

Wetting Transition in Lutidine-Water Mixtures

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A predicted general property of liquid mixtures, the transition from complete to partial wetting at a temperature away from the critical consolute point, is verified experimentally. The system 2,6-lutidine + water undergoes such a transition at $T - T_c \approx 15$ K, as indicated by the difference in capillary parameters measured by the capillary rise and meniscus curvature in thin Pyrex tubes above this temperature. The experiment provides an estimate of the differential binding energy between the two species of fluid molecules and the wall.

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The physical background of *wetting* is less well understood than desirable in view of its great technological importance. Cahn¹ recently pointed out a new general relation for phase-separated liquid mixtures in contact with a third medium w (walls, air, etc.): At a temperature close to a critical consolute point, $T - T_c \rightarrow 0$, one of the two phases (α, β) will *completely* wet w forming a thin film of, say, β material between α and w . For $|T - T_c|$ sufficiently large, on the other hand, a transition to *partial* wetting will take place and the β film will disappear.

The prediction is based on the temperature dependence of the three interface energies (or tensions) $\sigma_{\alpha\beta} \propto |T - T_c|^\mu$ and $\sigma_{\alpha w} - \sigma_{\beta w} \propto |T - T_c|^\beta$ with $\mu \approx \frac{4}{3}$ and $\beta \approx \frac{1}{3}$. Obviously, $\sigma_{\alpha w} > \sigma_{\alpha\beta} + \sigma_{\beta w}$ for $|T - T_c| \rightarrow 0$, which is the condition for complete wetting; but $\sigma_{\alpha w} < \sigma_{\alpha\beta} + \sigma_{\beta w}$ for sufficiently large $|T - T_c|$.

Cahn,¹ Moldover and Cahn,² and other authors^{3,4} verified experimentally the first part of this prediction, viz., the formation of wetting films at the fluid-air interface near T_c . We present here experimental evidence for the second part, viz., the transition from complete (CW) to partial (PW) wetting at some temperature T_{WT} .

Since the disappearance of a very thin film is not easy to observe directly, we chose an indirect method and measured the meniscus height h as a function of $|T - T_c|$ in a small capillary tube inserted between the two phases of a phase-separated liquid mixture [Fig. 1(a)]. Note that the capillary is completely immersed in the fluid. The value of h depends on the balance of gravitational and interface forces:

$$h = \frac{2[\Delta\sigma/(c_\alpha - c_\beta)]}{ag(\rho_A - \rho_B)} \equiv \Lambda_h^2/a. \quad (1)$$

Here, a , g , ρ_A , and ρ_B are the capillary radius, gravitational acceleration, and densities of the

pure components A and B , respectively; c_α and c_β are the concentrations (by volume) of the A - and B -rich phases, respectively; and $\Delta\sigma$ is the difference in interface energies between αw and βw . The quantity Λ_h^2 is known as the capillary parameter which is independent of a .

For CW, we assume that a film of β -phase material is firmly attached to the glass walls yielding $\Delta\sigma = \sigma_{\alpha\beta}$; for PW, $\Delta\sigma = \sigma_{\alpha w} - \sigma_{\beta w}$. Hence, on the basis of the present simplified approach,

$$\Lambda_h^2 \propto |T - T_c|^A, \quad (2)$$

where $A \approx 1$ for CW, $A \approx 0$ for PW, since $A = \mu - \beta$ for CW, and $A = \beta - \beta$ for PW. Thus, the wetting transition should manifest itself in this model as an abrupt change in slope in a plot of Λ_h^2 vs $|T - T_c|$.

Mixtures of lutidine with water⁵ and Pyrex

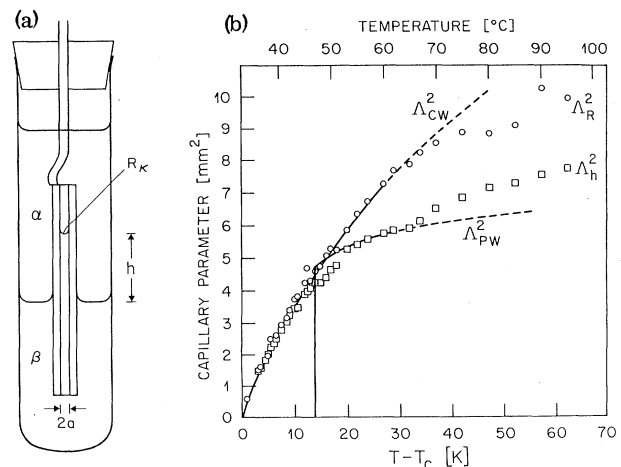


FIG. 1. (a) Experimental setup. (b) Experimental Λ_h^2 (squares) and Λ_R^2 (circles) vs temperature together with fitted curves of Λ_{CW}^2 and Λ_{PW}^2 vs $T - T_c$. Solid curves: calculated from coexistence curve and Eqs. (5); dashed portions: extrapolation for $T > 60^\circ\text{C}$.

