

Cloud-Point Measurements for the Mixture Tertiary Butyl Alcohol, Secondary Butyl Alcohol, and Water¹

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Cloud point measurements are presented for the ternary mixture of tertiary butyl alcohol (tBA), secondary butyl alcohol (sBA), and water. At a zero tBA concentration the system displays a large immiscibility gap, but with an increasing proportion of tBA, the gap pinches off at a critical double point to a closed loop and a lower gap, then the loop shrinks and disappears at a hypercritical point, leaving only the lower gap. This behavior is shown to be semiquantitatively similar to the behavior of sBA/water with increasing pressure. If a pseudobinary assumption is made, the shape of the cloud-point curves can be shown to be qualitatively similar to coexistence curves in binary mixtures, with an exponent of $\beta \approx \frac{1}{2}$. Near the critical double point this exponent appears to double.

KEY WORDS: aqueous systems; alcohol; cloud points; phase equilibria.

1. INTRODUCTION

Liquid mixtures display a fascinating variety of miscibility-immiscibility phase transition phenomena [1, 2]. These phenomena are important not only from a practical point of view in various chemical engineering applications but also from a fundamental standpoint regarding the molecular sources of the behavior and the details of the phenomena.

This paper presents cloud point and critical point data for a ternary mixture of tertiary butyl alcohol (tBA), secondary butyl alcohol (sBA), and water. The cloud point is the temperature at which the system nucleates from one liquid phase to two. The tBA is totally miscible with water at all equilibrium temperatures, whereas sBA is only partially soluble with water. It is reasonable to argue that mixtures of these two butyl alcohol isomers with water should display varying degrees of miscibility. This is in fact

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borne out by the data presented here. The interesting feature of these phase diagrams is that the butyl alcohol mixtures show, in sequence with increasing tBA concentrations, a large region of immiscibility with a single upper critical point, a closed-loop two-phase region above a second two-phase dome, and finally, shrinkage of the closed loop, leaving only the lower two-phase dome. At concentrations between these three major regions, double critical points occur. This behavior is completely analogous to the phase diagram of sBA with water with increasing pressure [3].

Such closed-loop and multi-critical point phase diagrams have been the subject of both theoretical and experimental investigations in the past. A qualitative description [4] of the interactions responsible for such behavior as presented here is that at high temperatures entropy dominates the free energy and the system mixes. As the temperature is lowered the mixing entropy term becomes less dominant and energetic dislike of the two components causes them to separate. The reluctance to miscibility of the phases at still lower temperatures is caused by favorable directional bonding (hydrogen bonding in the butyl alcohol plus water mixture), which is now entropically allowed at low temperature. Finally, a second phase separation at still lower temperatures may occur due to more favorable directional bonding between like molecules [5].

These qualitative ideas have been incorporated into theoretical models of these systems. These models include the decorated Ising lattice model of Wheeler and Anderson [6-8], a lattice-gas model with directional interactions due to Walker and co-workers [9-11], a two-component lattice model due to Huckaby and Bellemans [12], and a phenomenological multiple-energy state model due to Goldstein [13]. These models have shown impressive success in predicting the general features of the phase diagrams, critical-exponent renormalization, successful correlation of model parameters to real molecular parameters, and reproduction of the asymmetry of the coexistence curves.

In this paper we analyze the shape of the cloud-point curves by assuming that they are coexistence curves of a mixture of "butyl alcohol" (both isomers) and water. This shape bears a semiquantitative similarity to the coexistence curves of the sBA plus water system as a function of pressure. We also show that the critical exponent for these cloud-point curves is $\beta \approx \frac{1}{3}$ as for real coexistence curves in binary mixtures but tends to double near the critical double point.

2. EXPERIMENTAL METHOD

The materials used were water (H_2O), distilled and deionized; secondary butyl alcohol (2-butanol) from Aldrich Chemical Company, their

Gold Label grade; and reagent-grade tertiary butyl alcohol (2-methyl-2-propanol), which was fractionally distilled in our laboratory.

