THE JOURNAL OF
PHYSICAL CHEMISTRY

VOLUME 58 AUGUST 18, 1954 NUMBER 8

THE EFFECTS OF HYDROSTATIC PRESSURE AND CENTRIFUGAL FIELDS UPON CRITICAL LIQUID-LIQUID INTERFACES

BY J. H. HILDEBRAND AND B. J. ALDER

Department of Chemistry and Chemical Engineering, University of California, Berkeley, California

J. W. BEAMS AND H. M. DIXON

Rouss Physical Laboratory, University of Virginia, Charlottesville, Virginia

Received March 27, 1954

Hydrostatic pressure applied to the system *n*-perfluoroheptane–2,2,4-trimethylpentane, raises the critical temperature for the appearance of the liquid–liquid interface at a uniform rate of 0.06656° per atmosphere between 1 and 64 atmospheres. In the system perfluoromethylcyclohexane–carbon tetrachloride, the rise through the same interval is 0.03875° per atmosphere. Centrifugal fields raise the apparent critical temperature linearly; at an acceleration of 10^8 cm. sec.$^{-2}$ a rise of 10° was found in the case of the former system and 7.7° for the latter. Subtraction of the hydrostatic pressure upon the interface from the centrifugal weight of liquid "above" it leaves, in the case of the former system, a rise of 1.9° at this acceleration to be attributed to a sedimentation effect arising from the large difference, 1,017, in the densities of the pure components at 25°. In the case of the latter system, where the density difference is only 0.180, the residual effect is not more than 0.2°, which lies within the limits of error of the experiment.

One of us[1a] not long ago described a hypothetical picture of the micro-effects of changing temperature in the critical region, and added: "If this is a reasonably accurate description of the process, there would seem to be room for slight disagreement as to the precise value of the critical temperature, particularly if we remember that we are observing," in the appearance of an interface, "the effects of small differences in density, which depend upon the gravitational field, and could be markedly changed in a centrifugal field." This paper describes an experimental study of the effects of a centrifugal field, which may be called a sedimentation effect, upon two different non-polar liquid pairs. One pair consisted of *n*-perfluoroheptane and 2,2,4-trimethylpentane ("isoöctane") whose densities, 1.707 and 0.690, respectively, at 25°, are very different; the other was perfluoromethylcyclohexane and carbon tetrachloride, whose densities, 1.795 and 1.615, are near together. The liquid–liquid curve for the former system was determined by Hildebrand, Fisher and Benesi,[2] the latter by Hildebrand and Cochran,[3] and with great precision by Zimm.[4]

The Effect of Hydrostatic Pressure.—Two non-polar liquids which differ sufficiently in their internal attractive forces to yield two liquid phases normally mix with considerable expansion and heat absorption,[1b] because the mixing process substitutes contacts between unlike molecules for contacts between like molecules, with a weakening of the internal forces, because the attraction between unlike molecules is normally closer to a geometric than to an arithmetic mean. In the case of the first pair, the expansion is as much as 4.9 cc. per mole of mixture, according to unpublished measurements kindly put at our disposal by Professor Robert Dunlap, of the University of Maine. The hydrostatic pressure of the liquid "above" the interface (in the sense of the centrifugal field) will add its component to the expected sedimentation effect, therefore one of us (Alder) measured, in the absence of a centrifugal field, the change in the critical temperature of the interface caused by hydrostatic pressure.

A mixture of the critical composition, 55.0 volume per cent. of isoöctane for the former system,

---

[1] (a) J. H. Hildebrand, *J. Colloid Sci.*, **7**, 551 (1952). See also (b) G. Jura, D. Fraga, G. Maki and J. H. Hildebrand, *Proc. Natl. Acad. Sci.*, **39**, 19 (1953).

[2] J. H. Hildebrand, B. B. Fisher and H. A. Benesi, *J. Am. Chem. Soc.*, **72**, 4348 (1950).

[3] J. H. Hildebrand and D. R. F. Cochran, *ibid.*, **71**, 22 (1949).

[4] B. H. Zimm, THIS JOURNAL, **54**, 1306 (1950).

56.0 volume per cent. of CCl_4 for the latter, was confined over mercury in the closed limb of a V-shaped tube. Air pressure, measured by a Bourdon gage,[5] was applied to the mercury in the other limb, and the temperature observed at which the interface just appeared. The liquid mixture could be stirred when necessary by a steel pellet moved by an external magnet. The results are given in Table I. The rise in the critical temperature is quite linear with pressure as shown by the correspondence between observed and calculated temperatures for the simple relations given.

