

Partitioning of polystyrene latex spheres in immiscible critical liquid mixtures

P. D. Gallagher* and J. V. Maher

Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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We have made a systematic survey of the behavior of colloidal polystyrene latex spheres (PLS's) in critical mixtures of 2,6-lutidine plus water at temperatures where the liquid mixture separates into two immiscible phases. By varying the particle size, particle-surface charge density, and global PLS concentration, we observe a robust and reversible set of phenomena that include the partitioning of the particles into a preferred phase at temperatures close to T_c with a subsequent population of the interface between the liquid phases as the temperature is quenched deeper into the two-phase region. These results are shown to be in good qualitative agreement with thermodynamic models if the models are extended to include the singular temperature dependence of the particle-liquid and liquid-liquid interactions near the critical point. We also observe crystalline ordering of particles on the interface when the population of PLS's on the liquid-liquid interface is high.

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I. INTRODUCTION

The behavior of colloids and macromolecules in multi-phase, immiscible liquid mixtures is a topic of long-time interest and of considerable practical importance. Due to the small size of the particles dispersed in the liquid mixture, Brownian motion is efficient in redistributing the particles to an equilibrium configuration with the lowest total free energy. Consequently, there can be a partitioning of a majority of the particles into a preferred phase where the particle-liquid interaction is most favorable, or alternately, onto an interface between two liquid phases where, due to the reduction in the liquid-liquid area, the total surface energy is effectively reduced. Simple thermodynamic models based on arguments of this kind have been developed and extended [1-3] to include effects of gravity, particle shape, and/or particular features of the particle-liquid interaction. Partitioning particles into a preferred phase is a technique which is used for the separation of polymers and biological macromolecules, usually using aqueous, two-phase polymer solutions [2, 3].

Recently, colloidal suspensions in critical binary liquid mixtures have received renewed attention as candidate systems in which to study wetting phenomena because of the large amount of area present for a given amount of colloid. Beysens and others [4] reported observations of aggregation phenomena in systems of colloidal silica dispersed in mixtures of 2,6-lutidine and water (LW) in the one-phase region. They interpreted the aggregation as being related to wetting transitions expected near the critical point of the binary liquid mixture. In another paper [5] we argue against the interpretation that the aggregation is caused by prewetting transitions, but the dependence of the aggregation on the solvent composition does clearly indicate a relationship to wetting phenomena.

Near the critical point of a binary mixture many of the important quantities which characterize the system are described by power laws in the reduced temperature,

$t \equiv \frac{T}{T_c} - 1$, with universal exponents which do not depend on the details of the specific system. The two primary interactions which should govern the wetting behavior of the system are the interaction energy of the colloidal particle surface with the liquid mixture, and the surface energy (i.e., surface tension) of the interface between the two liquid phases. With the ansatz that the interaction energy between the liquid and the colloidal particle depends only on the local composition of the liquid mixture near the particle surface [6], then the difference in this interaction energy for a particle in one or the other liquid phase should vary as the composition difference between the two phases, α and β , i.e.,

$$\sigma_{\alpha x} - \sigma_{\beta x} \approx \sigma_x^{(0)} t^{\beta_1}, \quad (1)$$

where $\sigma_{\alpha x}$ ($\sigma_{\beta x}$) is the surface energy per unit area for a colloidal particle in the α (β) phase, $\sigma_x^{(0)}$ is an amplitude which depends on the specific details of the colloid particle-liquid mixture interaction, and β_1 is a universal exponent which describes the difference in composition between the two phases near a (two-dimensional) surface ($\beta_1 \approx 0.8$) [6].

Similarly, the surface tension between the α and β phases is expected to behave as

$$\sigma_{\alpha\beta} \approx \sigma_{\alpha\beta}^{(0)} t^\mu, \quad (2)$$

where $\sigma_{\alpha\beta}^{(0)}$ is an amplitude which depends on the specific liquid mixture (a typical value for binary liquid mixtures is ≈ 12 dyn/cm [7]), and $\mu \approx 1.3$ is the surface tension exponent.

Standard wetting arguments for a system near a critical point and in the presence of a flat wall [6] consider the configuration of the movable liquid interface relative to the location of the immovable wall. However, in a

colloidal system the very small size of the particles (the “walls”) causes them to be much more movable than the liquid interface, and consequently the interpretation of the phase behavior in terms of wetting arguments is significantly modified. However, the important energetics which govern the behavior of the colloidal particles in the thermodynamic models depend on the critical properties of the liquid mixture in the same fashion as in the wetting arguments. As a consequence, an analogy to the argument for a necessary crossover in the wetting behavior near the critical point can be constructed for a system with “movable walls.”

