Phase Behavior of Colloids in Binary Liquid Mixtures

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Partially miscible binary liquids containing silica colloids show equilibrium phase boundaries and critical lines. The phase separation is ternary in nature, and measurements allow construction of the ternary phase prism for colloids dispersed in binary fluid mixtures. Comparison with earlier aggregation studies strongly suggests that the aggregation phenomena observed for colloidal particles in binary liquid mixtures is in fact a true phase separation in the ternary mixture. [S0031-9007(97)02376-4]

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Beysens and Esteve [1] made the first observation that when dispersed in small quantities in lutidine/water mixtures charged silica colloids flocculate reversibly within the homogeneous liquid phase near the lutidine/water miscibility gap. Subsequently, particle aggregation phenomena have been reported in several other phase-separating binary mixtures [2,3]. The usual explanation is that particles aggregate because of preferential adsorption of one of the components of the solvent onto the particle surface as the binary liquid phase boundary is approached. Although it is clear that the particle stability is affected by the presence of the miscibility gap, the particles have always been assumed to not change the solvent phase diagram. Hence the particle aggregation curve is shown as being separate from the binary liquid phase separation curve.

The stability of colloidal particles depends on the potential of mean force between them, and there is an immense literature addressing the effect of various additives (e.g., electrolytes or polymers) on the interparticle potential [4,5]. For example, recently [6] silica particles have been shown to aggregate into two liquidlike coexisting phases deep within the homogeneous phase of an aqueous surfactant solution, and colloidal crystals form in dilute dispersions of polystyrene particles in aqueous surfactant solutions near the solvent phase boundary [7]. The latter observation is qualitatively similar to the particle aggregation phenomena discussed earlier. The present study is an attempt to link all these observations, and we present results that strongly support the idea that the particle aggregation phenomena observed in binary liquid mixtures in fact is a phase separation within the overall ternary mixture. This view is in accord with a theory recently developed by Lowen [8].

Phase behavior observations are made for negatively charged Ludox silica particles dispersed in either 2-butoxyethanol (C_4E_1)/water mixtures or in lutidine/water mixtures over a wide range of concentrations and temperature. Aqueous solutions of ethoxylated alcohol surfactants like C_4E_1 display upper miscibility gaps similar to those in the simple binary mixture of lutidine and water. The choice of a surfactant system as the solvent phase stems from a motivation to address the issues related to the effect of complex structures on colloid stability. Ludox is used as the colloid because the small particles (24 nm diameter) are less likely to settle than the larger silica or polystyrene particles (>0.1 μm diameter) used in previous aggregation studies.

2-butoxyethanol (C_4E_1) and 2,6 methyl pyridine (lutidine) were purchased from Aldrich and had stated purities of 99 + %. Water was distilled and deionized (MilliQ), and Ludox (a stable colloidal dispersion) was supplied by Dupont as a 50 wt % dispersion in water with a pH of 9.

Phase behavior was studied by measuring the phase boundaries, tie lines, and the critical line. Phase boundaries were identified by either the visual observation of

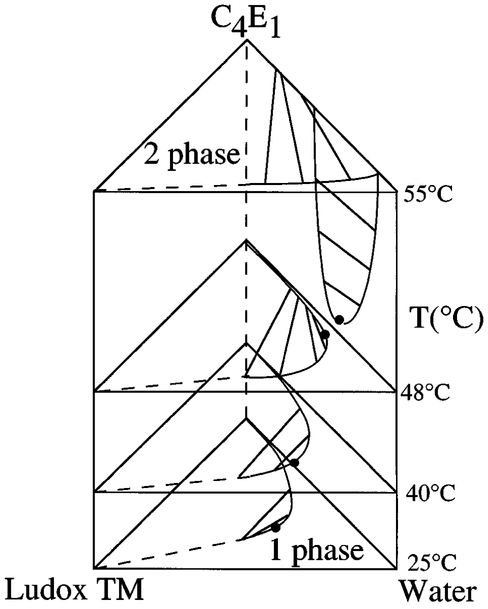

FIG. 1. The ternary phase prism for mixtures of water/Ludox/C_4E_1 showing phase boundaries and tie lines. The curved solid lines are the two-phase boundaries, and the straight lines within the two-phase regions are the tie lines. The broken line regions of the phase boundaries are smooth extrapolations and have not been measured. The dark points are the critical points.