capillaries with radii $a = 0.3, 0.5,$ and 0.8 mm were chosen for the experiment. The capillaries and glass containers were first cleaned with RBS 50,⁶ then with a mixture of acetone, NaOH, and H₂O, and rinsed with distilled water and methanol. The lutidine⁷ concentration was 31.4% by volume which is close to critical, with $T_c = 33.0 \pm 0.3$ °C.⁸ The temperature, which was controlled to < 0.05 K, was raised in steps of ≤ 0.5 K close to T_c , and in > 1 K intervals above 40 °C. It should be noted that the 2,6-lutidine-water system has an inverted coexistence curve so that the system exists in two phases when $T > T_c$. After each step, a sufficiently long time was waited for the system to reach equilibrium. Intermittent plugs of α or β material were removed by moving the capillary up and down. The equilibrium meniscus height h was measured for different vertical positions of the capillaries with respect to the external meniscus to exclude errors due to possible pinning at the walls.

Since the relation $h \propto a^{-1}$ was experimentally well satisfied (with a systematic slightly positive deviation for $a = 0.3$ mm), we present our results in terms of Λ_h^2 vs $T - T_c$ in Fig. 1 (open squares, averages for the three radii). The data points lie on a slightly bent curve for the first 10 to 15 K above T_c . The data can be fitted by a power law with exponent 0.97 in agreement with Eq. (2) for CW. At higher temperatures, > 48 °C, Λ_h^2 increases at a much slower rate but is far from being temperature independent, as expected from Eq. (2) for PW.

Since the system is rather far from criticality, the simplest explanation of the gradual bending over would be an influence of correction to scaling terms.⁹ Alternatively, a wetting transition could take place near 48 °C, but then the Λ_h^2 vs $|T - T_c|$ dependence would be more complicated than anticipated. To distinguish between the two possibilities, we also determined the meniscus radius of curvature R which provides an independent measure of the relevant parameters:

$$R = \frac{2[\sigma_{\alpha\beta}/(c_\alpha - c_\beta)]}{hg(\rho_A - \rho_B)} \equiv \Lambda_R^2/h. \quad (3)$$

The new capillary parameter Λ_R^2 equals Λ_h^2 for CW, i.e., $R = a$, but not for PW ($R > a$). R was determined experimentally from photographs of the meniscus. The meniscus contour was digitized, corrected for the cylindrical optics of the bath, container, and capillary, and computer fitted to a circle. The resulting R values scattered considerably, since the fitting procedure

is sensitive to the exact shape of the contour which could not always be photographed with sufficient contrast and magnification. Still, the averages of Λ_R^2 yield a fairly smooth curve sufficient for comparison with Λ_h^2 [Fig. 1(b)].

At small $T - T_c$, Λ_R^2 clearly coincides with Λ_h^2 . However, Λ_R^2 vs $T - T_c$ continues to rise smoothly beyond $T - T_c = 15$ K (48 °C) at least up to 40 K (73 °C). Thus, a distinct gap opens above 15 K yielding strong evidence for a wetting transition at this temperature.

We shall next discuss the capillary parameters in terms of the more realistic gradient-energy approach already used by Cahn.¹ In essence, the interface energies are expressed as an integral over a term $\propto (\nabla c)^2$, a concentration-dependent chemical potential Δf , and a local wall-fluid interaction Φ which depends on the surface concentration c_s only. The resulting expression for the total free energy across an interface (coordinate x),

$$\Delta F = \Phi(c_s) + \int_0^\infty [\Delta f(c) + \kappa(\nabla c)^2] dx, \quad (4)$$

is minimized to provide the concentration profile and ΔF itself. Note that Cahn's correction to Δf for the slight bulk undersaturation in a one-phase system¹ is not required in the presence of the second phase. Equation (4) assumes an extremely short-range fluid-wall binding force which has recently been put into question.¹⁰ The assumption, however, is certainly adequate for the macroscopic quantities considered here.