We have made a general survey of the behavior of polystyrene latex spheres (PLS's) in binary liquid mixtures of 2,6-lutidine plus water as a function of temperature in the two-phase region. In addition to the interaction between the binary solvent mixture and the colloidal surface, the behavior of the system could also be influenced by additional features of the colloidal suspension, such as the particle size and shape, particle number density, and the mass density of the colloidal particles relative to the liquid mixture. While *a priori* there is no reason to expect a simple description of the behavior of this ternary system, our observations reveal a robust set of phenomena which are seen in all of our samples in spite of changes in the solvent concentration, the particle size, the surface charge on the PLS, and the global PLS concentration. Furthermore, we have made crude measurements on a set of samples in which a critical mixture of isobutyric acid and water (IBW) was used as a solvent in place of LW; all phenomena to be discussed below for our extensive measurements of LW were also observed at least qualitatively for IBW. In a limited temperature range near T_c the behavior we observe seems consistent with thermodynamic models using wetting energetics, while at temperatures farther from T_c additional features are observed (again robust) which are related to the interaction between PLS particles.

The organization of the paper is as follows. In Sec. II we describe sample preparation and characterization and we also give a brief description of our experimental procedures. Since many techniques were eventually used to study the general phase behavior of this system, some of the experimental details are deferred to subsequent sections where results from a particular measurement are discussed. In Sec. III we present our results and discussion. This section is organized phenomenologically into four subsections, each of which describes distinct features of the phase behavior. The first three of these subsections describe equilibrium phenomena in three separate temperature regimes: partitioning of the PLS's into a preferred phase near the critical temperature T_c ; farther from T_c , PLS population of the interface; and farther still from T_c , crystalline order on the liquid interface. The fourth subsection describes interesting kinetic effects seen in reaching the equilibrium states discussed in the first three subsections. This fourth subsection also provides a brief discussion of the irreversible aggregation of colloidal particles which occurs only if the temperature is pushed too far into the solvent's two-phase region. Finally, in Sec. IV we present our conclusions.

II. EXPERIMENTAL PROCEDURES

We used monodisperse, charge-stabilized polystyrene latex spheres prepared using a surfactant-free emulsion polymerization technique, where stabilization against aggregation is provided by a net surface charge density from sulfonate end groups preferentially located on the surface of the sphere [8]. The surface charge density was measured by the manufacturer using conductometric titration techniques [9]. In the solvent mixture these charged particles are expected to be screened by counterions when separated by distances larger than the Debye screening length. For a salt-free LW or IBW mixture (LW is a weak base and IBW is a weak acid) standard ion concentration estimates suggest the Debye screening length ℓ_D to be ~ 10 nm. Our most concentrated samples have mean particle spacings of $6 \mu\text{m}$. Thus for a homogeneous equilibrium state, the particles are approximately non-interacting. (Our estimate of ℓ_D arises from using the reported [10] value of the LW solvation constant to estimate a hydroxide concentration $[\text{OH}^-] \simeq 4.5 \times 10^{-4}$ mol/l. This, along with an equal positive lutidine ion concentration and equal concentrations of positive and negative ions normally present in filtered reagent grade distilled water leads to a total ion concentration of 1.8×10^{-3} mol/l. At even the highest PLS concentration, $\phi = 10^{-3}$, the ion concentrations added to the solutions by the PLS stock solution should be less than 10^{-4} mol/l and thus are ignored in this estimate. Assuming all valence numbers to be unity and using a linear interpolation between the dielectric constants [11] at 35°C of water (75) and lutidine (7.5), we can use the standard expression [12] for the Debye screening length ℓ_D to estimate $\ell_D \simeq 10$ nm.)

For each of the two liquid mixtures (i.e., LW and IBW) we have prepared samples using five different types of polystyrene latex spheres. Their properties are listed in Table I. Using types A–C allowed us to vary the particle radius from 0.5 to $1.5 \mu\text{m}$ while maintaining nearly the same surface charge density of $5.7 \mu\text{C}/\text{cm}^2$. Similarly, using types D and E allowed us to vary the surface charge density by an order of magnitude for particles of nearly the same size, i.e., $d = 0.37 \mu\text{m}$. In order to study the effect of the global concentration of PLS's in the mixture, samples of type-A PLS's in LW were prepared at five different global volume fractions of PLS's, each differing by a factor of 10, in the range $10^{-7} < \phi < 10^{-3}$. This range allows visual observations of extreme volume fractions but exceeds the useful range for standard light-scattering

TABLE I. Diameter and surface charge density of PLS's as reported by the manufacturer.