the meniscus or by turbidity measurements. Phase boundaries at constant temperature were obtained by varying the concentrations (in wt %) of Ludox and surfactant. Their temperature variation was obtained along paths of several fixed binary ratios [water/surfactant (C_w/C_s), water/Ludox (C_w/C_l), or surfactant/Ludox (C_s/C_l)], while varying the concentration of the third component. The ternary phase diagram is constructed by combining all of these independent observations. Critical temperatures (T_c, ±50 mK) and critical concentrations (C_c, ±0.5%) are obtained using the equal volume criteria for phase separations within 50 mK of the mixed phase.

Light scattering measurements are performed using a Brookhaven apparatus (Model BI 9000) and an Ar-ion laser (488 nm wavelength). Transmission is kept above 0.4 to avoid multiple scattering, and the scattered intensity is corrected for changes in sample volume, sample turbidity, and the particle form factor.

Figure 1 shows the ternary phase prism for Ludox particles dispersed in C_4E_1/water. The vertical axis is temperature, and each triangle is a constant temperature phase diagram with the three corners representing 100 wt % concentration of the marked component. The cubic phase boundary on the C_4E_1/water plane is the upper miscibility gap for the C_4E_1/water binary mixture with its T_c at 49 °C at 29 wt % C_4E_1 (C_c). In the presence of particles, the ternary mixtures phase separate at temperatures below the binary phase boundary. These phase boundaries are shown by solid curves within each triangle (at each temperature). Two liquidlike phases coexist inside each curve. For a majority of the phase space, the coexisting phases are either rich or lean in colloids. The solid lines within the two phase region are the tie lines and the filled circles are the critical points. This is the first time such a ternary phase prism has been constructed for complex systems containing colloidal particles.

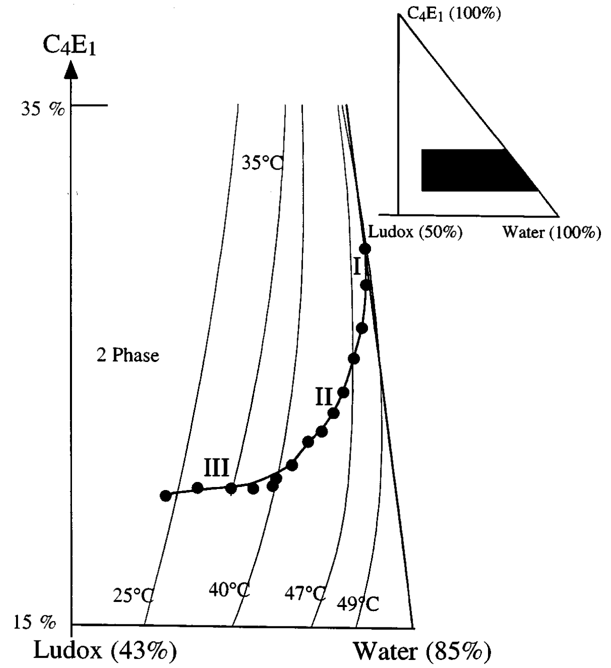

FIG. 2. One-phase to two-phase boundaries at different temperatures (shown in Fig. 1) are projected into the same triangle. Only the region around the critical points (filled circles) are shown. Regions I, II, and III are discussed in the text.

The phase boundaries at different temperatures, shown in Fig. 1, are projected over a limited concentration range onto the same triangle in Fig. 2. The two phase region reaches progressively further into the water corner as T increases, reflecting the decreasing mutual miscibility of the three components with increasing temperature. The dark filled circles are the critical points. The critical line begins at the binary C_4E_1/water critical point. At 10 wt % Ludox (C_{lc}), the critical coordinates change to $C_{sc} = 22.5$ wt % C_4E_1 and $T_c = 45°$ C. Further addition of Ludox causes very little change in the critical C_4E_1 concentration, while the critical temperature decreases continuously. As a consequence of the formation of equal volumes of the coexisting phases near the critical point, the tie lines near the critical line are perpendicular to the critical line. Hence the change in the critical point compositions as Ludox concentration increases determines the direction in which the phase coexistence changes.

