

Acetone impurity effects on the binary fluid mixture methanol–cyclohexane

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Measurements on the coexistence curves of the binary fluid mixture methanol–cyclohexane with increasing amounts of acetone impurity showed essentially linear changes in the critical temperature and critical concentration with impurity. Adding 1.0% acetone impurity caused the critical temperature to decrease by 3.4 K, the effective critical exponent β to increase and the critical concentration, as measured by volume fraction methanol, to decrease by 0.005.

I. INTRODUCTION

The mutual miscibilities of pure liquid–liquid mixtures have been well characterized as a critical phenomena.^{1,2} Liquid–liquid phase transitions have been observed by a number of investigators^{2–6} over the years. The highest temperature where phase separation occurs is known as the (upper) critical consolute point. It is characterized by a critical temperature and a critical composition. For any pair of fluids that has a critical point, the mutual miscibility of the liquids produces a coexistence curve that has a universal shape. The location of the critical point depends on the components used, but the shape of the curve is common. There is an advantage in studying such universal quantities as the critical exponents since they remain invariant; thus, information gained on one fluid mixture can be applied to all.⁷

Theoretical predictions of impurity effects on binary fluid mixtures have focused on two effects: (1) the critical temperature and (2) the critical exponents. The critical temperature effect has been explained by various means^{8,9} but these provide more interpretation than prediction.¹⁰ For small amounts of impurity, the critical temperature is expected to change linearly. Impurity effects on critical exponents are explained by a “mobile electron Ising ferromagnet” model.¹¹ This is appropriate since ferromagnets are in the same universality class as binary fluids, and impurities in fluids are not bound in space. This theory utilizes the critical temperature dependence as one measure of the system’s susceptibility to impurities. A dilution parameter x is defined: $x = f(T_c - T_{c0})/T_{c0}$, where $T_c(T_{c0})$ is the critical temperature of the impure (pure) system and f is a constant of order unity. A given critical exponent is expected to increase linearly with x . In the limit as $x \rightarrow 1$, the exponent approaches its “fully renormalized value.”¹¹

Several experiments have been done on the effect of impurities on the critical temperature. Typically, impurities that are soluble in only one component raise the critical temperature linearly^{8–10,12–14}; impurities soluble in both components tend to lower the critical temperature.¹⁰ The coexistence curve was not directly used as a means of determining the critical temperature in any of these experiments. The method of mapping the coexistence curve yields much more precise values of the critical temperature, since the influence of the prepared fluid composition can be eliminated. Since

the critical composition is also affected by impurities, it is important to utilize just such a technique, which is independent of the composition, for determining T_c .

The amplitudes and critical exponents are also affected by impurities. Goldburg and Pusey¹⁵ found the critical exponent γ to change when using very large amounts of impurity (50% mole fraction). Zollweg, and Wolk *et al.* have both observed¹⁶ a fully renormalized value of β in ternary mixtures at the Plait point. Bloeman *et al.*¹⁷ and Anisimov *et al.*¹⁸ have observed an impurity effect on the amplitude of the heat capacity anomaly and some effect on the critical exponent α . However, neither group could determine a value for α when impurities were present. Such experiments assume the system to be at the critical point, which implies the correct critical composition as well as critical temperature. However, Bak and Goldburg¹³ have observed an impurity effect on the critical composition. Thus, it is possible for experiments done with impurities using the critical composition of pure systems to be not sufficiently close to the true critical point to determine precisely either the amplitude or the critical exponent.

In a previous experiment,¹⁹ we investigated the effect of a water impurity on the critical temperature, composition, and exponent β in the system methanol–cyclohexane. Water is an impurity soluble in only one of the components used, and, as others have observed,^{8–10,12–14} produces a linearly increasing critical temperature with impurity concentration. A linear increase in the critical composition was also apparent. The effective critical exponent β increased more rapidly than expected from the theory, but the effect of correction-to-scaling terms^{2,20} on the theory cloud is applicability.

This paper describes a subsequent experiment: the effect of an acetone impurity on the critical temperature, critical composition, and critical exponent β in the binary fluid mixture methanol–cyclohexane. Acetone is soluble in both components and thus is expected to lower T_c . Small amounts of acetone impurity did result in appreciable shifts in the critical parameters.

