

Critical point shifts in binary fluid mixtures

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An empirical observation is made of an apparent universal shift in the consolute point (X_c = critical composition, T_c = critical temperature) of binary fluid mixtures when the system identity is perturbed. The shift in a "pure" system's critical point (X_{co} , T_{co}) when perturbed becomes (X_c , T_c) which seems to obey $(T_c - T_{co})/T_{co} = (X_c - X_{co})/X_{co}$. This relation has been observed to hold in a wide range of systems including closed-loop coexistence curves (guaiacol-glycerol-water, or tertiary butyl alcohol in secondary butyl alcohol and water), deuterated systems (methanol-cyclohexane, or isobutyric acid-water), impurities added to methanol-cyclohexane, the molecular weight dependence in polystyrene-methylcyclohexane, and the pressure dependence of methanol-cyclohexane.

Universal behavior within a universality class has been well documented¹ close to the critical point for critical exponents, critical amplitudes (through two-scale-factor universality), and correction-to-scaling amplitudes. But the location of the critical point, and how it might be affected by perturbing the system, has not been predicted to show universal features. The location of a critical point has intrinsically been a system-dependent feature.

It is well known that perturbations of a binary fluid mixture, through the addition of impurities, pressure or electric field, will cause the critical temperature to change. But there have been few reports of the shift (or lack thereof) of the critical composition as a result of such perturbations. In some cases, a shift in the critical composition would not be observable due to the technique used, and in other experiments the uncertainty in the critical composition is relatively large. The coexistence curve needs to be well-measured to obtain an accurate determination of the critical composition.

There are no theoretical expectations for any particular shift in critical composition, should one be observed. In fact, few experimenters would have thought to look for any systematic changes in the critical composition since simple models of binary mixtures (van der Waals,² regular solutions,³ etc.) have not predicted a relationship between the critical temperature and critical composition as the system is perturbed. It can be shown⁴ from Prigogine and Dufay³ that an impurity will cause a critical temperature shift equal to the critical composition shift only when the solubility in the two components are roughly the same.

Never the less, it was reported several years ago that two different impurities (water⁵ and acetone⁶), with vastly different solubilities in the two components, caused a systematic shift in the critical temperature and composition of the methanol-cyclohexane system. If $X_{co}(T_{co})$ is used to indicate the "pure" system's critical composition (temperature) and $X_c(T_c)$ the system's new critical composition (temperature) after an impurity is added, then it was observed⁶ that the scaled shift in critical temperature was just equal to the scaled shift in critical composition

$$\frac{T_c - T_{co}}{T_{co}} = \frac{X_c - X_{co}}{X_{co}} \quad (1)$$

This empirical relation suggests that impurities which cause a change in critical temperature will also cause a change in critical composition. Because the critical temperature for binary liquid mixtures is typically a factor of 600 times larger than the critical composition, the shift in the critical temperature is much more apparent. Before testing this relation in other mixtures, the composition variable choice used in X_c needs to be noted.

The choice of the best composition variable to form the order parameter for binary fluid mixtures is still not determined.¹ As a result, each investigator chooses a convenient composition variable, usually mole, mass, or volume fraction. The scaled shift in the critical composition will depend slightly on the composition variable, but when the critical point shifts are small, then the scaled shift of $(X_c - X_{co})/X_{co}$ using one composition variable is just proportional to the scaled shift using another composition variable. Thus, the trend in the scaled shift in X_c as the perturbation changes will not depend on the composition variable. When reporting and using the critical composition in this paper, the author's choice is used whether it be mole fraction, mass fraction or volume fraction. Indeed, it is not possible to convert between volume fraction and the other two variables without detailed knowledge⁷ of the excluded volume, a quantity not measured for most systems.

The component used to determine the composition variable is arbitrary (e.g., the critical composition of the deuterated isobutyric acid and deuterated water system can be stated as 0.882 mole fraction D_2O or as 0.118 mole fraction deuterated isobutyric acid).⁸ Using component 1 vs component 2 in the composition variable only affects the scaled shift in X_c when the critical composition of the pure system is not close to one-half in that composition variable. In this paper, a convention is adopted to use the component that gives the shift in the critical composition of the same sign as the shift in the critical temperature.

The empirical observation given by Eq. (1) will be tested here by a richer variety of influences on the system identity; influences that maintain the basic identity of the components and thus act as a perturbation to the system. Thus, it will be important to look for experiments where some perturbing influence was systematically applied to a binary mix-

ture, and where the coexistence curve was carefully measured to observe (or not observe) the small shifts in X_c suggested by Eq. (1).

