Effect of Third Component on Liquid-Liquid Critical Point

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The upper critical solution temperature of a binary pair varies linearly with the mole fraction of a dilute solute, and to a good approximation, the effects are additive for several dilute solutes. Data are reported for the systems hexane–nitrobenzene and hexane–nitroethane with solutes isoprene, maleic anhydride, and 4-methyl-*cis*-4-cyclohexene-1,2-decarboxylic anhydride.

The effect of small amounts of a third component on the critical point of a binary mixture is of interest for both theoretical and practical reasons. The understanding of a solute behavior near the limit of infinite dilution in a solution near its critical point is central to the understanding of the critical phenomenon itself (*15*). Moreover, experimentally, it is important in the investigation of critical phenomena to have some measure of the relative effect of trace impurities on the properties being investigated. Experimentally liquid-liquid critical points are much more accessible than the mathematically equivalent vapor-liquid critical phenomena; therefore, only the former will be considered here.

The theory of liquid-liquid equilibria in ternary (and some quaternary) solutions has been investigated rather thoroughly for the special case of strictly regular solutions by Meijering (*8, 9*), but this provides little guidance for real solutions. The regular solution theory of Hildebrand and Scott (*5, 6*) is somewhat more useful and will be exploited below; but, in fact, it is valid only for systems of relatively low polarity, and few of these form immiscible mixtures. Wagner (*14*) developed from general thermodynamic considerations an expression applicable to more general cases, but its utility is limited by the extensive information required—for example, the second derivative of the partial molal entropies.

Rice and coworkers (*7, 10*) developed a similar expression from a consideration of the effect of an impurity on interfacial tension, a result in certain limits equivalent to Wagner's. This result too is more interpretive than predictive; therefore, to characterize any system of special interest, in general an experimental investigation is required. A typical study of this type is the recent work of Hales et al. on the effects of several third components on the critical point of the water–triethylamine system (*4*).

We report the effect of some impurities on the upper consolute points of two liquid-liquid systems, hexane–nitrobenzene and hexane–nitroethane. These studies were made in conjunction with investigations of the rate of a chemical reaction at a liquid-liquid critical point (*12, 13*) with the purpose of being able to predict the variation of the upper critical solution temperature with the extent of reaction of the dilute solutes. The solutes studied, therefore, were a diene, isoprene, and a dienophile, maleic anhydride, as well as the adduct of the Diels-Alder condensation of these two species, 4-methyl-*cis*-4-cyclohexene-1,2-dicarboxylic anhydride.

Experimental

Materials. *n*-Hexane was distilled at a 15:1 reflux ratio in a 1-m column packed with glass helices to remove olefins. A middle cut (bp, 68.0–68.1°C) was taken and treated with molecular sieves to remove water. The hexane was tested for olefins with concentrated sulfuric acid and was better than 99.9% pure. This result was confirmed by vpc. All chromatographic analyses were made on a Beckman GC-5 equipped with dual 6-ft, ⅛-in. o.d. columns with 3% SE-30 on Gas-Pack F and dual hydrogen flame detectors.

Nitrobenzene was extracted with 2*M* NaOH, washed with distilled water, shaken with dilute HCl, again washed with distilled water, and dried with $CaSO_4$. Distillation was in a 1.5-m column packed with nichrome helices (50 theoretical plates) at 4–5 mm Hg (65–72°C) under nitrogen; heating lasted no more than 8 hr. The first 10 and last 30% of the distillate were discarded. The nitrobenzene was stored in brown glass bottles at 0°C in contact with CaH_2.

Nitroethane was washed with concentrated H_2SO_4 until the acid layer was colorless. It was then washed with water, 5% aqueous Na_2CO_3, and again with water. It was triply distilled from $CaSO_4$ in the same 1.5-m column, and the first and last 20% were discarded. The nitroethane was stored in brown bottles at 0°C. It contained less than 0.1% impurities by vpc.