All mixtures were made volumetrically and the results are quoted in this way. Stock solutions with a total volume of 100 ml were made up of the two butyl alcohols. These mixtures are called butyl alcohol (BA) and labeled by their tBA concentration X_{tBA} , where $X_{tBA} = V_{tBA} / (V_{tBA} + V_{sBA}) = V_{tBA} / V_{BA}$, where V is the volume. Butyl alcohol plus water mixtures for cloud-point studies were created by mixing volumes of the stock BA solutions with volumes of water in glass ampoules. These volumes were measured with a digital pipette, whose calibration was checked, and the total volume was always 5 ml. The glass ampoules were made of standard Pyrex glass tubing, 12-mm I.D., and were scrupulously cleaned and dried before filling. Once filled, the ampoules were frozen in liquid nitrogen and flame-sealed. Care was taken to ensure against microleaks and alcohol pyrolysis. The ampoules were labeled as binary mixtures by their BA concentration, $X_{BA} = V_{BA} / (V_{BA} + V_{H_2O})$. Of course the BA had a concentration of tBA as described above so a given ampoule was described by both its BA concentration relative to the total volume and its tBA concentration relative to the total volume of BA. The probable error in X_{tBA} and X_{BA} was 0.1% (relative error, 0.2%).

Cloud-point measurements were made typically by placing eight ampoules in a rotatable holder which was immersed in a large ($3 \times 11 \times 15$ -in.) bath. Linkage from the holder to the top of the bath allowed the observer to agitate the samples thoroughly. The bath contained either methanol or water, which was pumped by a refrigerated/heated circulator. Temperature control was $0.01^\circ C$. The ampoules were well illuminated and observed through a large window on the side of the bath. Cloud points were determined visually as the temperature changed at a rate of $\sim 0.5^\circ C/min$ going from the one-phase into the two-phase regime. Cloud points were typically very sharp and usually reproducible to $0.1^\circ C$.

An interesting shear thinning phenomenon occurred near the critical double point (CDP). If the temperature was held constant, a sample which was thoroughly opaque with cloudiness in the two-phase region could be agitated and become perfectly clear as if in the one-phase regime. With time of the order of minutes, the sample would slowly opalesce and then, finally, after several minutes to half an hour, would regain its original cloudiness. The phenomenon seems to be similar to that described by Pine et al. [14], who saw suppression of the critical point in a binary mixture by tens of millikelvins. Our systems showed suppression of the phase transition by a Kelvin degree or more and hence may make for a useful system to study these nonequilibrium phenomena. For the purpose here, however, it was a considerable nuisance and forced us to proceed very slowly in the pinch-off

region near the CDP and added additional error to the determination of cloud points in this region.

A series of measurements was also performed to determine the critical curve (or plait curve) of the system. As the critical point is approached from the two-phase region, ampoules not having the critical-point concentration would show their equilibrium meniscus position to pass out of either the top or the bottom of the sample. This equilibrium meniscus position was determined by thoroughly agitating the system in the two-phase region at a given temperature and then waiting for the system to separate completely. At the critical-point concentration, the meniscus will stay fairly close to the center of the sample. By using this technique, the critical or plait point was determined for a number of the mixtures.

3. RESULTS AND DISCUSSION

3.1. General Phase-Diagram Properties

The cloud point data are presented in Fig. 1, where the system is represented as a pseudobinary system of butyl alcohol and water. Qualitatively, the trend toward increasing solubility with increasing tBA concentration is seen. The pure sBA system with water ($X_{tBA} = 0$) displays a large miscibility gap topped by an upper critical solution temperature (UCST) at 117°C (not shown in Fig. 1) [3]. This gap pinches in slightly near 0°C. The addition of tBA pinches this region in further, until finally, at $X_{tBA} = 9.1 \pm 0.1\%$ the gap pinches off near a critical double point. Further addition of tBA shrinks the closed loop and pushes the lower gap to yet lower temperatures. At an X_{tBA} value between 40 and 41% the upper loop disappears near $\sim 70^\circ\text{C}$ at a hypercritical point.

Figure 2 displays the critical curve (locus of plait points) of the system as a function of the tBA concentration. This may be considered a side view of Fig. 1. The points of infinite slope are the hypercritical point at $\sim 70^\circ\text{C}$ and $X_{tBA} = 40.5 \pm 0.5\%$ and the critical double point at 2.5°C and $X_{tBA} = 8.0 \pm 0.1\%$.

