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Citation: J. Chem. Phys. **68**, 3099 (1978); doi: 10.1063/1.436150
View online: https://doi.org/10.1063/1.436150
View Table of Contents: http://aip.scitation.org/toc/jcp/68/7
Published by the American Institute of Physics

Effect of centrifuging on fluctuations in the critical liquid–liquid region[a)]

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(Received 26 April 1977)

This paper presents a reassessment of an earlier paper on the elevation of the critical temperature, t_c, of liquid–liquid mixtures in a centrifugal field and in a uniform pressure field. Two systems are used: one whose components have nearly the same density, the other whose densities differ widely. We find that with the first pair pressure raises t_c by the same amount whether applied by external compression or by a centrifuge, where the centrifugal force produces the same pressure. With the second pair there is a small additional increase in t_c which we attribute to stretching of the range of the thermal fluctuations. We confirm this effect and its magnitude by a theoretical analysis.

In 1954, Hildebrand, Alder, Beams, and Dixon[1] published observations on "The Effect of Hydrostatic and Centrifugal Fields Upon Critical Liquid–Liquid Interfaces." A group of authors[2,3] have asserted that those observations are not equilibrium ones because they can be interpreted by a mathematical analysis based upon a hypothetical sedimentation process that leads to a hydrodynamic instability, and consequently turbulence, that was confused with critical behavior. We wish to restate and amplify the experimental facts and give an explanation of them based on equilibrium theory.

We reported a study of the displacements of critical temperatures by centrifuging two liquid mixtures, one whose components differ in density very greatly, the other very little. The main purpose of our study was to learn whether a large disparity in density between a pair of liquids would introduce what we called a "sedimentation effect," not intending that term to be taken literally. In the critical region we do not deal with clusters that are permanently of a different density than the surrounding medium, but instead with microregions that owing to fluctuations are temporarily denser than the mean and in the next instant less. As we shall see, the centrifugal field can only interact with spatial gradients in these fluctuations, not with the local fluctuations themselves.

To emphasize that the two systems behave experimentally identically even though the possibility of hydrodynamic instabilities exists in only one of the two systems, we present Fig. 1 and the following table that gives the pertinent parameters of the two systems:

	A		B	
	$C_7F_{16}+$	C_8H_{18}	$C_6F_{11}CF_3+$	$C\,Cl_4$
Density at 25°	1.707	0.690	1.795	1.622
Critical volume frac.	0.45	0.55	0.44	0.56
Volume/mole	227	165	195	97
Critical temperature	22.2°		25.8°	

Liquid–liquid solubilities for system A had been determined by Hildebrand, Fisher, and Benesi,[4] and for B by Hildebrand and Cochran.[5] Alder determined critical temperatures at a series of uniform pressures up to 65 atm. Beams and Dixon determined consolute temperatures in high centrifugal fields. The hydrostatic and centrifugal results are compared in Fig. 1 for systems A and B. The pressure produced in the centrifuge is readily calculated from the rotor speed and the weight of the liquid above the miniscus. If the weight of the liquid is calculated from the mean density in system B (1.70 g/cc) the shift of the critical temperature with rotor speed is quantitatively accounted for. On the other hand, for system A an effective density of 1.25 g/cc would make the hydrostatic and centrifuging results correspond while the mean density is 1.15 g/cc.

The actual density of the critical mixture is, in fact, even slightly less than the mean because of volume expansion upon mixing. Jura, Hildebrand, Fraga, and Maki[6] determined this density to be 1.12 g/cc, which has to be upped by about 1% to account for compressibility of the system under the pressure generated by the centrifuge. This difference between the effective density and the actual density translates into an additional shift in system A over and above that due to the hydrostatic pressure of the order of 1° at the highest rotor speed. This comparison between systems A and B makes unlikely the occurrence of an entirely different phenom-

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[a)] Work was performed in part under the auspices of the U.S. Energy Research and Development Administration under contract No. W-7405-Eng-48.

[b)] Deceased.