Table I

Effect of Hydrostatic Pressure upon the Critical Temperature of Interfaces

C_7F_{16}–i-C_8H_{18}			C_7F_{14}–CCl_4		
	t_c			t_c	
P, atm.	Obs.	Calcd.	P, atm.	Obs.	Calcd.
1.00	22.30	...	1.00	26.21	...
9.25	22.85	22.87	11.60	26.63	26.62
20.50	23.60	23.60	21.00	26.99	26.99
33.80	24.48	24.48	39.15	27.69	27.69
64.05	26.51	26.49	64.60	28.70	28.67
$\Delta t/\Delta P$	0.06656°/atm.			0.03875°/atm.	

In the case of C_7F_{14}–CCl_4, our value for t_c at 1 atmosphere is lower than those previously reported for this system. This may be the result of the care we took to purify our CCl_4 from traces of CS_2, which raises t_c, as might be expected. The behavior of these two-component systems under hydrostatic pressure is analogous to that of a one-component system, where Schneider and Habgood[6] found that the form of the liquid–vapor coexistence curve is very dependent upon the height of the column above the meniscus.

Volume Change upon Mixing.—The change in volume upon mixing can be related to the shift of the interface temperature with pressure by aid of the equations of regular solution theory which, although ignoring the clustering in the immediate vicinity of the critical point, have been used successfully to calculate critical compositions and temperatures.[7]

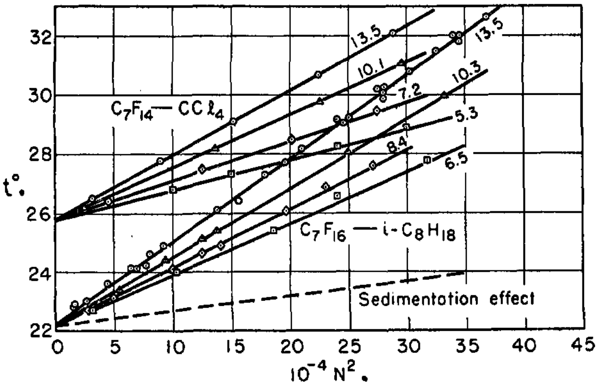

Fig. 1.—Effect of rotor speed upon t_c for different liquid depths, in mm.

Including the Flory–Huggins expression for entropy in the equation for activity, and setting its first and second derivatives with respect to composition equal to zero, yielded the following equations for critical composition and temperature

$$\frac{\varphi_1}{\varphi_2} = \left(\frac{V_2}{V_1}\right)^{1/2} \quad (1)$$

$$RT_c = 2\phi_1{}^2V_1(\delta_2 - \delta_1) \quad (2)$$

Here the ϕ's denote volume fractions, the V's molar volumes, the δ's solubility parameters. This permits us to write

$$RT\left(\frac{\partial \ln a_2}{\partial P}\right)_{T,\phi} = \bar{V}_2 - V_2 = V_2\phi_1{}^2\left(\frac{\partial(\partial_2 - \delta_1)^2}{\partial P}\right)_{T,\phi}$$

$\bar{V}$ is partial molar volume. We have found by experiment that $RT_c = A + BP$, hence, by equation 2

$$B = 2\phi_1{}^2V_1\left(\frac{\partial(\delta_2 - \delta_1)^2}{\partial P}\right)_{T,\phi}$$

and thus, $\bar{V}_2 - V_2 = (B/2)\ (V_2/V_1)$. Calculating the volume change upon mixing from $\Delta V^M = B/2(\mathrm{v}_1(V_1/V_2) + \chi_2(V_2/V_1)$ we obtain for the system C_7F_{16}–i-C_8H_{18} at the maximum, 2.6 cc. per mole of mixture, rather less than the value calculated from Dunlap's densities. For C_7F_{14}–CCl_4 it is 1.5 cc.

The effect of centrifugal fields was investigated by Beams and Dixon at the University of Virginia in the vacuum contained centrifuge there developed.[8] It is hardly necessary to repeat here any details of its construction and operation, except as follows. Rotor speeds were determined to at least 0.5%. Temperatures, measured before and after each run, seldom differed by more than 0.1° because of the large heat capacity of the Duralumin rotor.

The separation into two phases starts at the "bottom" or peripheral end of the rotor cell, where the pressure is highest. It is observed as a sharp line of separation between the liquids both directly and by the schlieren optical method. The latter is more sensitive, but both give essentially the same results. When using the schlieren method, one notices as the rotor speed is slowly increased, with temperature constant, that within one or two r.p.s. turbulence begins in the cell and the liquids separate near the periphery of the cell. If, now, the rotor speed and temperature are held constant, the line of separation stays at a constant radial distance near the periphery. If, next, the rotor speed is increased, the line of separation moves toward the axis of rotation, and if the rotor speed is continually increased the interface moves upward.

The relation between rotational speed, N, in revolutions per second, and the observed temperatures of separation is shown in Fig. 1 for different depths of liquid in the cell, ΔR. It is to be seen that the centrifugal fields applied produce changes of many degrees in the temperature of separation.