Extrapolation of the critical curve in Fig. 2 to $X_{tBA} = 100\%$ (i.e., no sBA) suggests a critical point on top of a two-phase region at $T = \sim -35^\circ\text{C}$ in the binary mixture of tBA plus water. From Fig. 1, one can speculate that this critical point would occur near a tBA volume fraction of $\sim 50\%$, which corresponds to a mole fraction of $\sim 16\%$ tBA in water. Dynamic light-scattering evidence for critical phenomenon-type fluctuations in supercooled solutions of tBA and water was given by Euliss and Sorensen [15], who speculated that tBA may show a miscibility gap with

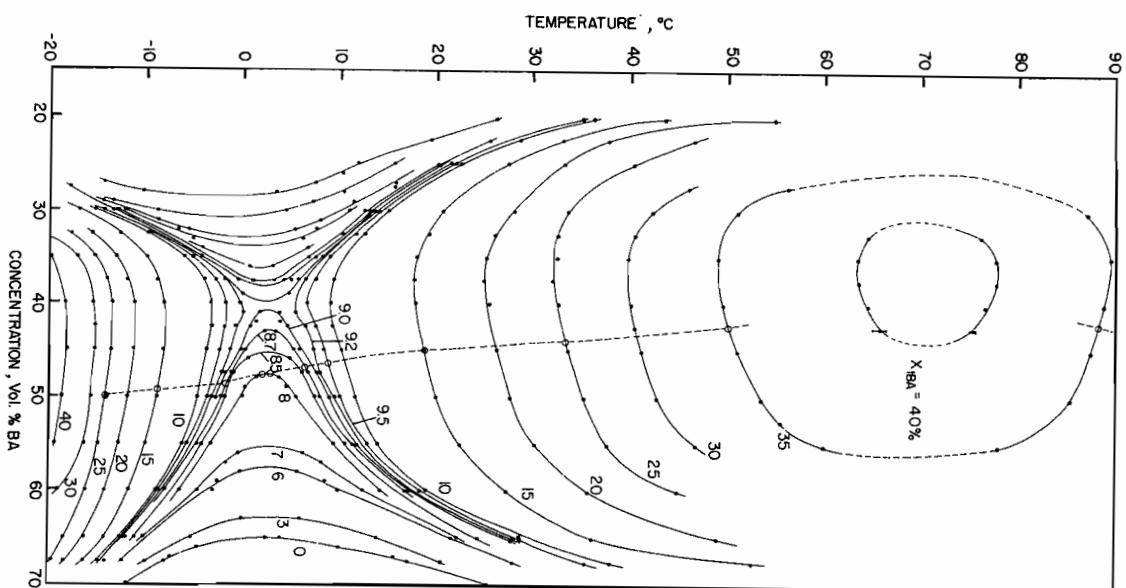


Fig. 1. Cloud-point curves for the system of tertiary butyl alcohol (tBA), secondary butyl alcohol (sBA), and water. The data are points; the lines are eye-drawn fits. The concentration of BA is the volume concentration of the sum of both butyl alcohols in the total aqueous system. X_{tBA} is the volume concentration of tBA in the total BA. The dashed line and the associated open circles represent the critical curve.

water in the supercooled solution. Corroboration of this speculation was given by Bender and Pecora [16], who also performed dynamic light-scattering measurements on this system and showed that the effective concentration fluctuation correlation length peaked near 14 mol% tBA for equilibrium temperatures and increased slightly with decreasing temperature. From the descriptive picture of these multiloop phase transitions described in Section 1 [4], one may infer that this possible critical point and subsequent phase transition in binary solutions of tBA and water is driven by water–water hydrogen bonding at extreme supercoolings. The mole fraction of $\sim 16\%$ tBA is consistent with ideas that supercooled water forms open clusters of roughly six molecules per cluster [17–20].

Figure 3 compares these cloud-point curves to the coexistence curves of the pure sBA plus water system as a function of pressure [3]. The

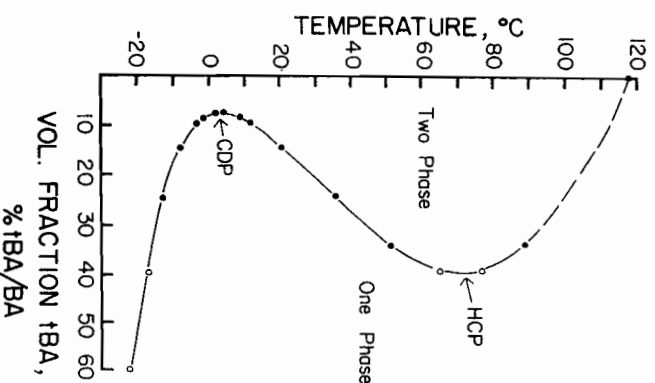


Fig. 2. Critical curve of the tBA-sBA-water system. Filled circles represent the actual determination of the critical point; open circles are inferences from the cloud-point curve. CDP is the critical double-point; HCP is the hypercritical point.