| Type | d (μm) | σ ($\mu\text{C}/\text{cm}^2$) |
|------|-----------------------|--|
| A | $0.555 \pm 2.9\%$ | 5.70 |
| B | $1.014 \pm 7.6\%$ | 5.77 |
| C | $1.46 \pm 3.3\%$ | 5.56 |
| D | $0.378 \pm 5.9\%$ | 3.85 |
| E | $0.371 \pm 2.3\%$ | 0.38 |

measurements, since strong multiple scattering occurs in the most concentrated sample, while in the most dilute samples the very weak scattering from the PLS particles is overwhelmed by scattering from critical fluctuations in the solvent. For all the data shown in this paper we used PLS in LW mixtures. However, as was mentioned above, some of the experiments were crudely repeated with IBW as a solvent mixture and these indicated that our general observations were robust against changes in the solvent mixture. Both binary solvent mixtures contained water as one component (to ensure compatibility with the PLS's which are originally suspended in distilled water). Also, both mixtures have been well studied and have convenient critical temperatures, although for the LW system the coexistence curve is inverted (i.e. has a lower consolute point). For LW, the lower critical temperature is $\approx 33.8^\circ\text{C}$ [13], and for IBW the upper critical temperature is $\approx 26.12^\circ\text{C}$ [14].

We prepared the solvent mixtures by weight from filtered, reagent grade 2,6-lutidine [15] (or isobutyric acid [16]) and water and then added a diluted suspension of PLS's in water. The final composition of the PLS plus binary solvent mixture was near the published values for the critical mass fraction ($c_c = 0.29$ for LW [13], and $c_c = 0.39$ [14] for IBW). The overall uncertainty of the sample composition prepared in this way is less than 1% for both the solvent mass fraction and the volume fraction of polystyrene spheres. We verified that the samples were near their critical composition by phase separating each sample at several temperatures and measuring the volume of each phase. We fit the relative volumes to the expected shape of the coexistence curve resulting in best-fit values for both the critical temperature T_c and the coexistence temperature T_{cx} . Using this procedure, the coexistence temperatures of our samples never differed from the critical temperature by more than 10^{-4} K.

Due to the singular temperature dependence of the important quantities near the critical point, good temperature control was necessary for these experiments. We used a Tronac temperature controller with a well-stirred water bath around the sample to maintain an overall temperature stability of better than ± 0.5 mK over many hours and even days, much longer than needed to attain equilibrium and make light-scattering measurements. Our experimental procedure consisted of vigorously stirring the samples (after temperature equilibrium had been reached within the water bath) using a teflon-coated magnetic stir bar sealed inside each glass sample tube. After phase separation, we combined a variety of techniques to monitor such features of the behavior as (1) how the PLS particles distributed themselves between the two phases or at the interface, (2) changes in the measured size of individual PLS particles which might indicate wetting or adsorption layer growth, and (3) aggregation or structure in the PLS distribution which would indicate significant PLS interactions. These techniques included visual observations which were effective in determining which of the two liquid phases was preferred by the particles and whether a large number of particles were present on the interface, since the strong scattering

of light by the large spheres resulted in a milky appearance in regions where the local PLS concentration was high. For particles dispersed uniformly in one of the two bulk phases, we used standard light-scattering techniques including measurements of the particle structure factor (from the angular distribution of light) and diffusive relaxation (through dynamic light scattering). The size of the particles could be determined from both the particle structure factor, and from the diffusion constant. In the case of the dynamic light-scattering (DLS) measurements, the sphere radius was obtained using the Stokes-Einstein relationship for the diffusion constant and an independent determination of the viscosity of the surrounding liquid phase. We used our measurements of the liquid coexistence curve together with published viscosity data for the LW system [17] as a function of temperature and composition to determine the viscosity of the solvent mixture. As a check, we measured the viscosity of LW mixtures (no spheres) at many different compositions and temperatures with a Cannon-Fenske capillary viscometer and always obtained good agreement with the published data. We also consistently obtained good agreement in the measured sphere size from both static and DLS measurements, and we estimate the overall uncertainty in the sphere size determined from either technique to be about 10%. Measurements of the intensity for off-specularly reflected light from the interface (after subtraction of the bulk phase scattering which, in turn, was measured by orienting the laser to miss the interface) allowed us to monitor changes in the concentration of PLS's on the interface.

III. RESULTS AND DISCUSSION

A. Bulk partition (temperatures near T_c)

For all of the samples phase separated near T_c we have observed a noticeable partitioning of a majority of the PLS's into one of the two bulk phases, which we term the preferred or wetting phase. This segregation of the PLS's is not only evident from the milky, white opalescence of the more populated phase, but also from light-scattering measurements made through each phase which demonstrate a large difference in the amplitude of light scattered by the PLS. Figure 1 shows results from angular distribution measurements through the upper and lower phases of a critical LW mixture containing $0.555\text{-}\mu\text{m}$ PLS's (type A) at equilibrium 100 mK above the critical temperature. In the wave-number range probed by our experiment, the Lorentzian structure factor this far from the critical point for light scattered by bulk solvent fluctuations is nearly constant. However, the spheres are large enough to display a strong wave-number dependence, with the first minimum in the structure factor clearly visible. The dashed lines represent best fits to the data using the Rayleigh-Debye approximation for the sphere scattering [18] plus a constant intensity background which accounts for both the bulk critical scattering and instrumental background. For this sample, the large amplitude of the PLS scattering is evident in the