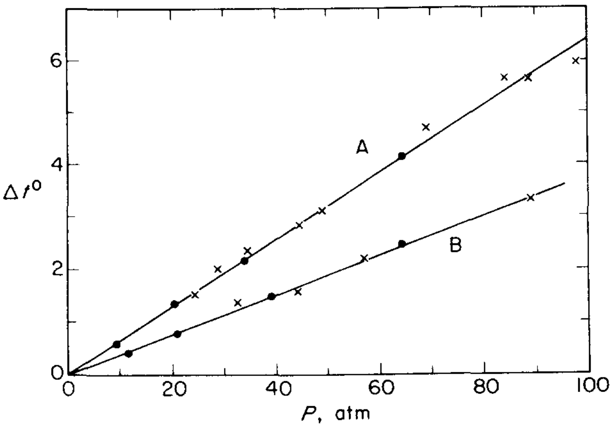

FIG. 1. Elevations of critical temperatures by a uniform hydrostatic pressure (solid circles) and centrifuging pressures (crosses) for the liquid–liquid system A: $C_7F_{16} + i\ C_8H_{18}$, and B: $C_6F_{11}CF_3 + C\,Cl_4$. The calculated pressure in the centrifuge in system A uses an effective density of 1.25 g/cc while for system B the mean density of 1.70 g/cc was used.

enon in one of the systems and led us to the conclusion of a small actual shift of the critical temperature in system A.

The shift, furthermore, appears also to be unrelated to any hydrodynamic instability on the basis of an unobservable change in the location of the phase boundary as long as the ultracentrifuge is maintained at constant speed and constant temperature. To be sure, when the rotor speed increases, large convective turbulence is observed due to transfer of liquid components in the cell, but this turbulence stops after a few minutes when the rotor speed is held constant. The very sensitive Philpot–Svensson–Schlieren optical system employed would have shown even small turbulences. As the rotor speed was further increased, and then maintained at the higher speed, the boundary would reform after an initial turbulent period at a position further away from the peripheral wall of the cell and remain there during the entire period of observation.

The true equilibrium state of the system after very long centrifugation can be calculated by thermodynamics. At equilibrium for a column of fluid of 1 cm height enormous concentration gradients would develop so that the concentration at the bottom would no longer be near the critical concentration. The establishment of this equilibrium concentration can, however, be extremely slow compared to our observation times. It is for this reason that we extrapolated our results to zero column height since under those conditions the concentration gradient is eliminated. The independence of the shift, within experimental error, over column heights of about $\frac{1}{2}$ to $1\frac{1}{2}$ cm at given rotor speed leads us to believe that the establishment of the equilibrium concentration profile is slow, although the extrapolation to zero height is larger than one might wish.

It is in any case hard to understand why a turbulent boundary would persist for any length of time. The adiabatic conditions for convective turbulence are only readily exceeded near the critical point because of the divergent heat capacity. This gives rise to very efficient and rapid centrifugally driven heat and mass transfer in the region of the liquid column that is near critical conditions. Otherwise, the column is, in fact, more stable the higher the rotor speed, because the higher the pressure gradient that is developed, the more difficult it becomes to exceed the adiabatic conditions that lead to turbulence. This, it seems to us, qualitatively accounts for the stabilization of the column within several minutes, although the much slower molecular processes of diffusion, by which the equilibrium concentration profile is established, are not perceptible during the time of observation.

A shift of the critical temperature of about 1° seems reasonable in view of the many observations that show significant enhancement of fluctuations within that temperature range near the critical point. For example, observations by Zimm[7] on the turbidity of mixture B shows a rapid rise as the critical point is approached from above within 1°. An analysis by Debye[8] shows that this is due to concentration fluctuations. Concentration fluctuations are also responsible for the near doubling of the diffusion coefficient of a foreign gas (CH_4) within 1° of the critical temperature of a mixture similar to B, namely, $C_6F_{11}C_2F_5$ and $C\,Cl_4$, as observed by Hildebrand and Lamoreaux.[9] These fluctuations cannot be neglected near the critical point and invalidate the conclusion on purely thermodynamic grounds that a centrifugal potential cannot shift a chemical equilibrium. That conclusion is based on the conservation of mass in chemical systems and leads to the independence of the chemical potential on the centrifugal field, but ignores that, at the critical point, the work necessary to create large density fluctuations becomes vanishing small.