The coexistence curve of 2,6-lutidine-water system, plotted in Fig. 2 (dotted curve), is highly asymmetric.⁵ This implies an asymmetric chemical potential Δf . Similarly to Beaglehole,¹¹ we assume for the two branches $i = \alpha, \beta$ of the coexistence curve $\Delta f_i = b_{4i}(\zeta^2 - \zeta_i^2)^2$. The ζ 's are concentrations (by volume) measured from the top of the Δf potential hill between the coexistence values $\zeta_\alpha, \zeta_\beta$. To account for the asymmetry, we allow for different values of $b_{4\alpha}, b_{4\beta}$ and $\zeta_\alpha, \zeta_\beta$ for the two branches of the coexistence curve and a shift of the origin of ζ on the c axis with varying $T - T_c$. The two coefficients $b_{4\alpha}, b_{4\beta}$ which are a measure for the size of the potential are coupled to each other by the condition $\Delta f_\alpha = \Delta f_\beta$ for $\zeta = 0$.

For a rough measure of the asymmetry, we assume heuristically that the ratio of Δf curvatures at ζ_β and ζ_α is proportional to the ratio of the slopes of the coexistence curve. This relation, together with $\zeta_\alpha - \zeta_\beta = c_\alpha - c_\beta$, provides ζ_α and ζ_β for each temperature. The square root of

the resulting chemical potential is crucial for Cahn's wetting theory on which our calculation is based.¹² Therefore, $\Delta f^{1/2}$ vs c was also plotted in Fig. 2 for various temperatures. The increasingly pronounced asymmetry (with increasing T) is clearly seen. The break in curvature at the center maximum, caused by the composite expression for Δf , has a minor influence on the interface energies and profiles. The wall binding

$$\Lambda_{CW}^2 = (2\zeta_\alpha^2/C_g)(1+g_A^3)/(1+g_A), \quad (5a)$$

$$\Lambda_{PW}^2 = [2/C_g \zeta_\alpha(1+g_A)] [\zeta_\alpha^3(1-g_A^3) + g_A^3(\zeta_\alpha^2 + \zeta_{s0}^2)^{3/2} - (\zeta_\alpha^2 - \zeta_{s0}^2)^{3/2}]. \quad (5b)$$

$g_A \equiv \zeta_\beta/\zeta_\alpha$ accounts for the asymmetry. The constants $C_g \equiv 3g(\rho_B - \rho_A)/4(\kappa b_{4\alpha})^{1/2}$ and $\zeta_{s0}^2 \equiv \varphi/2(\kappa b_{4\alpha})^{1/2}$ normalize the gravitational and short-range interface energy with respect to the gradient energy. We neglect here the weak temperature dependence of κ , characterized by the critical exponent η . Note that for $g_A=1$ (symmetric Δf), Λ_{PW}^2 becomes almost independent of ζ_α and hence $T - T_c$. In Fig. 1, a good fit of Λ_{CW}^2 to the experimental Λ_R^2 was found for $C_g=0.058 \text{ mm}^{-2}$. Λ_{PW}^2 could be fitted to the experimental Λ_h^2 data quite well in between 20 K (53 °C) and 35 K (68 °C) with $\zeta_{s0}=0.413$ and $T_{WT} \approx 48$ °C. These values should be roughly correct since other models for Δf which we also tried gave similar results.

From C_g and ζ_{s0} , one can calculate $\varphi=8.4 \text{ nJ/mm}^2$ and $(\kappa b_{4\alpha})^{1/2}=24.6 \text{ nJ/mm}^2$. The value of φ may be interpreted as the differential bind-

energy is assumed to be simply¹¹ $\Phi = \varphi\zeta_s$, where φ is independent of ζ and T .

The concentration profile, determined from Eq. (9) of Ref. 1, is identical to Beaglehole's result for PW but has a more complicated shape for CW. Equation (4) provides the interface energies $\Delta F_{\alpha w}$, $\Delta F_{\beta w}$, and $\Delta F_{\alpha\beta}$. Minimization of the total energy of the fluids in the capillary yields for CW and PW, respectively,

ing energy of the two molecular species of the mixture with the pyrex walls. The central maximum of $2(\kappa\Delta f)^{1/2}$ just touches the line $\varphi = \text{const}$ for $\zeta_\alpha = \zeta_{s0}$ (Fig. 2); for smaller ζ_α , Λ_{PW}^2 is undefined. If the wall-fluid interaction is restricted to a molecular monolayer, a binding energy of about 6 meV/molecule is estimated. This value indicates a small difference in binding energy for water and 2,6-lutidine molecules as compared to the energy of adsorption of water on silica (100 to 200 meV).¹³ A small difference is necessary for a wetting transition to occur within the experimental temperature regime. As a final countercheck, we measured h vs $T_c - T$ in a methanol-cyclohexane mixture of critical composition. This mixture reportedly² has no wetting transition in the experimental temperature range. A smooth curve Λ_h^2 vs $|T - T_c|$ was found in this case, i.e., the obvious bend seen in the lutidine-water mixture was absent here.