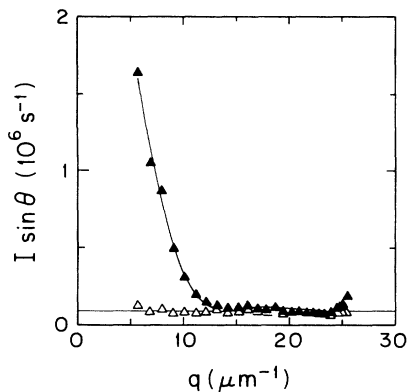


FIG. 1. Intensity of light scattered as a function of wave number from the upper (light triangles) and lower (dark triangles) phases of a PLS/LW mixture separated ≈ 100 mK above T_c . The solid line is a fit to the data.

lower, water-rich phase but undetectable from the constant background in the lutidine-rich, upper phase. This strong partitioning of type-A ($0.555\text{-}\mu\text{m}$) PLS's in LW mixtures was observed over our full range of global PLS volume fraction, $10^{-7} \leq \phi \leq 10^{-3}$.

The choice of which phase wets the PLS is observed to be sensitive to the surface charge density of the PLS and to the properties of the liquid mixture, and not to the size or concentration of particles in the mixture. We separated mixtures containing each of the five PLS types in both LW and IBW mixtures to determine the wetting phase. For both liquid mixtures (LW or IBW) we found that the high surface-charge-density particles (types A–D) preferred the water-rich phase while the low surface-charge-density particles (type E) preferred the phase rich in the nonaqueous component. Our results are summarized in Table II. This suggests that the surface charge density of the particles determined whether they were wet by the water-rich phase and that the pH of the solvent mixture was not important.

Since almost all of the particles are in the preferred phase at temperatures close to T_c , it is difficult to determine the relative population of particles between the two phases from measurements of a single sample at fixed PLS concentration. Instead, we have estimated the ratio of the PLS concentration between the two phases, called the partition coefficient K_p by combining light-scattering measurements made through the upper and lower phases of five different LW mixtures, all phase separated at the same temperature and containing the same

TABLE II. Wetting phase as a function of PLS type. *W* refers to wetting by the water-rich phase, and *L* and *I* to wetting by the lutidine- or isobutyric acid-rich phase, respectively.

| Liquid mixture | PLS type | | | | |
|----------------|----------|---|---|---|---|
| | A | B | C | D | E |
| LW | W | W | W | L | L |
| IBW | W | W | W | I | I |

particle type (type A), but with different global PLS concentrations. In samples with a low global PLS concentration, we are able to measure the amplitude of the PLS scattering in the wetting phase, but it is too weak to measure in the nonwetting phase. At much higher global PLS concentrations, we can measure PLS scattering amplitudes in the nonwetting phase, but the sphere concentration in the wetting phase is too high for meaningful light-scattering measurements. If we assume that the relative sphere population between the phases is independent of the global particle concentration, we can estimate the partition coefficient from the ratio of global PLS concentrations ϕ_1/ϕ_2 needed to give the same scattering intensity in the unpreferred phase at ϕ_1 and in the preferred phase at ϕ_2 . The assumption that K_p is independent of ϕ is equivalent to assuming negligible interparticle interactions and is therefore more reasonable for the more dilute mixtures but could fail for the more concentrated ones. As was noted above, the mean particle spacing is more than 500 Debye screening lengths for even the most concentrated samples so this technique should provide a reasonable lower bound on the partition coefficient. Figure 2 shows results from measurements of the angular distribution through the lutidine-rich phase (nonwetting) of a concentrated sample ($\phi_1 \approx 10^{-3}$) and from the water-rich phase (wetting) of a dilute PLS/LW mixture ($\phi_2 \approx 10^{-6}$), both separated at the same temperature. Here, the amplitude of the light scattered by the PLS's is nearly equal in the two phases.