The tie lines and the critical line orientations with respect to the phase boundary clearly show the changing partitioning of the three components between the

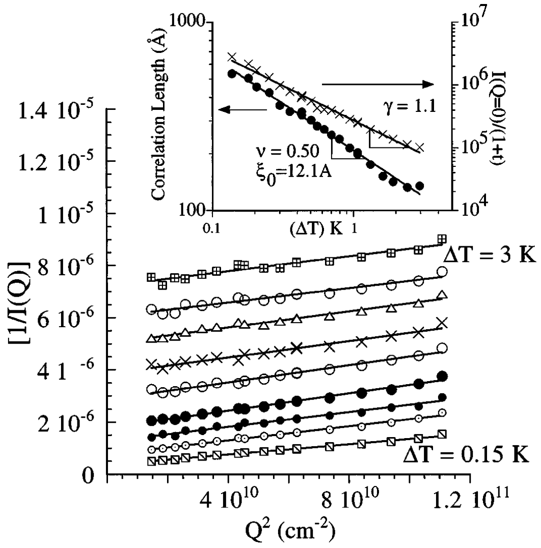

FIG. 3. The reciprocal of the scattered intensity I as a function of square of the scattering vector Q on approach to a critical point ($C_{lc} = 20\%$, $C_{sc} = 20.1\%$, and $T_c = 39.59$ °C) in region III, shown at several $\Delta T = (T_c - T)$ values. The straight line fits at each ΔT give I_0 and ξ according to Ornstein-Zernike theory $1/I(Q) = [1/I_0][1 + (Q\xi)^2]$, where $Q = (4\pi n/\lambda)\sin\theta/2$. λ the wavelength of light, n the refractive index. I_0 the intensity scattered at $Q = 0$, and ξ the correlation length. Inset: I_0 and ξ are plotted against $T_c - T$ in a log-log plot to obtain critical exponents according to $I_0/(1 + t) \sim [\Delta T]^{-\gamma}$ and $\xi \sim [\Delta T]^{-\nu}$; $t = \Delta T/T_c$.

coexisting phases as a function of temperature and composition. For very small particle concentrations, the tie lines are nearly parallel to the C_4E_1/water binary axis, implying equal partitioning of Ludox between the surfactant-rich and water-rich coexisting phases (region I in Fig. 2). For critical temperatures below 43° C, which correspond to Ludox concentrations above 15 wt% (region III), the tie lines are almost parallel to the C_4E_1/Ludox binary axis. Therefore in region III there is almost equal partitioning of water between the particle-rich and surfactant-rich coexisting phases. For intermediate particle concentrations, as the particle concentration decreases, the critical temperature increases and the tangents to the phase boundary at the critical line tilt continuously towards the C_4E_1/water binary axis (region II). This is a clear indication of ternary phase behavior.

Light scattering measurements are performed near the critical point in region III. Ornstein-Zernike theory predicts linear variation of the reciprocal of the scattered intensity with the square of the scattering vector. This is clearly seen here (Fig. 3). The intensity at zero scattering angle I_0, which is proportional to the osmotic compressibility, and the correlation length ξ [calculated using the intercept and slope of Fig. 3 at each $(T_c - T)$] both show power law divergences (Fig. 3, inset). These data further support that the observed colloidal instability is a true thermodynamic phase transition. The universal