The type of perturbation varies considerably. Impurities added to a binary mixture cause the critical temperature and composition to vary. This was reported for six sets of water⁵ and acetone⁶ impurity concentrations in methanol–cyclohexane, where the coexistence curve was mapped by a refractive index technique and the critical compositions were calculated from the shifts in the curves and from the prepared composition. One point was also observed⁹ in the closed-loop coexistence curve guaiacol–glycerol with a water impurity where the upper consolute point's shift was used here. Another, more systematic, study of the closed-loop coexistence curve secondary butyl alcohol in water has recently been done with tertiary butyl alcohol added as an impurity to shrink the curve to a double critical point.¹⁰ This experiment measured the cloud point for nine different impurity concentrations and found a large change in both the critical composition (in volume fraction) and temperature of the lower critical solution points.

A different type of perturbation occurs when deuterium is substituted for hydrogen. A shift in the critical point has been reported for an undeuterated versus a completely deuterated system: isobutyric acid and water,⁸ where the mole fraction shift in X_c is used because of the large effect the excess molar volume has on volume fraction in this mixture.⁷ Gulari, Chu and Woermann¹¹ observed a shift in the critical composition (measured in mass fraction) equal to the shift

in critical temperature in the isobutyric acid–water system under isotopic exchange.¹² Another system, methanol–cyclohexane, has had a fixed amount of deuterated cyclohexane added, which caused a shift in the critical point.^{13,14} This system has also been studied with progressively larger amounts of deuterated methanol to produce a set of critical points.¹⁴ Mole fraction was used as the composition variable in these last two deuteration experiments on methanol–cyclohexane.

A very different type of perturbation occurs when one varies the molecular weight of polystyrene in methylcyclohexane, a system which is believed to behave as a binary fluid mixture.¹⁵ The theoretical expectations for the critical composition and temperature dependence on molecular weight come from the Flory–Huggins (mean field) equation¹⁶ which depends on the segment–solvent interchange energy to give a dependence between X_c and T_c but not the slope of one in Eq. (1). The range of polystyrene molecular weights in methylcyclohexane measured by Dobashi *et al.*¹⁵ varied over a factor of 10 and resulted in a wide range of values for (X_c, T_c) where X_c was reported as a volume fraction. Since this system has no pure state, the middle of the range of critical points was used as (X_{co}, T_{co}) .

The shifts in the critical point resulting from these perturbations on five very different systems give 28 data points indicating the scaled shift in the critical temperature $(T_c - T_{co})/T_{co}$ as a function of the scaled shift in the critical composition $(X_c - X_{co})/X_{co}$ as shown in Fig. 1. The straight line is not a fit to the data but is a line of slope 1.0,