To determine K_p , we plot the measured PLS scattering amplitude from each phase of the liquid mixture as a function of the global PLS concentration. The scattering amplitude should depend linearly on the particle concentration, but with a slope which depends on the relative refractive index between the sphere and the surrounding liquid, which will obviously be different in each phase. Therefore, we linearly extrapolate the scattering amplitudes measured in each phase to a low, arbitrary concentration ($\phi = 10^{-8}$) and divide each intensity at

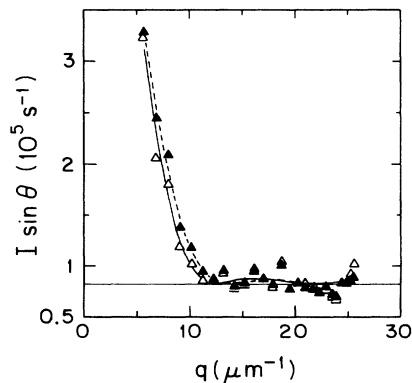


FIG. 2. Intensity of light scattered as a function of wave number from the upper phase (light triangles) of a concentrated ($\phi = 10^{-3}$) PLS/LW sample, and from the lower phase (dark triangles) of a dilute sample ($\phi = 10^{-6}$ g/ml), both phase separated ≈ 100 mK above T_c .

this concentration by the slope to correct for the difference in the refractive indices before taking the ratio to estimate K_p . This is shown in Fig. 3 for five samples separated approximately 100 mK above T_c , where we obtain $K_p \sim 2300$.

Recently, Boucher [3] has reviewed thermodynamic models which describe the partitioning of macromolecules between two immiscible liquid phases. These models generally treat the particles located in each of the liquid phases as separate systems of noninteracting, “ideal-gas”-like particles, with an additional term added to the particle free energy describing the interaction of the colloidal surface with the surrounding liquid. By requiring equilibrium between the two “systems,” the ratio of the particle concentrations between the two phases can be determined. For spherical particles of radius r_1 one obtains

$$K_p \equiv \frac{n_\beta}{n_\alpha} = \exp \left[(4\pi r_1^2) \frac{(\sigma_{\alpha x} - \sigma_{\beta x})}{k_B T} \right], \quad (3)$$

where k_B is the Boltzmann constant, and n_α (n_β) is the number concentration in the α (β) phase. With the assumption that the interaction difference between the particle and each of the two phases should vary as the composition difference between phases at the surface [Eq. (1)], we expect that $\ln K_p$ should behave as a power law in the reduced temperature with an exponent β_1 . This is consistent with the expectation that the partition coefficient approaches 1 at the critical temperature where the two phases are identical. This result was first anticipated and tested by Bronsted and Warming [1] using chromium hydroxide and arsenious sulphide solutions in near critical water-isobutyl and alcohol-ethanol mixtures. Their analysis was based on mean-field expectations and yielded an exponent near $\frac{1}{2}$. Due to the onset of population of the liquid/liquid interface by the PLS particles (to be discussed below), we have not been able to observe sufficient temperature dependence in our measurements of the partition coefficient to determine an exponent.

We have looked for the formation of wetting layers on

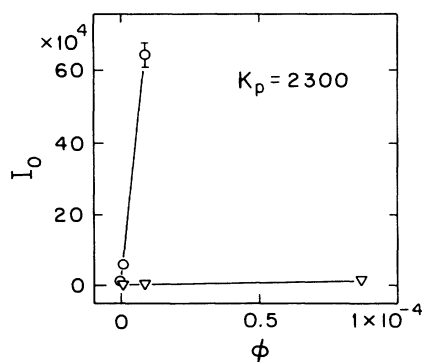


FIG. 3. Intensity (arbitrary units) of static light scattered from colloidal spheres in the upper (triangles) and lower (circles) phases of five different LW/PLS samples at the same temperature but with different global PLS concentrations ϕ .

the particles by measuring both static angular distributions and photon autocorrelation functions to monitor the effective size of the spheres. We have observed no change in the effective size from that reported by the manufacturer (and confirmed by us using both static and DLS measurements of spheres dispersed in water) in either phase in this temperature region. This is demonstrated in Fig. 2 where the sphere structure factors measured in the wetting and nonwetting phases of PLS/LW mixtures separated 100 mK above T_c are nearly identical. We estimate that, with an experimental resolution for the sphere size of nearly 10% for both DLS and angular distribution measurements, we would be sensitive to wetting layers whose thickness was of the order of two to three correlation lengths of the critical liquid mixture at temperatures closest to T_c . This lack of evidence of a wetting layer is easy to understand for the preferred phase where no such layer should exist and for most temperatures in the nonpreferred phase where layers as thick as ten correlation lengths would be too thin to be observed. However, our observations near T_c are very reliable, and we do not understand why layers thicker than two to three correlation lengths do not appear on the particles which are forced into the nonwetting phase at large values of ϕ .