Isoprene was distilled in a 0.5-m column packed with nichrome helices to remove dimer and then stored in brown bottles at 0°C. The isoprene purity by vpc was better than 99.7%.

Maleic anhydride was vacuum sublimed to remove maleic acid. The purified material was stored and loaded into closed containers in a dry box. As a test of purity, a portion was washed with distilled benzene, decanted, and dried. The weight of residue indicated less than 0.5 wt % maleic acid.

4-Methyl-*cis*-4-cyclohexene-1,2-dicarboxylic anhydride (MCDA) was made by the direct Diels-Alder condensation of isoprene and maleic anhydride in ethyl acetate, to which a trace of hydroquinone had been added to suppress free-radical addition. The product was purified by repeated recrystallization from a mixed solvent of ethyl acetate and ligroin (mp, 66–67°C).

Apparatus and procedure. The coexistence curves for the two binary mixtures hexane–nitrobenzene and hexane–nitroethane were determined from a set of samples made up to composition by weight and sealed into 7-mm pyrex tubes about 9 cm long. A short length of glass rod was placed in each tube as a stirrer. These tubes had been first cleaned with a potassium dichromate-concentrated sulfuric cleaning solution and rinsed several times with distilled water. Because of the enormous effect of water on the critical point, complete dryness of the tubes was assured by holding them at 350°C while flushing with dry nitrogen to remove all traces of water vapor before filling.

The constant temperature bath was controlled to ±0.005°C by a proportional-integral controller, with temperature fluctuations observed on a Hewlett-Packard quartz crystal digital thermometer. The thermometer used to measure the bath temperature had 0.1°C divisions and could be read with an eyepiece to ±0.01°C. The thermometer was calibrated against a thermometer calibrated by the National Bureau of Standards.

An apparatus was constructed to rotate the tube end over end inside the temperature bath, so that the glass

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rod stirrer would fall through the liquid, causing mixing. The apparatus consisted of a submerged horizontal drive shaft with a fuseholder perpendicularly attached to one end. The sealed glass tube was placed in the fuseholder, and the shaft was rotated by a rubber pulley connected to a 4-rpm electric motor mounted on a platform above the water level.

The temperature of the bath was set above the separation temperature of each mixture, and the mixture was thoroughly stirred by rotating the tubes. The temperature of the bath was lowered in successive steps of 0.1°C with intermittent stirring. As the separation temperature was approached, the bath temperature was lowered in steps of 0.01°C and maintained for 10-15 min at each level to let the mixture come to equilibrium. Visual observations were made during this time for a meniscus. The highest temperature at which a meniscus was observed was taken as the separation temperature. All separation temperatures were reproducible to ±0.01°C. In the critical composition region, opalescence made visual observations of a meniscus difficult, requiring equilibration times of up to half an hour.

The effect of impurities on the critical point was determined by essentially the same technique. Weighed amounts of each third component, up to about 1 mol %, were added to the binary solvent mixture at its critical composition, sealed in tubes, and measured as above.

In the mixture with more than one solute—reacting mixtures containing both the diene and dienophile plus possible condensation product—the critical point was determined by a laser light-scattering method (*12, 13*). The solution was confined inside a small (about 15 ml) flask equipped with optical windows at a 90° angle to each other and magnetic stirring. The flask was immersed within two nested temperature-controlled water baths, with the temperature stability of the inner bath better than ±0.001°C, as determined with a quartz crystal thermometer (Hewlett-Packard Model 2801A). Tubes through the baths were provided as a water-free optical path for incident light from a helium-neon gas laser, and the scattered light at 90° was detected by a 1P28 electron tube powered by batteries for stability, with output to a picoammeter (Kiethly Instruments Model 414A) and a millivolt recorder. Sensitivity tests showed that this arrangement permitted rapid détection of the critical point to better than ±0.01°C (*12, 13*).