Now there are two obvious ways to subtract the hydrostatic contribution in order to verify the existence of a pure sedimentation effect. The former is given by $2\pi^2\rho N^2(R_p{}^2 - R_s{}^2)$, where ρ is the density

---

(5) *For details regarding the pressure system see* E. W. Haycock, B. J. Alder and J. H. Hildebrand, *J. Chem. Phys.*, **21**, 1601 (1953).

(6) W. G. Schneider and M. W. Habgood, *ibid.*, **21**, 2080 (1953).

(7) J. H. Hildebrand and G. R. Negishi, *J. Am. Chem. Soc.*, **59**, 339 (1937); J. H. Hildebrand, *ibid.*, **59**, 2083 (1937); J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes," Reinhold Publ. Corp., New York, N. Y., 1950, Chap. XVI.

(8) J. W. Beams, *J. Wash. Acad. Sci.*, **37**, 221 (1947).

of the liquid above the interface, R_s the radial distance to the surface, and R_p, the radial distance to the periphery, 6.20 cm., where the interface first appears. The value of ρ cannot be fixed with any certainty. According to the measurements of Dunlap, its value for a mixture of the composition we used should be close to 1.10 at 25°, but since the denser component has separated below the interface when this becomes visible, this may be regarded as a maximum value. If we calculate the hydrostatic pressure when $R_p = 7.2$ cm. and $R_s = 6.55$ cm. and $N^2 = 30 \times 10^4$ sec.$^{-2}$, assuming $\rho = 1.10$, we obtain 57.9×10^6 dynes cm.$^{-2}$ or 57.2 atmospheres. This alone, at the rate of 0.06656°/atm., would give a rise of 3.8°. The rise observed under these conditions was 5.3°, leaving 1.5° as the contribution of the sedimentation effect. The maximum in the solubility curve might be shifted by pressure to a different composition, but it is hardly to be expected that any such shift could be very far, and if it occurs it would have affected the static and centrifuge results nearly equally, except that the centrifugal field gives rise to a density gradient according to which the above difference could be regarded as a minimum.

Another, and we believe preferable, method of separating the sedimentation effect is to extrapolate to zero height above the interface. Figure 2 shows $R_p^2 - R_s^2$ plotted against Δt_c for five different values of N^2. The intersections of these lines with the zero ordinate may be taken as the value of the sedimentation effect at different centrifuge speeds. The dotted line in Fig. 2 represents this effect. Its value at $N^2 = 30 \times 10^4$ is 1.9°, agreeing satisfactorily with the above minimum of 1.5° for the same speed of rotation.

The same method of extrapolation applied to the system C_7F_{14}–CCl_4, whose components differ much less in density, gives intercepts amounting to not more than 0.2°, well within the experimental limits of uncertainty, and we have not thought it necessary to plot them. In this case, the rise found in the centrifuge corresponds closely with the rise calculated for the hydrostatic pressure alone. In the critical mixture, the density, calculated on an additive basis, is 1.67 at 25°. The actual value for the upper phase is doubtless smaller. When $N^2 = 30 \times 10^4$, $\Delta R = 1.35$ cm., the calculated hydrostatic pressure is 173 atm., and the calculated rise is 6.7° (also a maximum). The rise observed was 6.6°.

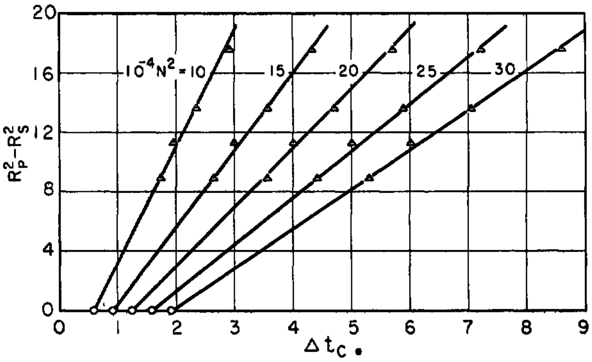

Fig. 2.—Extrapolation of Δt_c to zero liquid depth for constant rotor speeds: system C_7F_{16}–i-C_8H_{18}.

Discussion.—If these mixtures, in the region of light scattering, corresponded to ordinary emulsions, with globules of one density dispersed in a medium of different density, the sedimentation could be analyzed after the manner used by Perrin. These mixtures differ from true emulsions, however, in that they have a cell-like structure, made up of micro-regions which contain the components in different proportions, separated by density gradients instead of abrupt boundaries. The components of a critical mixture are present in nearly equal volume,[2,3] and the regions cannot properly be regarded as, respectively, outer and inner. As the temperature is lowered, the "cells" become larger and the composition gradients steeper, and eventually yield interfaces sharp enough to reflect light. Separation into upper and lower phases is brought about by the action of gravity or of a centrifugal field upon the regions of different density.

We have no desire to monopolize the theoretical analysis of these observations, and invite the attention of the investigators now interested in critical phenomena.

This work was supported, in part, by the Atomic Energy Commission.