RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 27, NUMBER 5 MAY 1983

Impurity effects in a near-critical binary-fluid mixture

J. L. Tveekrem* and D. T. Jacobs
Department of Physics, The College of Wooster, Wooster, Ohio 44691

(Received 16 August 1982)

Measurement of the coexistence curve of the binary-fluid mixture methanol-cyclohexane with increasing amounts of water impurity showed essentially a linear dependence of the critical temperature, critical exponent β, and critical concentration with impurity. Adding 0.10 vol% water impurity caused the critical temperature to increase by 3.8 K, the effective critical exponent β to increase by 0.0021, and the critical concentration, as measured by volume fraction of methanol, to increase by 0.004. Surface wetting was also observed in the impure samples and observations are reported on one impure mixture.

It is commonly assumed that impurities have an insignificant effect on critical phenomena in fluids, providing only an uninteresting shift in the critical temperature. However, various investigators have reported not only substantial shifts in the critical temperature,[1-4] but also changes in the critical composition[3,5] and critical exponents.[6,7] Furthermore, impurities affect the amplitude of the heat-capacity anomaly[5] and are expected to affect other amplitudes as well. Investigators have also used impurities to move the critical point when measuring surface wetting.[4] Impurities have a significant impact on experimental and theoretical work in critical phenomena.

To predict the critical exponent dependence on impurity, Fisher and Scesney[8] define a "dilution parameter" $X=f(T_c-T_{c0})/T_{c0}$, where T_c is the critical temperature of the impure system, T_{c0} is the critical temperature of the pure system, and f is a constant of order unity whose value depends on the precise definition of X. Fisher and Scesney argue f should be between 0.6 and 0.9; we take f to be 1 in this paper. The critical exponent β is predicted[8] to increase linearly with X: $\beta=\beta_0[1+X\alpha'/(1-\alpha')]$ where β_0 is the coexistence curve exponent for the pure system, and α' is the heat-capacity exponent for the pure system. In the limit as X goes to 1, the exponent β approaches the "fully renormalized" value.

Experiments investigating impurity effects suffer from one or more of the following difficulites: only one impurity level is measured so no clear trend can be established, relatively large amounts of impurity are used, the amplitude of the measured effect becomes too small to determine a value for the critical exponent, and/or the location of the critical point is uncertain.

This experiment provides the first systematic measurement of impurity effects on the critical temperature, critical composition, and critical exponent β in a binary-fluid mixture. Precise measurements were made on the coexistence curve of methanol-cyclohexane with small amounts of water impurity. These measurements revealed appreciable shifts in the critical parameters. We also report on observations of surface wetting in one of the impure mixtures.

Matheson, Coleman, and Bell spectrophotometric grade methanol and cyclohexane were used without further purification. The fluids were put into a cell which was sealed to prevent evaporation or contamination of the fluids. Before filling, the cell was baked overnight and allowed to cool in a dry nitrogen atmosphere. The composition of the "pure" mixture was measured to be 29.3 ± 0.1 wt.% methanol with a total volume of 6.2 ml. After the coexistence curve was determined on this "pure" sample, subsequent coexistence curves were measured after introducing small (12–25-μl) amounts of distilled water into the cell. Four coexistence curves were thus measured: the "pure" original mixture, 0.4%, 0.6%, and 0.8% by volume added water. The most impure mixture was analyzed using Karl Fischer titration[9] and contained (0.85 ± 0.03)% by volume water. The composition of the mixtures (wt.% methanol) was not changed significantly by the small amounts of water added. Using the same mixture and varying only the water content ensured that any systematic differences between data sets must be due to the water impurity.

In order to determine the coexistence curve, the concentration of one fluid in each phase must be measured as a function of temperature. The refractive index was used as a measure of volume fraction, the order parameter which usually provides a more symmetric coexistence curve[10] in binary-fluid mixtures. It has been shown[11] that the refractive-index difference between two phases is proportional to the difference in volume fraction between the phases. The refractive index of each phase was determined at 632.8 nm with a resolution of 0.000 15 and with a reproducibility typically better than that. Refractive-index data were taken approximately every 3 to 24 h with longer times necessary for fluid equilibrium when close to T_c. The cell was shaken after temperature equilibrium to assure efficient mixing across the meniscus. The temperature was controlled within maximum excursions of ±1.5 mK over 24 h. Details on the cell, refractive-index measurement, and temperature control are given elsewhere.[12]

Surface wetting, which has been observed[13,14] in several systems lately, became noticeable in our experiment as water impurity was increased. In the mixture containing 0.8% added water, a fairly flat bubble appeared in the upper phase against the glass window when far below the critical temperature ($19\ \mathrm{K} < T_c - T < 49\ \mathrm{K}$). Over the region $3.4\ \mathrm{K} < T_c - T < 19\ \mathrm{K}$ no bubbles were observed in either phase. When closer than 3.4 K to critical, one to three spherical bubbles with a mean diameter of 0.4 mm appeared on the bottom of the cell. These spherical bubbles persisted in the one-phase region ($-1.5\ \mathrm{K} < T_c - T < 3.4\ \mathrm{K}$) even after vigorous shaking.