II. EXPERIMENTAL DETAILS

Spectrophotometric grade methanol (J.T. Baker) and cyclohexane (Kodak) were used without further purification to prepare the “pure” sample. The fluids were put into a cell which was sealed as before¹⁹ to prevent evaporation or contamination. The composition of the pure mixture was measured to be 29.6 ± 0.1 wt. % methanol with a total volume

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of 6.8 ml. After the coexistence curve was determined on this pure sample, subsequent coexistence curves were measured after introducing small amounts of spectrophotometric grade acetone (with a negligible water content—0.1%) into the cell. Four coexistence curves were thus measured: the pure original mixture, 0.52%, 1.05%, and 1.53% by volume added acetone. The composition of the mixtures (wt. % methanol) was not changed significantly by the small amounts of acetone added. Using the same mixture and varying only the acetone content ensured that any systematic differences between data sets resulted from the acetone 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 curve² in binary fluid mixtures. It has been shown⁵ 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 3–24 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.⁶

III. EXPERIMENTAL OBSERVATIONS

Surface wetting, which has been observed^{21,22} in several systems lately, was noticeable in our experiment and changed character as acetone impurity was increased. By observing the phases against the aluminum side wall and the curvature of the meniscus between the lower and upper phases, we could make qualitative observations of wetting. The lower phase has a lower refractive index than the upper phase. This lower phase preferentially wets the walls and completely surrounds the upper phase when at temperatures well below critical. Such complete wetting could be observed not only by the curvature of the meniscus but also by the total internal reflection which occurred at the side wall. When close to the critical point, this wetting disappeared: the meniscus between the upper and lower phases had no curvature, nor was there any total internal reflection at the side wall. The location of the transition from “complete” to “no” wetting changed roughly linearly with impurity. In the pure sample, complete wetting was observed for all temperatures below 5° from critical; for the 1.5% impure sample complete wetting occurred for $T_c - T > 0.75^\circ$. No wetting was observed when within 0.75° of critical for the pure sample and when within 0.3° for the 1.5% impure sample. The transition region was gradual and could be monitored by the height above the meniscus of the horizontal line demarcating total internal reflection. That complete wetting occurs far from T_c while there is no apparent wetting close to T_c is similar to our previous observations,¹⁹ yet contrary to what

has been predicted²³ and observed^{21–22} on other systems. It is possible that the upper phase is still wetted when close to the critical point by a film of the lower phase that is too thin for total internal reflection to take place.

It is not clear how thick the films on a side wall may become. For an approximate thickness, one can use the ellipsometry results²² for films lying on top of the upper phase and measured to be no more than 100 nm. This would intrude a lower-phase film that is 10^{-5} of the optical path length of the bulk upper phase. If the film wets the glass windows to a uniform thickness, then the film would only shift the light but not change the refracted angle. The curvature of the film at the air meniscus and at the meniscus between the phases would only shift the light vertically. Differential wetting between the aluminum side walls and the glass could deflect the beam horizontally; however, the film is very thin and no qualitative difference in wetting was observed. Thus, these films did not affect our refractive index measurements within experimental error.

The critical temperature in the 1.5% impure mixture increased slightly with time: about 5 mK/day. We experimentally determined that the critical temperature was drifting by monitoring the location of the coexistence curve with time. This small increase in T_c is attributed to a tiny leak in the vapor phase which would have resulted in a total loss of 0.1% of the fluid during the time the measurements used in this paper were taken. The data used here include only the early points for this impure sample so that the composition did not vary within its experimental error.