B. Initial population of interface (intermediate temperature range)

In addition to the partitioning of the colloidal particles into a preferred bulk phase, we have also observed a striking temperature dependence to the presence of spheres at the interface between the liquid phases (i.e., to the meniscus). This is an equilibrium phenomenon which is quite robust, being observed in all of the samples we made, and furthermore is reversible with temperature. Similar to our interpretation of the partitioning of particles into a preferred phase as a manifestation of wetting, we believe that the observed temperature-dependent migration of spheres to the interface is related to wetting transitions which are expected near T_c [6]. The interface population can be described in terms of three different temperature regions. First, there is the part of the two-phase region, beginning at the critical temperature T_c , which we have discussed in Sec. III A above. This region is characterized by a “clean” interface, i.e., there is an unobservably low concentration of PLS at the meniscus. In this region, observations reveal a flat and uniformly reflective (shiny) interface with no evidence of PLS population, even when the PLS population of the preferred bulk phase is very high ($\phi \approx 10^{-3}$). Second, beginning rather abruptly at a temperature which we call the “particle wetting temperature” T_w (in anticipation of our interpretation in analogy to wetting phenomena), we observe the onset of preferential adsorption of PLS particles on the meniscus. Here, we observe an increasing cloudiness of the interface, nonuniform reflectivity (especially when the meniscus is illuminated from behind with light incident near the critical angle for total internal reflection), and an increase in the intensity of light scattered nonspecularly from the

interface. This adsorption of particles on the interface increases as the temperature is moved farther from T_c (for typically 100–500 mK) until the onset of the third temperature regime with the appearance of highly concentrated “patches” or “islands” of PLS particles on the interface. As the temperature moves into this third region (farther from T_c) the islands grow in size. The third temperature region is characterized by high concentrations of PLS and significant interparticle interactions at the liquid interface, and we defer a more detailed discussion of its features to a later section, concentrating in this section on the transition from the first to the second temperature region.

We have attempted to extend our visual observations of the onset of interface population near T_w by measuring the scattering intensity from the interface when a laser beam is totally internally reflected from the meniscus in the upper, lutidine-rich phase of a PLS (type *A*) plus LW mixture. The detector was positioned away from the specular direction of the reflected beam but in the forward direction (typically at $\theta \approx 30^\circ$) where the scattering from the $d = 0.555\text{-}\mu\text{m}$ particles was strong. To remove the contribution to the total intensity from light scattered from composition fluctuations in the upper phase, a second intensity measurement was made with the laser beam in the upper phase but missing the interface. Subtraction of the two measurements removed most of the bulk contribution to the total signal and emphasized the surface scattering contribution. This excess surface intensity is shown in Fig. 4 as a function of the temperature difference from T_c for a (type-*A*) PLS plus LW sample. The onset of interface population at T_w is determined from both visual observations and from the first sign of a systematic increase in the excess surface intensity. The large increase in this intensity at larger temperature differences coincides with the appearance of concentrated “islands” of PLS on the interface, which results in very intense coherent scattering from the meniscus. The subsequent decrease in intensity at higher temperatures is an artifact of our experimental geometry, since the increasing curvature of the meniscus with temperature eventually

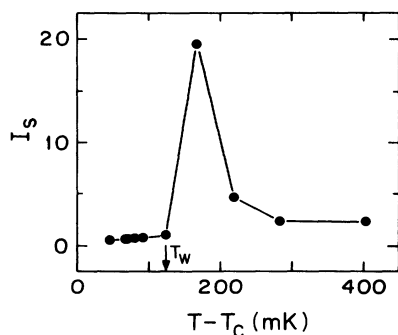


FIG. 4. Intensity (arbitrary units) of light scattered from the interface of a separated LW/PLS mixture as a function of $|T - T_c|$. Onset of particle population of the interface is indicated at T_w . Reduced I_s at $T - T_c > 200$ mK is discussed in the text.

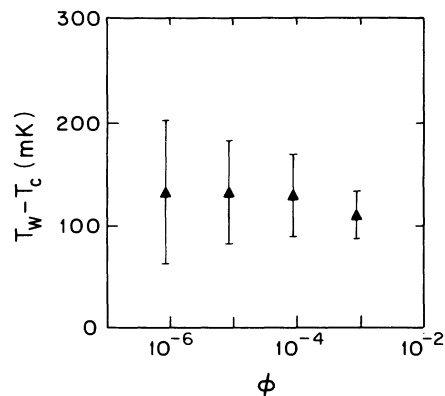


FIG. 5. Offset of interface population temperature T_w from critical temperature T_c for indicated values of PLS volume fraction.

blocked much of the light scattered from the meniscus (visual observations showed no decrease in the interface population at these temperatures).

As can be seen from Fig. 5, there was no measurable change in the particle wetting temperature (T_w) when the concentration of PLS was changed; however, the onset of clumping into concentrated islands of PLS clearly occurred closer to T_w for samples with a higher global PLS concentration. T_w was different for particles with different surface charge densities. For LW mixtures containing PLS types *A*, *D*, and *E*, Fig. 6 shows that the measured population temperature relative to the critical temperature was $|T_w - T_c| = 100 \pm 40$, 25 ± 15 , and 60 ± 30 mK, respectively (with the type-*E* particles populating the interface from the upper phase as was discussed above). Since particles of types *A*, *D*, and *E* are all approximately of the same size, this shift in T_w suggests a continuous change in the wetting behavior of the PLS particles with surface charge density. High-charge-density particles are wet by water and have a T_w relatively far from T_c . Then, as the surface charge is de-