Preferential wetting of the lower phase on the glass and aluminum cell wall was also observed to change with temperature in this same mixture. Such wetting was observable both as a bending of the meniscus between the phases at the wall and by total internal reflection. The reflection occurred in the upper phase at the wall when the lower refractive index, lower phase wet the wall. A gradual transition from complete wetting of the upper phase by the lower phase when well below critical ($7\ \mathrm{K} < T_c - T$) to no wetting when close to critical ($T_c - T < 0.4\ \mathrm{K}$) was observed. This is inconsistent with the predicted[15] and observed[14] behavior of complete wetting close to T_c and partial wetting far from T_c. We reconcile this difference by assuming that the impurity (water) preferentially wets the wall over either phase when the system is close to critical. This would be consistent with Rice's contention[16] that impurities affect surface tensions and with our observations of the critical temperature drifting with time.

The critical temperature in the impure mixtures decreased slightly with time. In the 0.8% mixture, the critical temperature had the largest drift: about 12 mK per day. We experimentally determined that the critical temperature was drifting by monitoring the location of the coexistence curve with time. This small decrease in T_c is attributed to water adsorbing gradually onto the walls and being thus removed from the mixture. Only 18 nl of water per day would have to be adsorbed to account for this drift. It is also possible that the spherical bubbles present were rich in water impurity, but their composition could not be deduced in our cell.

Each coexistence curve consisted of from 15 to 21 pairs of refractive indices as a function of temperature. The small drift in T_c was taken into account in presenting and fitting the data reported here. Those points closest to T_c for each curve are plotted in Fig. 1. The expected dramatic increase in T_c is readily observable by the relative vertical displacements of the coexistence curves. Each curve was fitted using a properly weighted linear least-squares routine[17] by the simple scaling relation[10] $\Delta n = Bt^{\beta}$, where Δn is the difference in refractive index (proportional to volume-fraction difference) between the upper and lower phases, B is an amplitude, t is the reduced temperature: $t = (T_c - T)/T_c$, and β is the effective critical exponent. All four curves were fitted well by this relation over the region $0 < T_c - T < 40$ K with small reduced χ squares and no systematic deviations (see Table I).

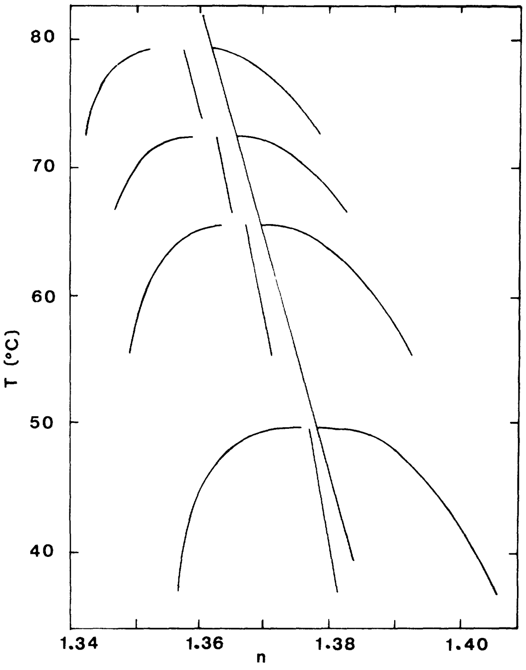

FIG. 1. Coexistence curves for methanol-cyclohexane with successive amounts of an impurity (water) added. For clarity, the individual points taken on each curve are not shown but are merely connected to form the curves illustrated. The vertical shift of the coexistence curves is due to the change in critical temperature; the lowest impurity sample has the lowest T_c (see Table I). The increasing separation between the diameters (short lines) and one-phase (long straight line) at the critical temperatures indicates an increase in the critical composition.

The critical temperature was determined by performing successive fits and finding the minimum in the reduced χ square while varying T_c. The critical temperature increased linearly with impurity [see Fig. 2(a)] by +3.8 K per 0.1 vol% water added to the mixture, which is much larger than reported earlier by Jones and Amstell.[1] Our results are consistent with previous investigations[1-4] which show that impurities soluble in only one component raise the critical temperature for an upper consolute point. Most impurities which are soluble in both components

TABLE I. Parameters determined from analyzing the coexistence curve for four mixtures of methanol-cyclohexane with water impurity over the temperature range t using simple scaling. χ^2 is the reduced χ square (Ref. 17). ϕ_c is the critical volume fraction determined from Fig. 1 as described in the text. One standard deviation errors are indicated in parentheses. The amplitude B in the simple scaling fits was found to be a constant 0.143 ± 0.002 as expected from the theory (Ref. 8).