In that respect the centrifugal field is different from other external fields. For example, as analyzed by Debye,[10] the shift of the critical point by an external electric field can be explained by the difference in work necessary to create the various local fluctuations themselves. The reason for this difference is that an external electric field can interact with the fluid directly via the dipole moment of its constituents or macroscopically through the dielectric constant.

The effect of the centrifugal field can only be through a change in the density gradient or in the correlation between fluctuations. It can be argued that the qualitative effect is to raise the critical temperature, as observed, since the centrifugal field, on the average, increases the range of the fluctuations. The range is determined by the distance between a concentration fluctuation and a correlated opposite fluctuation which necessarily accompanies it since the total concentration must be preserved. Near critical conditions this distance becomes of the order of the wavelength of light, leading to critical opalescence. The centrifugal field stabilizes those correlated pairs of fluctuations separated by larger distances where the denser end is nearer the periphery of the cell. Thus, in effect, the external field favors phase separation or raises the critical temperature. Another way to state this effect is that the average range of the fluctuations is increased in the presence of the field on energetic grounds so that at a higher temperature these fluctuations become comparable to the wavelength of light. Since the shift depends on the fluctuation range, consideration of a microscopic region that is denser than the mean in one instant and less in the next leads to no net effect.

The analysis follows Debye[8] both in concept and notation. The fluctuating part of the excess free energy density, δF, can be written as a sum of two terms,

$$\delta F/kT = (S + \Omega/kT)\eta^2/2 + (H/2kT)(\nabla\eta)^2 ,$$

where η represents the fluctuation in volume fraction. The first term is the only one present in a homogeneous system. Its coefficient consists of an entropy term S, namely, the second derivative of the entropy density, and an energy term Ω/kT. This coefficient vanishes at the critical point, since it is equivalent to setting the second derivative of the chemical potential equal to zero to determine critical conditions. The second term, involving gradients of the fluctuation, accounts for inhomogeneities in the density to first order and is essentially an interfacial energy term. The coefficient H does not vanish at the critical point. Debye showed its magnitude to be $\frac{1}{6}\Omega l^2$, where l^2 is the range of the intermolecular forces, that is the square of an atomic dimension.

The obvious effect of a centrifugal field is to make the various coefficients functions of the position, R, in the centrifuge. This causes the vanishing of the coefficient of η^2 to lead to new critical conditions; however, these are the ones that correspond to the shift caused by the hydrostatic pressure at R. This is consistent with the purely thermodynamic criterion that a centrifugal field leads to no shift of phase equilibria beyond that produced by the hydrostatic pressure. A new effect is, however, produced by the second term. H, being a function of R, modifies by partial integration the η^2 term by $\nabla^2(H/2kT)$ that leads to a shift of the critical temperature by $\nabla^2 H/2kS$. In view of the above comments on the magnitude of H, this shift is far too small to explain the observed one.

There exists, however, an additional effect due to the gradient in the external field produced by a centrifuge. This gradient leads to a difference in force, $\mathbf{F}_{\alpha\beta}$, experienced by particle α of mass, M_α, located at $\mathbf{r}_\alpha$ in the tube and particle β of mass M_β located at $\mathbf{r}_\beta$:

$$\mathbf{F}_{\alpha\beta} = \omega^2 M_\alpha \mathbf{r}_\alpha - \omega^2 M_\beta \mathbf{r}_\beta ,$$

where ω is the speed of rotation expressed in rad/sec. By introducing center of mass coordinates, this force can be rewritten as

$$\mathbf{F}_{\alpha\beta} = \omega^2[M_{\alpha\beta}\mathbf{R} + 2\mu_{\alpha\beta}\mathbf{r}_{\alpha\beta}] ,$$

where

$$M_{\alpha\beta} = M_\alpha - M_\beta, \qquad \mu_{\alpha\beta} = \frac{M_\alpha M_\beta}{M_\alpha + M_\beta} ,$$

$$\mathbf{R} = \frac{M_\alpha \mathbf{r}_\alpha + M_\beta \mathbf{r}_\beta}{M_\alpha + M_\beta}, \qquad \text{and } \mathbf{r}_{\alpha\beta} = \mathbf{r}_\alpha - \mathbf{r}_\beta .$$