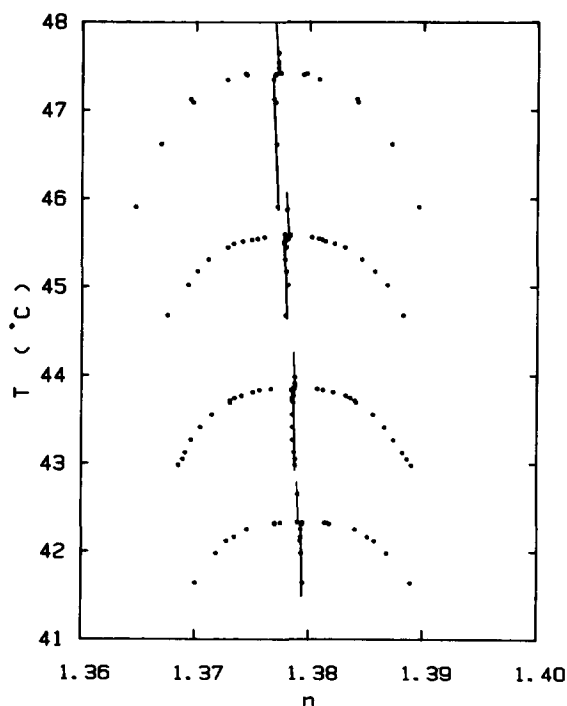


FIG. 1. Coexistence curves for methanol-cyclohexane with successive amounts of an impurity (acetone) added. The vertical shift of the coexistence curves is due to the change in critical temperature; the lowest impurity sample has the highest T_c (see Table I). A decrease in the critical composition is indicated by the decreasing separation between the diameters (longer straight lines) and the one phase (shorter lines) at each mixture's critical temperature.

IV. DATA AND RESULTS

Each coexistence curve consisted of from 15–20 pairs of refractive indices as a function of temperature. Those points closest to T_c for each curve are plotted in Fig. 1. The expected dramatic decrease in T_c is readily observable by the relative vertical displacements of the coexistence curves. Because of the small leak in the 1.5% impure sample, insufficient data were obtained on that sample to determine β . A properly weighted linear least squares routine²⁴ was used to fit the simple scaling relation² $\Delta n = Bt^\beta$ to each remaining curve. 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. The pure and 0.5% sample coexistence curves were fitted well by this relation over the region $0 < T_c - T < 20$ K with small reduced chi-squares and no systematic deviations. (See Table I.) The 1.0% impure sample showed systematic deviations when all 19 points were fitted using simple scaling. When the two points furthest from T_c ($T_c - T > 10^\circ\text{C}$) were eliminated, the fit was good with no systematic deviations.

The critical temperature was determined by performing successive fits and finding the minimum in the reduced chi-square while varying T_c . The critical temperature decreased linearly with impurity (see Table I) by +3.4 K per 1.0% acetone added to the mixture, which is much larger than reported earlier by Jones and Amstell.¹² Our results are consistent with previous investigations^{8–10,12–14} which show that impurities soluble in both components tend to lower the critical temperature while impurities soluble in only one component raise the critical temperature for an upper consolute point. The critical temperature has also been found¹⁰ 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; in this experiment, an addition of 0.5% acetone corresponds to an increase in x of 0.056.

The effective critical exponent β found using simple

TABLE I. Parameters determined from analyzing the coexistence curve for four mixtures of methanol-cyclohexane with acetone impurity over the temperature range t using simple scaling. The simple scaling fit to the 1.05% acetone sample excludes the two data points furthest from T_c . The effective critical exponent β is determined from simple scaling fits and χ^2 is the reduced chi-square (Ref. 24). ϕ_c is the critical volume fraction of methanol 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 0.145 ± 0.002 —a constant as expected from the theory (Ref. 11).

% Volume acetone (± 0.1)	0.00	0.52	1.05	1.53
Temperature range, t	$2 \times 10^{-6} \rightarrow$ 6×10^{-2}	$4 \times 10^{-5} \rightarrow$ 4×10^{-2}	$5 \times 10^{-4} \rightarrow$ 3×10^{-2}	$3 \times 10^{-5} \rightarrow$ 3×10^{-2}
T_c ($^\circ\text{C}$) (± 0.015)	47.410	45.560	43.853	42.33
β (± 0.002)	0.329	0.330	0.337	...
χ^2	0.44	0.23	0.18	...
ϕ_c (± 0.002)	0.304	0.301	0.299	0.296

scaling (Table I), changed with impurity much more than was anticipated. The expected change in β using Fisher's theory¹¹ is less than 0.001. Our previous experiment¹⁹ using water as an impurity also found much larger changes in β than expected. Goldberg and Pusey¹⁵ as well found a larger dependence of the critical exponent γ on impurity than predicted. Others¹⁶ have observed a fully renormalized value of β ($= 0.37$) at the Plait point.