hypercritical points (HCP) lie at roughly the same temperature and concentration (67 vs 70°C and 38 vs 34% by weight BA or sBA). If one uses a rough scaling factor of 20 atm/%tBA, cloud-point curves and coexistence curves roughly match. For instance, the HCP is at 840 atm in the pure sBA system; scale this by 20 atm/%tBA, $840/20 = 42\%$ tBA, which compares well with 40.5%. Continuing this scaling, Fig. 3 shows that the 800-atm coexistence curve is roughly similar to the 40% cloud-point curve, and so on. Hence there is a remarkable, semiquantitative relation between the phase behavior of sBA plus water with the addition of tBA and that with the application of pressure.

The cloud-point curve of a binary mixture is also the coexistence curve. Thus one may make a pseudobinary assumption that the cloud-point curves in Fig. 1 represent the coexistence curves of the binary mixture of butyl alcohol and water. This is, of course, an approximation because the butyl alcohol in each phase of the separated mixture may have different amounts of the two isomers. In fact the asymmetry of the critical curve relative to the cloud-point curves and the fact that the critical points are

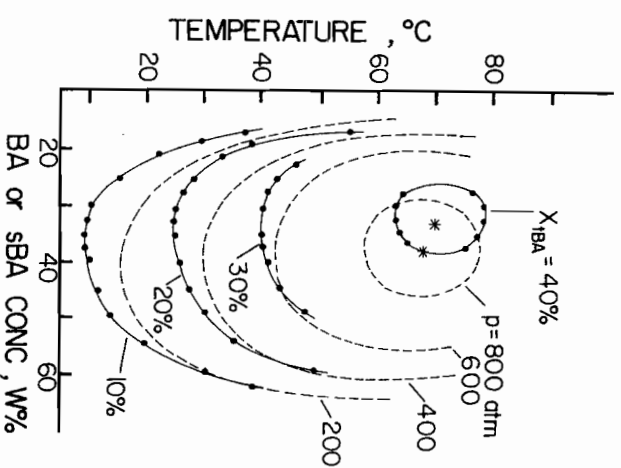


Fig. 3. Comparison of BA (=tBA + sBA) plus water cloud-point curves (solid lines) for various tBA concentrations to sBA plus water coexistence curves (dashed lines) for various pressures. The asterisks represent the hypercritical points.

not at temperature extremes of the cloud-point curves demonstrate the inaccuracy of the pseudobinary assumption for this mixture. Despite this, it is interesting to describe qualitatively the shape of the cloud-point curves with the usual equation used to describe the coexistence curve [21, 22]

$$(X_2 - X_1)/X_c = 2B(|T - T_c|/T_c)^\beta \quad (1)$$

In Eq. (1) X_1 and X_2 will be, for this analysis, the butyl alcohol concentrations at the two branches of the cloud-point curve at a given temperature, T . X_c is analogous to the critical point in a true binary mixture, the butyl alcohol concentration at the extremum of the cloud-point curve. T_c is the "critical temperature," i.e., the cloud-point extremum temperature.

To accomplish this analysis we plot, in Fig. 4, a double-logarithmic plot of $(X_2 - X_1)/X_c$ versus $|T - T_c|/T_c^{-1}$. We find, for tBA concentrations far from the pinched-off region near the critical double point, linear plots implying a power-law behavior and slopes yielding $\beta \approx \frac{1}{3}$. This is near the normal Ising value found in true binary mixtures [22]. For tBA concentrations near the CDP, however, the plots seem to cross over to exponents that are essentially doubled to $\beta \approx \frac{2}{3}$. This doubling is expected because our approach to the critical curve is tangential near the CDP [23]. This will cause exponent renormalization, in this case doubling, since the critical curve must be roughly quadratic near the CDP. Similar behavior has been