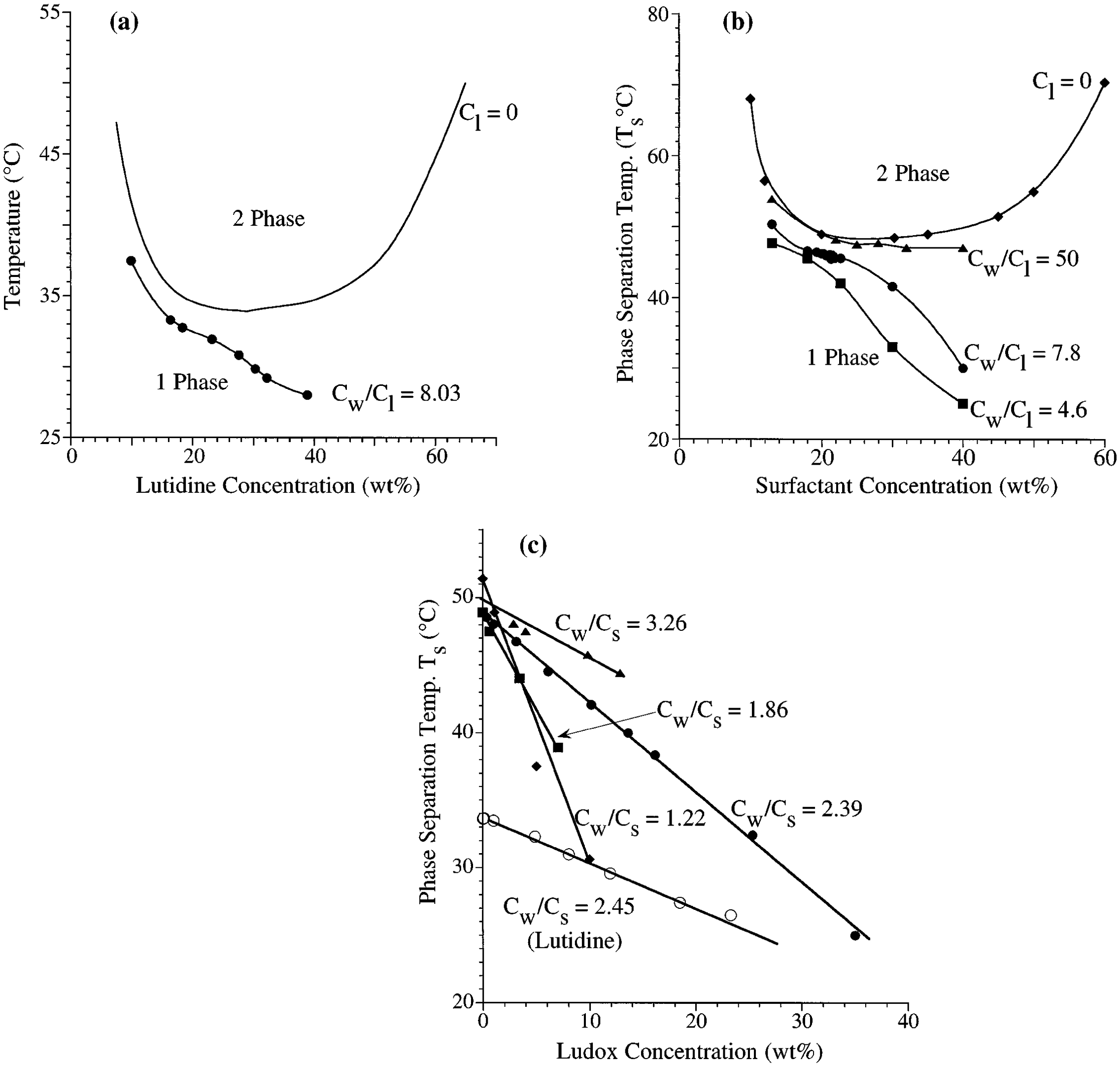

FIG. 4. Comparison of water/Ludox/2, 6 lutidine with water/Ludox/C_4E_1 mixtures. The one-phase to two-phase boundaries with temperature are similar for (a) water/Ludox/2.6 lutidine and (b) water/Ludox/C_4E_1. Similar patterns are seen for fixed water/Ludox weight ratios (C_w/C_l) in both systems, and adding particles to the surfactant solution distorts the cubic shape of the binary coexistence curve. Panel (c) shows the same effect for varying Ludox concentration at fixed water to surfactant weight ratios (C_w/C_s) for the C_4E_1 mixtures (solid symbols) and for varying Ludox concentration at fixed water to lutidine weight ratio (open symbols). Note that the phase-separation temperature for the binary mixture and those for the ternary mixtures fall on the same straight lines. The high temperature side of each curve represents the two phase region.