% Volume water (±0.1)	Temperature range t	T_c (°C) (±0.015)	β (±0.002)	χ^2	ϕ_c (±0.004)
0.05	3×10^{-6}–7×10^{-2}	49.725	0.325	0.88	0.302
0.45	6×10^{-5}–10^{-1}	65.597	0.338	0.45	0.319
0.65	2×10^{-4}–10^{-1}	72.494	0.338	0.77	0.323
0.85	5×10^{-4}–10^{-1}	79.465	0.344	0.62	0.331

lower the critical temperature.[2] The critical temperature has also been found[2] to change linearly with small amounts of impurity—particularly for impurities which raise T_c. The dilution parameter X is then also linear with impurity added; an addition of 0.04% water corresponds to an increase in X of 0.050.

The effective critical exponent β found using simple scaling (Table I) changed with impurity much more than was anticipated. β increased approximately 0.0021 for each 0.1% by volume added water. Figure 2(b) shows a comparison between our values and those calculated using Fisher's[8] theory. Goldburg and Pusey[6] also found a larger dependence of the critical exponent γ on impurity than predicted, when using very large amounts of impurity (50%-mole fraction). Zollweg[7] has observed a fully renormalized value of β in the ethanol-water-chloroform system at the Plait point.

The effective exponent β has been experimentally determined[10] in binary-fluid systems to be the same as the asymptotic ($T \rightarrow T_c$) exponent over the range of reduced temperatures studied here. Fisher and Scesney[8] found the temperature range used to fit coexistence curve data to not significantly affect their predicted behavior for β. Nevertheless, correction to scaling fits were attempted to determine if values of β consistent with Fisher's theory[8] could be obtained. Two correction terms[10] were needed ($\Delta n = Bt^{\beta} + Ct^{\beta+(1/2)} + Dt^{\beta+1}$) when β was fixed at the predicted value in order to fit the data as well as simple scaling had done. The need for correction terms should be evident by systematic deviations of our data from a simple scaling fit. The lack of such deviations leads us to have more confidence in the values of β as determined by simple scaling and presented in Table I.

The long straight line in Fig. 1 connects the one-phase points for the four data sets and indicates that the overall composition (i.e., volume methanol divided by total volume) of the mixture did not change appreciably. The negative slope reflects the temperature dependence of the refractive index. If the critical composition were constant, the separation between the diameter and the one-phase line at the critical temperature would be the same for each coexistence curve. Since the overall composition was constant, the increasing separation means the critical composition changed with impurity.

To calculate the change, the separation in refractive index was taken as the one-phase refractive index minus the diameter refractive index at the critical temperature. The refractive-index separation was converted to a volume-fraction change using the proportionality derived elsewhere.[11] The proportionality constant was weakly temperature dependent and

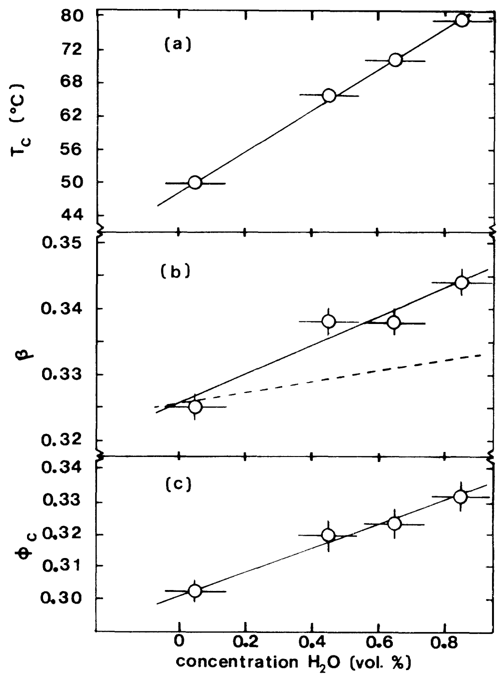

FIG. 2. Impurity effect on (a) the critical temperature; (b) critical exponent β, the dashed line from Fisher's theory (Ref. 8); and (c) critical concentration (volume fraction of methanol). Error bars are one standard deviation.

found to be 9.87 ± 0.02 for this mixture. The volume-fraction change was then added to the overall composition to find the critical composition. The results are presented in Table I and Fig. 2(c). The critical volume fraction of methanol increased by 0.004 per 0.1 vol% water added. Bak and Goldburg[3] have also noted a change in critical composition with impurity when studying phenol and water. The critical composition change is particularly important in experiments measuring amplitudes since they require a sample at its critical composition.

Impurities are not confined to causing a shift in the critical temperature. The impurity effects may or may not be small, depending on the system, but they are as important to consider as gravity effects or other complicating influences, especially when studying amplitudes.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are grateful to Professor S. C. Greer for helpful comments and to Bob Cohn for analyzing our mixture for water content.

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[*] Present address: Department of Chemistry, University of Maryland, College Park, MD 20742.

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