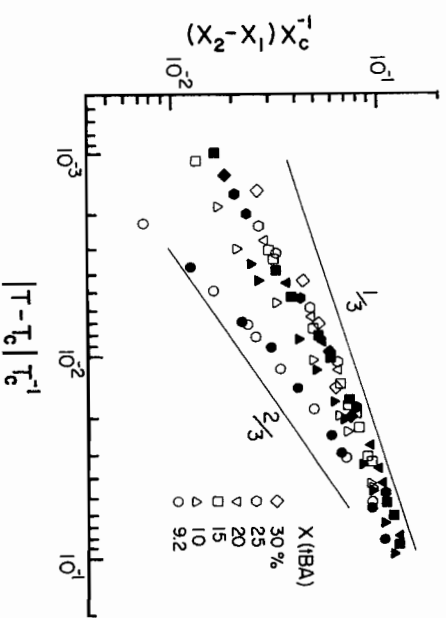


Fig. 4. Width of the cloud-point curve vs reduced temperature for various tBA concentrations. Filled symbols are for lower cloud-point curves; open symbols are for upper curves. Lines with slopes of $\frac{1}{3}$ and $\frac{2}{3}$ are drawn for comparison.

seen in gas-gas systems [24]. In conclusion, while the pseudobinary assumption for this mixture can be shown to be imperfect, it does allow for a qualitative description of the cloud-point curves.

4. CONCLUSION

Cloud-point curves in the mixture tBA, sBA, and water display an interesting variety of miscibility-immiscibility phase change behavior. The effect of adding tBA to the sBA plus water system is very similar to the effect of increasing pressure on the system. This suggests that the delicate interplay of energy and entropy effects on the phase behavior of the system is dependent on the properties of the interaction of the sBA with the water and this interaction can be changed in the same way by either the addition of tBA or the application of pressure. The shape of the cloud-point curves in the pseudobinary assumption is similar to that found in a true binary system with a critical exponent β consistent with the Ising value far from the critical double point and showing exponent doubling near this point.

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REFERENCES

1. J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures*, 3rd ed. (Butterworths, London 1982).
2. A. W. Francis, *Liquid-Liquid Equilibrium* (Wiley, New York, 1963).
3. T. Moriyoshi, S. Kaneshina, K. Ahara, and K. Yabumoto, *J. Chem. Thermodyn.* 7:537 (1975); W. Dolgolenko, Z. Phys. K. Chem. 62:499 (1908).
4. J. D. Hirschfelder, D. Stevenson, and H. Eyring, *J. Chem. Phys.* 5:896 (1937).
5. For an excellent heuristic description of these phenomena and photographs of the apparatus and work described in this paper, see J. S. Walker and C. A. Vause, *Sci. Am.* 256:98 (1987).
6. J. C. Wheeler, *J. Chem. Phys.* 62:433 (1975).
7. G. R. Anderson and J. C. Wheeler, *J. Chem. Phys.* 69:2082, 3403 (1978).
8. J. C. Wheeler and G. R. Anderson, *J. Chem. Phys.* 73:5778 (1980).
9. J. S. Walker and C. A. Vause, *Phys. Lett. A* 79:421 (1980); C. A. Vause and J. S. Walker, *Phys. Lett. A* 90:419 (1982); J. S. Walker and C. A. Vause, *J. Chem. Phys.* 79:2660 (1983).
10. R. E. Goldstein and J. S. Walker, *J. Chem. Phys.* 78:1492 (1983).
11. R. E. Goldstein, *J. Chem. Phys.* 79:4439 (1983).
12. D. A. Huckaby and A. Bellemans, *J. Chem. Phys.* 81:3691 (1984).
13. R. E. Goldstein, *J. Chem. Phys.* 83:1246 (1985).

14. D. J. Pine, N. Easwar, J. V. Maher, and W. I. Goldburg, *Phys. Rev. A* **29**:308 (1984).
15. C. W. Euliss and C. M. Sorensen, *J. Chem. Phys.* **80**:4767 (1984).
16. T. M. Bender and R. Pecora, *J. Phys. Chem.* **90**:1700 (1985).
17. C. M. Sorensen, *J. Chem. Phys.* **79**:1455 (1983).
18. F. H. Stillinger, *Science* **209**:451 (1980).
19. B. L. Halpapi and C. M. Sorensen, *J. Chem. Phys.* **77**:466 (1982).
20. R. J. Speedy, *J. Phys. Chem.* **88**:3364 (1984).
21. A. Kumar, H. R. Krishnamurthy, and E. S. R. Gopal, *Phys. Rep.* **98**:57 (1983), and references therein.
22. J. V. Sengers and J. M. H. Level Sengers, in *Progress in Liquid Physics*, C. A. Croxton, ed. (Wiley, New York, 1978).
23. R. B. Griffiths and J. C. Wheeler, *Phys. Rev. A* **2**:1047 (1970).
24. A. Deerenberg, J. A. Schouten, and N. J. Trappeniers, *Physica* **103**:183 (1980).