The term containing R is the one already dealt with, but the new term corresponds to an additional energy $U_{\alpha\beta}$ of $-\omega^2\mu_{\alpha\beta}r_{\alpha\beta}^2$ in the centrifugal field but absent in a uniform gravitational field. Hence, on the average, particle α feels a repulsive force due to all correlated particles of type β, which corresponds to an energy equal to

$$\langle U_{\alpha\beta}\rangle = -\omega^2\mu_{\alpha\beta}\int n_\beta C(r_{\alpha\beta}) r_{\alpha\beta}^2\, d^3 r_{\alpha\beta} ,$$

where n_β is the number density of particle β and $C(r_{\alpha\beta})$ is the correlation function which represents the average product of two fluctuations a distance $r_{\alpha\beta}$ apart divided by the average square of the fluctuation. In the absence of any correlation, $C(r_{\alpha\beta})$ vanishes and the effect disappears in as much as the centrifugal field cannot then develop any stress to extend the range of the fluctuation. In fluids not near critical conditions $C(r_{\alpha\beta})$ is short ranged, that is, of atomic dimensions, and the effect is entirely negligible. Near critical conditions, however, $C(r_{\alpha\beta})$ is long ranged, of the order of the wavelength of light, and according to the well-known Ornstein–Zernike formula, consistent with the free energy density expression above, is given by[11]

$$C(r) = \frac{kT}{4\pi H}\,\frac{e^{-Kr}}{r} ,$$

where K is the reciprocal of the range of the correlation, namely,

$$K^2 = (S + \Omega/kT)/H ,$$

which vanishes at the critical point. Hence,

$$\langle U_{\alpha\beta}\rangle = -6\omega^2\mu_{\alpha\beta}n_\beta kT/K^4 H .$$

To obtain the free energy density contribution proportional to η^2, the definition of this fluctuation variable must be introduced in the above expression. But first, that expression must be multiplied by the number density of particle α, summed over all possible values of α and β and integrated over volume to get the total energy contribution due to all possible such correlated pairs of fluctuations in the system. This straightforward procedure leads to an additional contribution due to stretching in a centrifugal field of

$$\frac{\delta F_c}{kT} = [-3\omega^2\rho_{12}^2/K^4(M_1 + M_2)H]\eta^2/2 ,$$

where ρ_{12} is the difference in mass density. This results in a shift, ΔT, of the critical temperature of

$$\Delta T = \frac{18\omega^2\rho_{12}^2}{(M_1 + M_2)l^2 S^2 k K^4} ,$$

where the estimate of $H = \Omega l^2/6$ has been introduced. For Ω/kT, the value S, given by the critical conditions in the absence of an external field, has been substituted. S in turn is estimated from regular solution theory.[12] This leads to a shift of the order of 0.1 °K at the highest speed of rotation, $\omega^2 \sim 10^7$ rad^2/sec^2, for system A, if the properties given in the table are substituted and $1/K$ is taken to be 5×10^{-5} cm and $l \sim 3\times10^{-8}$ cm so that $l^2 = 10^{-15}$. Thus the centrifugal field leads to a significant stretching of fluctuations of different densities separated by a distance of the order of magnitude of the wavelength of light. This is in qualitative agreement with the observations. Quantitative agreement cannot be expected until an upper limit on the range of the correlation, $1/K$, has been established from alternative considerations[13] involving the limitation on the range of the correlations by the presence of a density gradient in the mixture.

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