critical exponents γ and υ are lower than those expected for liquid-gas critical points [9], although the condition $\gamma = 2\upsilon$ is nearly satisfied. More careful measurements are required to determine whether the exponents are truly different from those of liquid-gas transitions.

To verify whether the observed ternary phase behavior is a general phenomena, the phase behavior of Ludox particles has also been studied in 2, 6 lutidine/water binary mixtures, for which $C_c = 29$ wt% lutidine and $T_c = 33.6°$C. As discussed above, particle flocculation has been reported in the vicinity of the phase boundary of 2.6 lutidine/water binary mixtures. Here we view the mixture as a true ternary system and two trajectories are followed in the phase prism by (1) varying lutidine concentration at a fixed water to Ludox ratio [Fig. 4(a)] and (2) varying Ludox concentration at a fixed water to lutidine ratio [Fig. 4(c)]. Also shown for comparison are the corresponding phase boundaries for Ludox particles in the C_4E_1/water mixtures [Figs. 4(b) and 4(c)].

The similarity in the shape of the phase boundary for particles dispersed in C_4E_1/water mixtures and in lutidine/water mixtures is striking. The phase separation temperature of the ternary system decreases continuously as the particle concentration increases. Narayan *et al.* [3] have reported a similar decrease in the flocculation temperature with increasing concentration of silica particles for particles in a mixture of 3-methyl pyridine, D_2O and H_2O. These similarities strongly suggest that the particle aggregation curves reported earlier in the vicinity of binary liquid phase boundaries are in fact the phase boundaries of the ternary systems at small particle concentrations. Therefore particle aggregation is due to a true ternary phase separation of the components. This similarity also rules out any important role for depletion forces induced by the C_4E_1 aggregates.

In the present phase behavior studies, a second phase separation in the solvent phase is observed when the phases that coexist at a lower temperature are further heated without mixing. When the system is continuously mixed and equilibrated while heating, however, the phase boundary of the binary liquid is not observed, and this must be the reason why an aggregation curve in addition to the phase separation curve is observed in earlier studies. In addition, the low particle concentrations used in previous aggregation studies likely precluded observation of the meniscus of a colloidal phase, and rapid sedimentation of the aggregated particles would hinder observation of equilibrium phase separation. Sedimentation time increases linearly as η/a^2 ($\eta =$ solvent viscosity; $a =$ particle or aggregate radius), so such time scales are short in aggregation experiments with large particles and aggregates. These time are long here because the Ludox particles are small ($a = 12$ nm).

Most recent theoretical approaches to this problem describe the colloidal instability as arising from interparticle attractions in the solvent phase [6,10]. The particles preferentially adsorb one of the components of the binary mixture as T_c is approached. Attractive interactions between these adsorbed layers cause colloidal instability and the particles partition into that phase rich in the preferred component. In the present systems, although particles partition predominantly into the wetting phase [11], the ternary system does not reduce to a pseudobinary system with particle number density as the order parameter. The phase separation process involves partitioning of all the components into coexisting phases *even at temperatures where the solvent liquids completely mix with each other.* Lowen [8] models the system as ternary by introducing solvent-particle interactions via the wetting properties of the solvent phase with the particles. Netz [12] shows that the colloid phase separation is due to the preference of the colloids for one of the components. It would be interesting to verify whether the ternary phase diagrams presented here can be explained within those scenarios.

In conclusion, we have constructed, for the first time, a ternary phase prism for binary liquids containing colloidal particles. The colloidal instability is shown to be a true thermodynamic phase transition (i.e., a liquid-gas transition) in the ternary system.

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