aust. J. Chem.*, **31**, 19 (1978).

(24) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, 1969.

$-T$ should give a straight line with slope β (see Figure 2). As can be seen in this figure, our data appears superficially to be well fitted by a simple scaling relation. However, a deviation plot (Figure 3A) shows systematic deviations which indicate the need for additional terms. The reduced χ^2 when using simple scaling is 3.0 where a value near 1 would indicate an acceptable fit. The values of the parameters for this fit are given in Table II. When the function was fitted to the data, the critical temperature was fixed. However, because of the uncertainty in T_c, a set of fits were performed where T_c was varied in 1-mK steps from -1 to 6 mK. The other parameters were fairly insensitive to this small change in T_c. The values of T_c reported in Table II are the values where the minimum in the reduced χ^2 occurred for the stated function.

The cause of the systematic deviation to a simple power law dependence could be either gravity effects, which become noticeable at temperatures close to T_c,[18] or corrections to scaling which become important far from T_c.[6] Thus, our data were partitioned and regions were fitted to our simple scaling formula. As shown in Table II, we found a good fit with no systematic deviations (see Figure 3B) when we excluded the three points furthest from T_c. This gave us a value of $\beta = 0.324 \pm 0.005$ and a reduced χ^2 of 0.41. Excluding the points close to T_c did not improve the fit, and hence we infer that gravity effects were not significant in this experiment.

Although there are only three points sufficiently far from T_c to observe corrections to scaling, fits were performed to the predicted functional form:[6]

$$\Delta n = A_1 \Delta T^\beta + A_2 \Delta T^{\beta+\Delta} + A_3 \Delta T^{\beta+2\Delta} + \ldots$$

where Δ is predicted to be 0.5. Others have found one correction term essential to obtaining a good fit when including data far from T_c.[4] All of our data could be fitted very well by using extended scaling with one additional term. A properly weighted nonlinear least-squares program similar to CURFIT[24] and written in Basic for our microcomputer was used to perform these fits. The value of Δ was fixed at 0.5. The results of these fits are shown in Table II. All of the fits were equally good (as shown by the reduced χ^2 values of $\simeq 0.37$), but, when $\Delta = 0.5$ ($A_3 = 0$), then β was large (0.34). If $2\Delta = 1.0$ (when $A_2 = 0$), then β was more reasonable (0.329) and in agreement with the value found for the subset of data closer to T_c. (That this first correction term has an exponent $\beta + 1$ could also imply an analytic correction instead of a Wegner correction.) When two correction terms are used, the fitted value of β is 0.33, but the parameter values are not well determined because of the few points involved and hence this result is not included in Table II.

Conclusion

We have performed the first precise measurements on the coexistence curve of the nonpolar binary fluid mixture perfluoroheptane–carbon tetrachloride near its consolute point. Neither gravity effects nor any anomaly in the rectilinear diameter was apparent in this system. The critical temperature was found to be 57.734 °C with a critical composition of 42.14 vol % perfluoroheptane. The critical exponent β was determined to be 0.324 ± 0.005, which agrees well with predicted values.[4,10,11] We could fit the predicted functional form for extended scaling to all of our data with the extended scaling exponent $2\Delta = 1$. Our data are not sufficiently numerous or precise to give much confidence to this value of Δ or to the amplitude of the correction term(s).