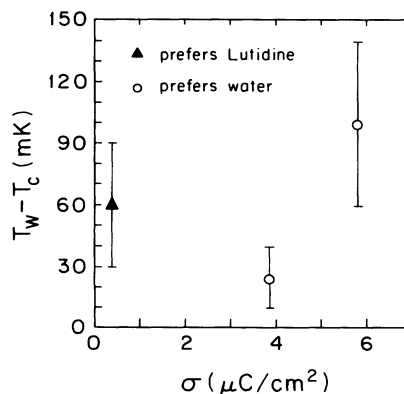


FIG. 6. Offset of interface population temperature T_w from critical temperature T_c for indicated values of PLS surface charge density σ .

creased, T_w moves closer to T_c , until at some point (below $3.85 \mu\text{C}/\text{cm}^2$) the particles change their preference to the lutidine-rich phase. Once the preferred phase is changed, further decreases in the surface charge density result in T_w moving away from T_c .

The thermodynamic models discussed by Boucher [3] also consider this preferential adsorption of colloidal particles to the interface between the liquid phases. In the same spirit as the previous discussion on bulk partition, particles located at the liquid interface are treated as a separate “system” in equilibrium with the two other “systems” which represent particles located in each of the other two liquid phases. The particle free energy for spheres on the interface contains, in addition to the usual “ideal-gas” terms, an additional term which accounts for the liquid-particle contact on both sides of the interface and for the reduction in the liquid-liquid surface area. Many other realistic features describing the particle-interface contact, some of which are reviewed by Boucher [3], can be included in this term, including the effect of particle shape, the contact angles with the liquid mixture, and the deformation of the liquid meniscus by gravity. For simplicity, we consider spheres of radius r_1 which “float” on a flat, horizontal interface with equal area hemispheres in each of the two liquid phases. The interaction term then will contain a positive contribution from the particle-liquid contact, $2\pi r_1^2(\sigma_{\alpha x} + \sigma_{\beta x})$, and a negative contribution caused by the reduction of the liquid-liquid contact area (equal to the cross-sectional area of the sphere), i.e., $-\pi r_1^2 \sigma_{\alpha\beta}$. The ratio of the PLS concentration at the meniscus (n_I) to that in the preferred bulk phase β (we let $\sigma_{\alpha x} > \sigma_{\beta x}$) is determined from the condition of equilibrium between the phases, and yields

$$\frac{n_I}{n_\beta} = \exp \left\{ \left(\pi r_1^2 \frac{\sigma_{\alpha\beta} - 2(\sigma_{\alpha x} - \sigma_{\beta x})}{k_B T} \right) \right\}. \quad (4)$$

Since β is the preferred phase, the interaction difference $(\sigma_{\alpha x} - \sigma_{\beta x}) > 0$ and the sign of the exponent depends on the magnitudes of the terms in the argument. Using the critical temperature dependence for the surface energies [Eqs. (1) and (2)], we conclude that the difference in the critical exponents $\mu > \beta_1$ should cause a necessary change with temperature in the sign of the exponent in Eq. (4). Therefore, there should be a crossover from partition primarily into the preferred bulk phase to preferential adsorption on the interface as the temperature difference from T_c is increased. This is in analogy with the standard argument [6] for a crossover from complete to partial wetting for a critical fluid against a flat wall. The temperature for the onset of migration is defined by the condition that

$$2(\sigma_{\alpha x} - \sigma_{\beta x}) = \sigma_{\alpha\beta}, \quad (5)$$

which, except for the factor of 2 (which arises from the spherical shape of the particle and our assumptions regarding the particle-liquid contact) is the same as the condition defining the wetting transition temperature in the standard wetting arguments [6]. While the importance of a low surface tension in ensuring bulk rather than

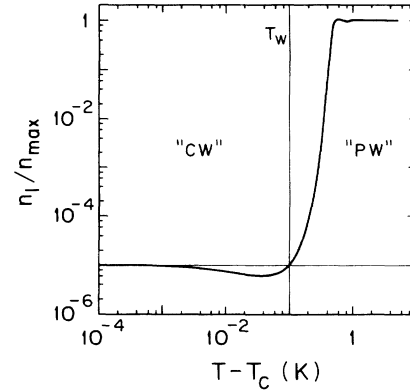


FIG. 7. Calculation from Eq. (4) of expected concentration of PLS’s (normalized to the concentration at close packing) at the LW interface as a function of the temperature difference from T_c .

interface population has long been recognized for polymer and biomolecular partition [2, 3], to our knowledge the necessary crossover with temperature near a critical point and the close relation to wetting arguments have not been previously appreciated.