Results and Discussion

The results of the coexistence curve determinations for the mixtures of hexane with nitrobenzene and nitroethane are given in Table I and shown graphically in Figures 1 and 2. All compositions were determined by weight and are accurate to at least three significant figures; the temperatures measured were reproducible to better than ±0.01°C.

A great many investigators have attempted to measure the critical solution temperature for the hexane-nitrobenzene system, and references compiled by Francis (*3*) include values ranging from 14-23°C. The higher values of the critical point could have been caused by small traces of water or water vapor in those experiments, whereas small quantities of olefins would result in lower values of T_C. Great care was taken in this work to assure dry, olefin-free samples.

Francis (*3*) suggested that the optimum value for the critical temperature is that of Woodburn and coworkers (*18*), 20.29°C. However, a recent Russian investigation (*1*) reports the critical point at 20.00°C and $(x_1)_C$ = 0.588, in good agreement with our values of T_C = 20.02°C and $(x_1)_C$ = 0.570.

Table I. Coexistence Curves for Binary Mixtures

Hexane(1)-nitrobenzene(2)		Hexane(1)-nitroethane(2)	
x_2	Phase boundary, °C	x_2	Phase boundary, °C
0.132	1.6	0.271	27.35
0.197	12.07	0.334	30.01
0.225	15.00	0.377	31.04
0.278	18.23	0.435	31.59
0.369	19.84	0.442	31.65
0.412	20.02	0.448	31.60
0.414	20.02	0.456	31.61
0.415	20.02	0.471	31.61
0.421	20.01	0.478	31.63
0.422	20.02	0.485	31.62
0.433	20.03	0.491	31.61
0.435	20.00	0.505	31.61
0.438	20.03	0.520	31.62
0.445	20.01	0.527	31.63
0.445	20.01	0.534	31.60
0.446	20.02	0.540	31.60
0.477	19.92	0.558	31.59
0.478	19.96	0.606	31.41
0.479	19.92	0.626	31.09
0.588	17.88	0.671	30.19
0.693	10.57	0.676	30.07
0.792	−6.3	0.723	27.71

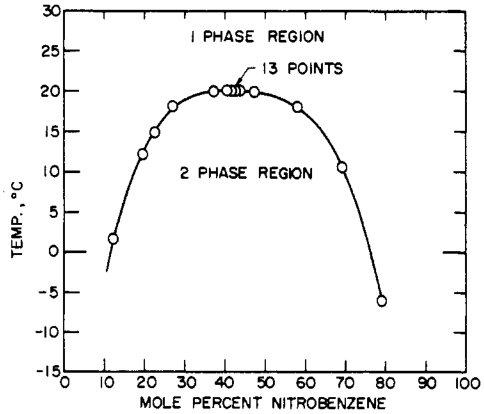

Figure 1. Coexistence curve for liquid-liquid phase boundary of hexane–nitrobenzene system

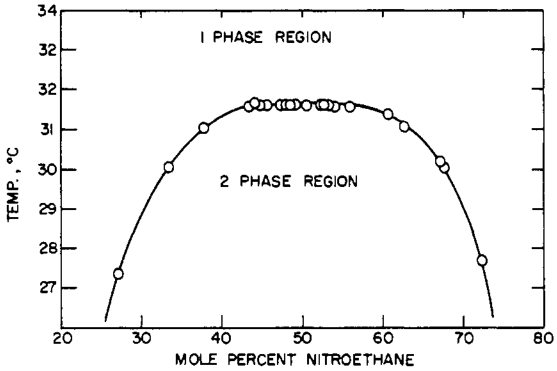

Figure 2. Coexistence curve for liquid-liquid phase boundary of hexane–nitroethane system