When we put all these findings together, our data indicate that the lutidine-water/Pyrex system undergoes a wetting transition near 48 °C, that the capillary method is suited to investigate the wetting behavior of phase-separated mixtures, and that our model with only two fitting parameters adequately describes this process.

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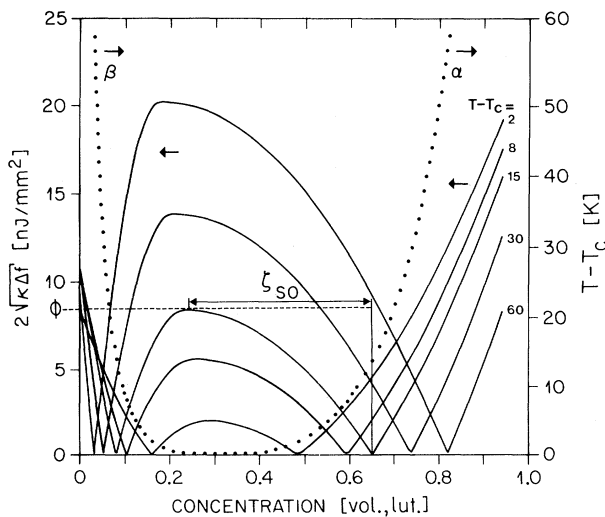


FIG. 2. Coexistence curve for lutidine-water (dotted curve), and $[\kappa\Delta f(c)]^{1/2}$ for various $T - T_c$. The dashed straight line represents the constant φ (8.4 nJ/mm²).

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Melting of Dislocation Vector Systems in Two Dimensions

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A Monte Carlo study of a system of interacting dislocation vectors reveals the possibility of two types of phase transitions. For a system with a large dislocation core energy, unbinding of dislocation pairs causes a continuous phase transition. With a small core energy a first-order transition is produced by formation of grain boundaries. This possibly resolves the discrepancy between the Kosterlitz-Thouless theory and previous computer experiments of atomistic systems.

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Among the various phase transitions taking place in two dimensions, melting is one of the still unresolved problems. On the one hand the renormalization method of Kosterlitz and Thouless¹ (KT) predicts a continuous phase transition due to dislocation unbinding, and its extension by Halperin and Nelson² and by Young³ (HNY) predicts two continuous phase transitions due to dislocation and disclination unbinding. On the other hand previous computer experiments⁴⁻⁹ on various atomistic systems indicate the melting transition to be first order.

The renormalization-group methods are calculating the free energy by the linear elasticity theory with additional dislocations,¹⁰ whereas atomistic systems contain furthermore effects such as anharmonicities, vacancies, and so on. If these neglected effects are important, the dislocation model is not sufficient to describe the melting transition. Recently, however, Chui¹¹ has pointed out that the first-order transition is possible even in a dislocation model if one considers the grain boundary excitation.¹²

In this paper I perform Monte Carlo simulations of dislocation vector systems with long-range interactions and a core energy, and investigate the order of phase transition taking place

there. The merit of simulating the dislocation vector system is that one can control the core energy directly.

The main finding is that both types of phase transition are possible depending on the core energy: a continuous phase transition for a large core energy and a first-order transition for a small core energy. The continuous transition is due to dislocation unbinding and the formation of free dislocations, as predicted by KT. The first-order transition is due to the nucleation of loops of grain boundaries, in agreement with computer experiments and Chui's prediction. Thus the disagreement between theories and experiments seems to be a consequence of differences in core energies.

I shall now explain details of the investigation. In the ground state, atoms order in a close-packed structure, i.e., triangular lattice in two dimensions. At high temperatures defects such as dislocations are possible as well as phonon excitations. Burgers vectors \vec{b} can be in six directions; $(\pm a_0, 0)$ and $(\pm a_0/2, \pm \sqrt{3}a_0/2)$, where a_0 is the lattice parameter. Instead of assuming dislocations with core radius a , I assume here that dislocations can be situated only on a triangular mesh site with lattice parameter $2a$. I also as-