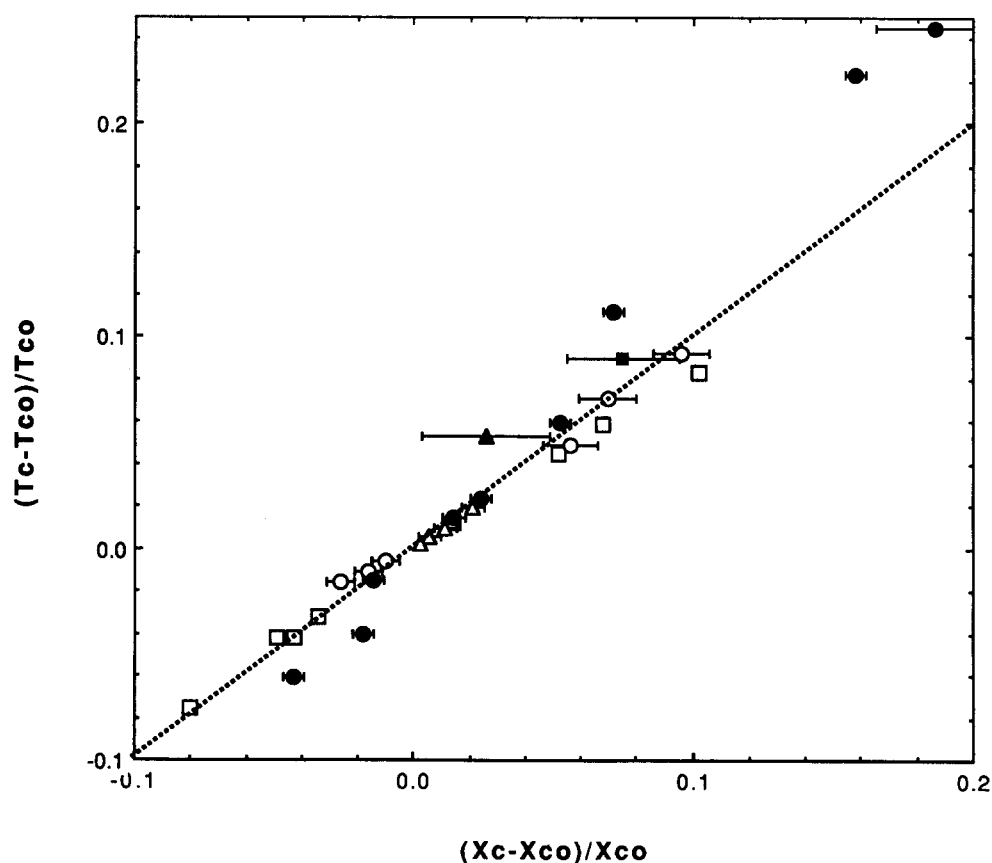


FIG. 1. The shift in a "pure" system's critical point (X_{co}, T_{co}) when perturbed becomes (X_c, T_c) which seems to obey $(T_c - T_{co})/T_{co} = (X_c - X_{co})/X_{co}$ (dashed curve). The data points are for the closed-loop coexistence curve guaiacol–glycerol–water (closed square: Ref. 9); deuterated methanol–cyclohexane (open triangle: Refs. 13 and 14) or isobutyric acid–water (closed triangle: Ref. 8) systems; impurities added to methanol–cyclohexane (open circle: Refs. 5 and 6); the molecular weight dependence in polystyrene–methylcyclohexane (open square: Ref. 15); and tertiary butyl alcohol in secondary butyl alcohol and water (closed circle: Ref. 10).

TABLE I. Parameter values resulting from a weighted, nonlinear, least squares fit of Aizpiri *et al.* (Ref. 17) isobaric data to the simple scaling expression $X = X_c + At \pm Bt^\beta$ where X is the mole fraction of cyclohexane in the methanol–cyclohexane system, $t = (T_c - T)/T_c$ is the reduced temperature, and β is a critical exponent fixed at 0.325. Correction to scaling functions did not significantly improve the fits, nor did they change the parameter values. Parameter errors are at the 68.3% confidence interval.

P (MPa)	T_c (K)	X_c	A	B
1.0	318.71 ± 0.08	0.4985 ± 0.0022	0.78 ± 0.16	0.911 ± 0.008
2.5	319.23 ± 0.09	0.4988 ± 0.0022	0.76 ± 0.17	0.911 ± 0.008
5.0	320.02 ± 0.08	0.4999 ± 0.0018	0.71 ± 0.14	0.914 ± 0.006
10.0	321.67 ± 0.09	0.5002 ± 0.0024	0.68 ± 0.19	0.912 ± 0.008
13.0	322.52 ± 0.11	0.5037 ± 0.0018	0.39 ± 0.21	0.925 ± 0.007

corresponding to Eq. (1), to guide the eye. The error bars on the data points are either those quoted by the author or are estimated to be ± 1 in the least significant digit quoted. The scaled critical temperature shift is much better determined in all the systems than is the scaled critical composition shift.

Finally, the pressure dependence of the critical point has been investigated. These experiments are more difficult to perform and tend to produce less precise coexistence curves than obtainable in a mixture at one atmosphere. However, many of these measurements are in the literature, but few have the requisite precision to observe shifts in the critical composition (in particular, with temperature control of a few milli-Kelvins when measuring the transition temperature). Aizpiri *et al.*¹⁷ have recently measured the transition temperature to a few mK for 23 compositions of methanol in cyclohexane at pressures ranging from 0.4 to 14.4 MPa. The authors fit the transition temperatures of each composition to a quadratic function of the pressure in order to interpolate

the transition temperature at a common set of pressures for all the compositions. These isobaric coexistence curves were then in turn interpolated by assuming an extended scaling function for each branch of the coexistence curve before arriving at a set of “data” they then fit to the same extended scaling function. Their results were internally inconsistent and unusable here. For example, at a pressure $P = 1.0$ MPa, the values they used for interpolation were $T_c = 318.84$ K and $X_c = 0.4412$ (“right branch”) or 0.5400 (“left branch”) while the final fitted results to the interpolated data were 318.728 K for T_c and 0.49852 for X_c .¹⁷