Often phenomena near a critical point are interpreted in terms of scaling laws, which in this case would take the form of

$$(x_1' - x_1'') = c(T_c - T)^\beta \qquad (1)$$

where c and β are constants. Although classical theory predicts the value of β as 1/2 (for example, Ref. *11*), more recently, both experiments and theory have indicated that the value is more likely close to 1/3 (*2, 11*). A least-squares fit of the data for the hexane–nitrobenzene system gives $c = 0.250$ and $\beta = 0.318$ with a percent deviation between the calculated and experimental coexistence curves of 0.2%. When β was forced to 0.333, the percent deviation was 0.6%. For the hexane–nitroethane system, $c = 0.302$, $\beta = 0.287$, percent deviation was 0.2%. When β was forced to 0.333, $c = 0.245$ and percent deviation was 1.8%. For comparison, in a recent study of the 3-methylpentane–nitroethane liquid-liquid equilibria, β was 0.34 ± 0.01 (*18*).

The effects of the added third components to the two critical mixtures are given in Table II and Figures 3 and 4. The precision of these results is equivalent to those above. Over the range investigated, the variation in T_c is within the accuracy of the data, extremely linear in x_3, the mole fraction of third component added. As expected, the most polar component, maleic anhydride, causes a sharp rise in the critical temperature (as would water, for example). The relatively nonpolar isoprene causes T_c to fall (as do other olefins), whereas the effect of MCDA is intermediate. Although the dipole moment of MCDA is almost as great as for maleic anhydride (*16*), it is a much larger molecule with a molar volume about twice that of maleic anhydride, so that the polar effects in solution are relatively less. These results agree qualitatively with the conclusions of Hales et al. (*4*), who explained the direction of change in terms of solubilities but did not observe linear behavior at the much higher concentrations they used. MacQueen et al. (*7*) did work at low concentrations for water as an impurity in the aniline–cyclohexane system and observed strictly linear dependence of T_c on x_3.

Strictly speaking, the critical temperatures reported for the three-component systems do not represent the actual determination of a critical point for the ternary system, but rather the determination of a phase boundary close to the critical point. The differences are negligible for the systems investigated here. The ternary mixtures were made up by adding a small quantity of the third component to a large excess of the binary at the critical composition of the binary. This, in effect, fixes the mole ratio of the first two components x_1/x_2, and by the phase rule this system can reach a critical point only if both temperature and pressure are permitted to vary: The pressure was not a variable but was 1 atm at all times.

Table II. Impurity Effects on Critical Points

Maleic anhydride		Isoprene	
$x_3 \cdot 10^3$	ΔT_c, °C	$x_3 \cdot 10^3$	ΔT_c, °C
Hexane–nitrobenzene system			
0.39	0.24	1.1	−0.11
0.85	0.44	5.2	−0.69
1.60	0.87	10.6	−1.50
3.7	1.97		
8.6	4.41		

Maleic anhydride		Isoprene		MCDA	
$x_3 \cdot 10^3$	ΔT_c, °C	$x_3 \cdot 10^3$	ΔT_c, °C	$x_3 \cdot 10^3$	ΔT_c, °C
Hexane–nitroethane system					
2.29	0.97	5.00	−0.74	4.0	0.82
5.02	2.19	13.38	−1.84	6.0	1.26
8.00	3.23	14.50	−2.11	8.1	1.69
9.25	4.01	21.95	−2.85	10.0	2.26
10.0	4.57	27.50	−4.05	15.6	3.26
10.3	4.70				
17.0	7.10				

The observations made represent only the phase boundary at a fixed ratio x_1/x_2 as a function of x_3. In fact, the top of the phase boundary curve is exceedingly flat (Figures 1 and 2 or Table I) so that a variation of several percent in the composition of the binary gives a variation in the temperature of the phase boundary no greater than the experimental uncertainty. For values of x_3 less than 1%, it seems most unlikely that the fixed ratio x_1/x_2 at the critical point of the binary pair could range outside this flat area of the curve. This assumption can be substantiated by a calculation given below. We assume that the phase boundary as measured at the fixed value of x_1/x_2 is, within experimental error, at the ternary critical temperature T_c.