Fisher and Scesney¹¹ found the temperature range used to fit coexistence curve data to affect their predicted behavior for β insignificantly. However, because of theoretical predictions and experimental verifications,²⁴ correction to scaling fits were attempted to determine if values of β consistent with Fisher's theory¹¹ could be obtained. The value of β was fixed at 0.328 and correction terms² were added

$$\Delta n = Bt^\beta + Ct^{\beta+1} + Dt^{\beta+1} + \dots$$

until the data were fitted as well as simple scaling had done. Two correction terms were necessary to improve the fits of the pure and 0.5% impure data. Two correction terms also allowed all the 1.0% impure data to be fitted with a small reduced χ^2 (0.4) and little systematic deviations. The lack of correction-to-scaling in theoretical predictions of impurity effects on exponents, coupled with the small number of points sufficiently far from T_c on these curves, precludes any firm conclusion on the impurity dependence of the exponent.

The short straight lines in Fig. 1 connecting the one phase points for the four data sets are collinear and indicate that the overall composition (i.e., volume methanol/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 within our experimental error, the increasing separation means the critical composition changed with impurity level. This critical composition can essentially be determined independently

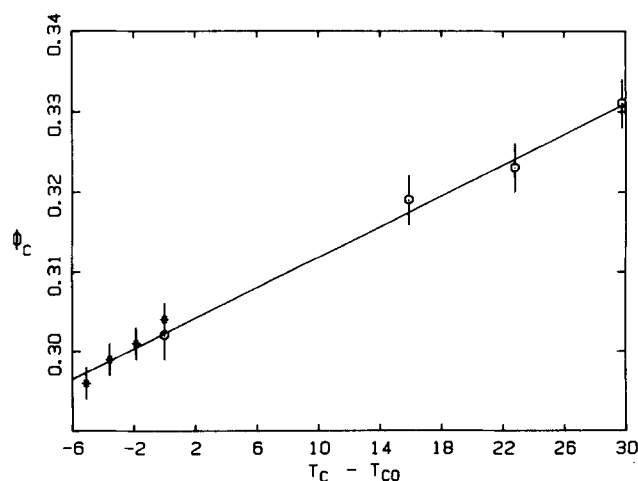


FIG. 2. The critical composition ϕ_c (volume fraction methanol) dependence on the critical temperature shift due to added impurity. The circles are from Ref. 19 when water was added as an impurity in methanol-cyclohexane. The stars are from this work (acetone impurity).

of the critical temperature.

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.^{5,19} The volume fraction change was then added to the overall composition to find the critical composition. The results are presented in Table I; the critical volume fraction of methanol decreased by 0.005 per 1.0 vol % acetone added. Bak and Goldburg¹³ have also noted a change in critical composition with impurity when studying phenol and water but did not quote a value. Our previous results¹⁹ also indicated a linear change in critical composition with water impurity. A universal dependence is noted when comparing the critical composition in that previous data with this experiment (see Fig. 2). The critical composition ϕ_c appears to depend linearly on the dilution parameter x or, equivalently, on the shift in critical temperature:

$$(\phi_c - \phi_{c0})/\phi_{c0} = k(T_c - T_{c0})/T_{c0},$$

where $k = 1.0$ as determined from the data in Fig. 2. Should this be further verified, it would greatly help experimenters in preparing their samples at the critical composition. The critical composition change is particularly important in experiments seeking to verify amplitude relationships which require the system to be at the critical point.