The isobaric coexistence curves as determined for Aizpiri¹⁷ were refitted directly in terms of an extended scaling, and also a simple scaling function for this paper. The errors in the transition temperature were taken as ten times the random error, which was necessary to account for the systematic fluctuations in transition temperature, which probably resulted from difficulty in maintaining sample integrity

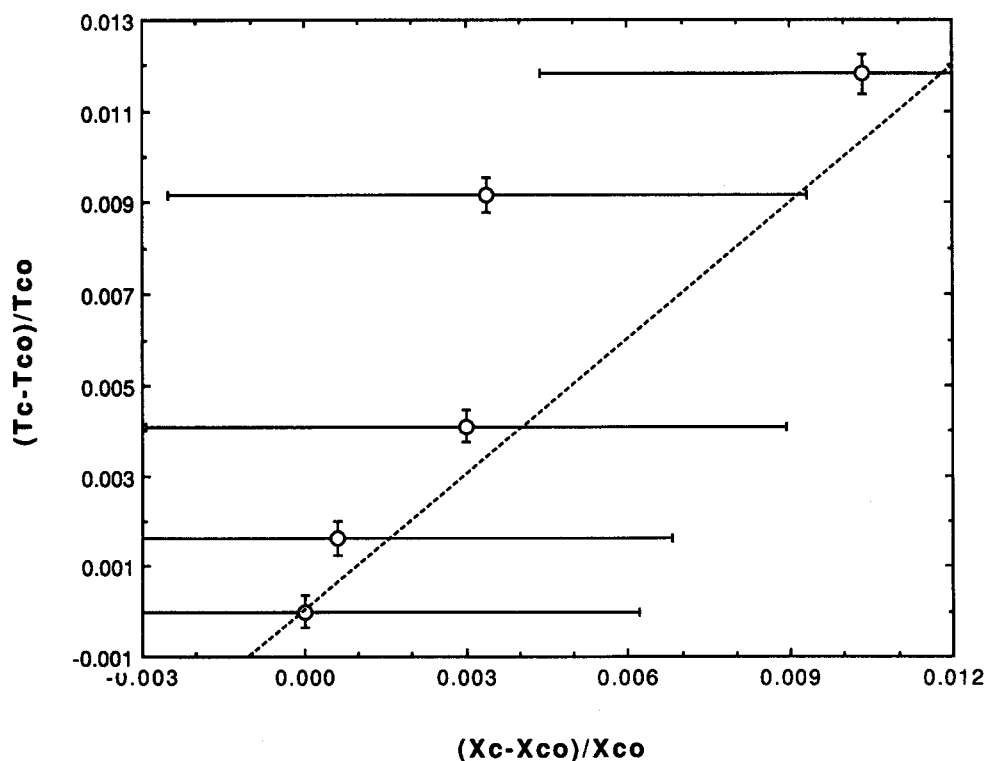


FIG. 2. Scaled critical temperature dependence on the scaled critical composition when pressure is applied to the methanol–cyclohexane system. The points are calculated from the results of the fits given in Table I to Aizpiri *et al.* (Ref. 17). The pressure values are 1.0, 2.5, 5.0, 10.0, and 13.0 which correspond to the points from the lower left to the upper right. The dashed line corresponds to a slope of 1.0 as given by Eq. (1) in the text. Error bars are one standard deviation.

(small traces of water cause a vast change in the critical temperature⁵), and an error of ± 0.0003 in mole fraction. The fits were done with a weighted, nonlinear, least-squares fitting routine¹⁸ which includes correlations among the parameters to determine the parameter errors. Simple scaling was adequate to fit the five isobars and determined the parameter values in Table I, where the errors are at the 68.3% confidence interval (one standard deviation). Using these results gives a scaled (relative to $P = 1.0$ MPa) critical temperature and composition dependence as shown in Fig. 2. The points suggest consistency with Eq. (1) (dashed line) but the errors on the critical composition determination are sufficiently large to allow no dependence at all.

While this set of pressure data are inconclusive, though suggestive, in supporting this universal dependence, Fig. 1 shows a clear dependence of the shift in the critical temperature on the shift in critical concentration suggesting that Eq. (1) holds for a wide variety of fluid mixtures when perturbed in very different ways. It appears that a universal shift in the critical point may occur when a system is perturbed by an external field, in these cases by "impurities" or by varying the molecular weight. The many experiments where such a dependence has been observed make it important for experimentalists and theorists to investigate this phenomena.

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