Primarily for qualitative comparison of the shapes of the curves, as well as for some verification of the above assumption, calculations have been made based on the regular solution theory of Hildebrand and Scott (*5, 6*). This theory of the liquid state, though strictly applicable only to systems of nonpolar or slightly polar molecules, has often given a reasonable qualitative picture of more polar mixtures and has the enormous advantage of having no adjustable parameters. Only the pure component properties need to be known.

The activity coefficient γ for a single component in a multicomponent mixture is given by

$$RT \ln \gamma_i = v_i(\delta_i - \bar{\delta})^2 \qquad (2)$$

where v is the liquid molar volume, δ_i is the solubility parameter of component i (the square root of the cohesive energy density, generally found from the enthalpy of vaporization), and $\bar{\delta}$ the volume-fraction average solubility parameter for the mixture. Once an analytical expression is available for the activity or for the Gibbs energy, it is straightforward to calculate the critical solution point by established means (*6*).

Calculations based on Equation 2 were made with known (*5, 6*) or estimated (*17*) values of the solubility parameters. The absolute values of T_c are in error by 50% and are not useful; rather the variation both of T_c and of the mole ratio x_1/x_2 as a function of x_3 are of interest. For the third components in the hexane–nitrobenzene system, the results of the calculations showed plots completely linear up to $x_3 = 0.01$, qualitatively similar to Figure 3; the calculated slopes were about 40% too low for the maleic anhydride and a factor of 2 too great (too negative) for the isoprene. In addition, since actual ternary critical points were calculated, the variation in the ratio x_1/x_2 was found directly and in no case exceeded 0.8%.

Similarly, in the hexane–nitroethane system, Equation 2 predicted a linear variation of T_c with x_3 up to 2% of the third component. Though the slopes for the three components were predicted in the correct order, quantitatively they were poor. Again, the variation in the ratio x_1/x_2 was small for low x_3; up to 1% of component three, the maximum variation was slightly over 3%. At 2% of the diluent, the calculated ratio x_1/x_2 at the critical point varied significantly more—in one case, over 7%, which could exceed the range of the flat portion of the phase boundary.

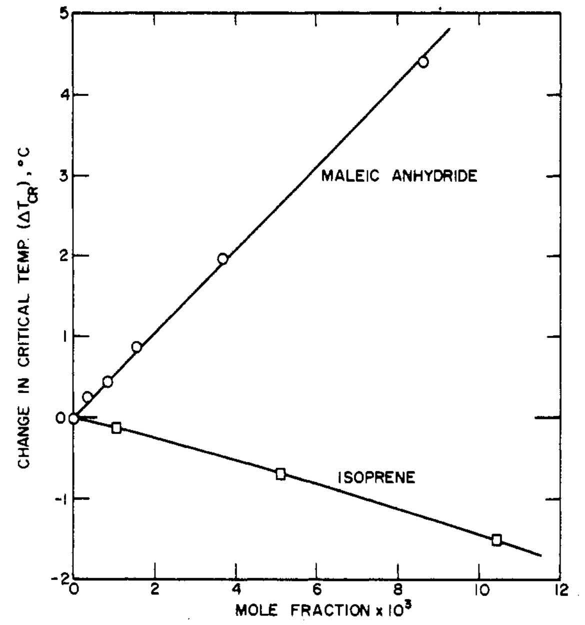

Figure 3. Effect of added third components on critical temperature of hexane-nitrobenzene system