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- ¹A. L. Sengers, R. Hocken, and J. V. Sengers, *Phys. Today* **30** (12), 42 (1976); S. C. Greer, *Acc. Chem. Res.* **11**, 427 (1978); G. Ahlers, *Rev. Mod. Phys.* **52**, 489 (1981); K. G. Wilson, *Sci. Am.* **241** (2), 158 (1979); J. F. Nagle and H. C. Scott, *Phys. Today* **31** (2), 38 (1978).
- ²S. C. Greer and M. R. Moldover, *Annu. Rev. Phys. Chem.* **32**, 233 (1981).
- ³S. C. Greer, *Acc. Chem. Res.* **11**, 427 (1978).
- ⁴S. C. Greer, *Phys. Rev. A* **14**, 1770 (1976).
- ⁵D. T. Jacobs, D. J. Anthony, R. C. Mockler, and W. J. O'Sullivan, *Chem. Phys.* **20**, 219 (1977).
- ⁶D. T. Jacobs, *J. Phys. Chem.* **86**, 1895 (1982).
- ⁷J. V. Sengers, in *Phase Transitions—Cargèse 1980*, edited by M. Levy, J. C. LeGuillou, and J. Zinn-Justin, (Plenum, New York, 1982).
- ⁸B. J. Hales, G. L. Bertrand, and L. G. Hepler, *J. Phys. Chem.* **70**, 3970 (1966).
- ⁹O. K. Rice, *J. Chem. Phys.* **64**, 4362 (1976).
- ¹⁰R. B. Snyder and C. A. Eckert, *J. Chem. Engin. Data* **18**, 282 (1973).
- ¹¹M. E. Fisher and P. E. Scesney, *Phys. Rev. A* **2**, 825 (1970).
- ¹²E. L. Eckfeldt and W. W. Lucasse, *J. Phys. Chem.* **47**, 164 (1943); D. C. Jones and S. Amstell, *J. Chem. Soc. (London)* **1930**, 1316.
- ¹³C. S. Bak and W. I. Goldburg, *Phys. Rev. Lett.* **23**, 1218 (1969).
- ¹⁴M. R. Moldover and J. W. Cahn, *Science* **207**, 1073 (1980); O'D. Kwon, D. Beaglehole, W. W. Webb, B. Widom, J. W. Schmidt, J. W. Cahn, M. R. Moldover, and B. Stephenson, *Phys. Rev. Lett.* **48**, 185 (1982).
- ¹⁵W. I. Goldburg and P. N. Puse, *J. Phys. (Paris), Colloq.* **33**, C1-105 (1972).
- ¹⁶J. A. Zollweg, *J. Chem. Phys.* **55**, 1430 (1971); L. E. Wold, Jr., G. L. Pruitt, and G. Morrison, *J. Phys. Chem.* **77**, 1572 (1973).
- ¹⁷E. Bloeman, J. Thoen, and W. Van Dael, *J. Chem. Phys.* **75**, 1488 (1981).
- ¹⁸A. Anisimov, A. V. Voronel, and T. M. Ovodova, *Sov. Phys. JETP* **34**, 583 (1972).
- ¹⁹J. L. Tveekrem and D. T. Jacobs, *Phys. Rev. A* **27**, 2773 (1983).
- ²⁰J. M. H. Sengers and J. V. Sengers, in *Perspectives in Statistical Physics*, edited by H. J. Raveche, (North-Holland, Amsterdam, 1981).
- ²¹C. Franck and S. E. Schantterly, *Phys. Rev. Lett.* **48**, 763 (1982); D. Beaglehole, *J. Chem. Phys.* **73**, 3366 (1980); D. Beysens and S. Leibler, *J. Phys. (Paris)* **43**, L133 (1982).
- ²²D. W. Pohl and W. I. Goldburg, *Phys. Rev. Lett.* **48**, 1111 (1982); J. W. Schmidt and M. R. Moldover, *J. Chem. Phys.* **79**, 379 (1983); M. R. Moldover and R. W. Gammon (to be published).
- ²³J. W. Cahn, *J. Chem. Phys.* **66**, 3667 (1977); G. F. Teletzke, L. E. Scriven, and H. T. Davis, *J. Chem. Phys.* **78**, 1431 (1983); H. Nakanishi and M. E. Fisher, *Phys. Rev. Lett.* **49**, 1565 (1982); E. Brezin and S. Leibler, *Phys. Rev. B* **27**, 594 (1983).
- ²⁴P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).