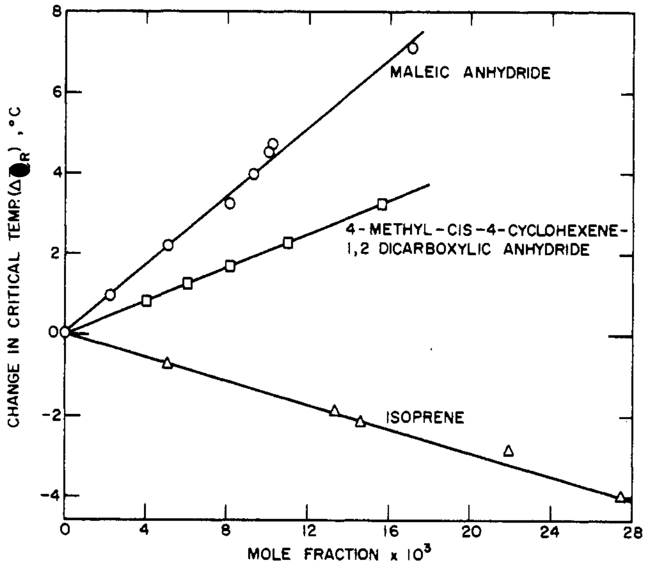

Figure 4. Effect of added third componets on critical temperature of hexane-nitroethane system

Table III. Effect of Multiple Solutes on Liquid-Liquid Critical Point

Solvent: n-hexane(1)-nitroethane(2) mixture
x_1/x_2 at the value of the binary critical point
Solutes: isoprene(3), maleic anhydride(4), MCDA(5)

Case 1:	$x_3 = 7.79 \cdot 10^{-3}$	$\Delta T_{c(3)} = -1.11$
	$x_4 = 6.11 \cdot 10^{-3}$	$\Delta T_{c(4)} = +2.65$
	$x_5 = 1.68 \cdot 10^{-3}$	$\Delta T_{c(5)} = +0.36$
		ΔT_c (calcd) = +1.90°C
		ΔT_c (exptl) = +1.96°C
Case 2:	$x_3 = 9.45 \cdot 10^{-3}$	$\Delta T_{c(3)} = -1.38$
	$x_4 = 7.79 \cdot 10^{-3}$	$\Delta T_{c(4)} = +3.36$
	$x_5 = 0$	$\Delta T_{c(5)} = 0$
		ΔT_c (calcd) = +1.98°C
		ΔT_c (exptl) = +2.05°C

Nevertheless, for small amounts of the solute ($x_3 < 0.01$), a linear variation is reasonable, from both experiment and theory. Such results suggest that for multiple dilute solutes in a critical mixture, the variation in critical point may be expressed as a type of Taylor series

$$T_{c(m)} - T_{c(12)} = (\partial T_c/\partial x_3)x_3 + (\partial T_c/\partial x_4)\, x_4 + \ldots.. \quad (3)$$

with the coefficients for each term taken as the slopes from plots such as Figures 3 and 4. Equation 3 allows us to predict the variation of the critical point with extent of reaction for dilute reactants (*12, 13*). Critical solution points were determined for a number of multicomponent systems by use of the laser light-scattering technique. Equation 3 was tested on these results and in all cases was successful within a few percent; two examples of such predictions are given in Table III.

Conclusions

The phase boundaries were determined for the liquid-liquid systems hexane-nitrobenzene and hexane-nitroethane. The effects of small amounts of a third component on the critical points were linear and to a good approximation, additive. Such results are qualitatively in agreement with the predictions of regular solution theory; however, this model is inapplicable for quantitative predictions in the highly polar systems studied.

Nomenclature

c = constant of proportionality, K^{-1}
R = gas constant, cal/g-mol, K
T = temperature, K
T_c = critical solution temperature, °C
$T_{c(12)}$ = critical solution temperature for the binary 1-2, °C
$T_{c(m)}$ = critical solution temperature for the multicomponent mixture, °C
v = liquid molar volume, cc/g-mol
x = mole fraction
x', x'' = mole fraction in coexisting phases

Greek Letters

β = exponent in scaling law
γ = activity coefficient
δ = solubility parameter $(\text{cal/cc})^{1/2}$
$\bar{\delta}$ = volume-fraction average solubility parameter

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