We have used Eq. (5) along with published values of the LW surface tension [7] and our measured particle wetting temperature ($T_w \approx 100$ mK) to determine $\sigma_x^{(o)}$ [of Eq. (1)] for use in Eq. (4). Figure 7 shows the resulting prediction of Eq. (4) for the surface concentration of $0.5\text{-}\mu\text{m}$ PLS’s in units of the close-packing concentration. In both our observations and the calculation, the concentration in the preferred bulk phase changes negligibly through the observed temperature region. The calculation indicates that the jump in population at the interface occurs in a narrow temperature region relative to the uncertainty limits of our measurements and thus should appear “sharp” in our observations. This is in excellent qualitative agreement with our observations in this temperature region.

C. Concentrated PLS structure at the interface (higher temperature range)

There is an abrupt appearance, at a temperature which depends on the global PLS concentration, of concentrated “islands” of colloidal spheres. These patches are noticeable as regions of lower reflectivity on the interface and from the intense surface scattering which results when they are illuminated by a laser. Their appearance is reminiscent of a two-dimensional phase transition (i.e., “clumping” transition [3]) to a high-concentration PLS “phase” on the interface. After their initial appearance these regions grow with subsequent temperature changes away from T_c until all or most of the available liquid-liquid surface area is occupied. We note that for the LW system, the Pyrex glass walls of the sample test tube are completely wet by the water-rich phase of the mixture [19] and consequently the available liquid interfacial

area includes a vertical interface near the glass test tube walls surrounding the upper, lutidine-rich phase. Since the mass density of the PLS particles is higher than that of either phase of the liquid mixture, the condensation of particles occurs first on the lower, horizontal meniscus and then proceeds to “grow” up the vertical interface as the temperature is quenched deeper into the two-phase region. These patches dissolve readily if the temperature is dropped below T_w .

We have studied this concentrated PLS “phase” on the vertical liquid interface by introducing a laser beam normal to the glass test tube wall in order to illuminate the layer of particles located near it. At a temperature where a wall layer of particles was present, the laser beam produced a striking diffraction pattern which consisted of either a sharp ring (which could arise from either liquidlike or polycrystalline order) or an annular pattern of Laue spots (clearly crystalline order). We assume that the sample is normally polycrystalline with the prominence of spots in some of our observations an accident of the location of the laser beam. Figure 8 shows the scattered intensity as a function of wave number as the photomultiplier is moved through a Laue-type spot from an illuminated sample of $d = 0.54\text{-}\mu\text{m}$ PLS’s in a LW mixture. The solid line indicates a best fit to the data using a Gaussian form which would be characteristic of a polycrystalline sample. The location of the peak maximum at $q = 13.02\text{-}\mu\text{m}^{-1}$ indicates a mean particle spacing close to that for close packing of spheres with the nominal diameter. The ratio of the peak width to peak position characterizes the typical extent of order in the PLS layer [20], and from our measurement we estimate that the crystalline order extends to $q/\delta q \approx 60$ particle diameters. We do not know if the crystalline order arises from direct Coulomb interactions between nearby particles whose spacing is less than the Debye screening length (which is possible at close packing) or from dipole interactions caused by the distorted ion-screening clouds due to the difference in polarizability of the two liquid phases [21]. Similar two-dimensional crystalline order

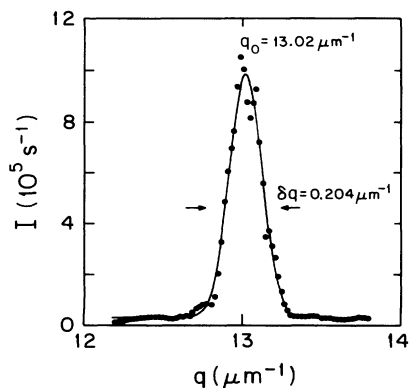


FIG. 8. Scattering intensity as a function of wave number for a “Laue spot” resulting from the diffraction of light incident on a (poly)crystalline PLS interfacial phase in a LW sample. The solid line is a best fit to a Gaussian form.

has been observed using polystyrene latex particles at a water-vapor interface [21], although the ability to control the surface population with temperature is probably much better for the critical system used in our experiments.

D. Kinetic and irreversible effects

We now comment on our observations regarding the kinetics of phase separation in the presence of the colloidal suspension. At temperatures close to T_c , where the interface is unpopulated, the rate of phase separation is not noticeably different from that for mixtures not containing spheres. The partitioning of particles into a preferred phase appears to have already occurred by the time the growing droplets are first visible by eye (i.e., several minutes). However, at temperatures above T_w , where the interface population is relatively high, the phase separation takes much longer to complete. At these temperatures, the PLS particles appear to find the many interfaces present in the separating mixture and remain there until the interfaces rupture during droplet coalescence. As PLS particles are forced off the available interfaces they collapse to the lower liquid-liquid meniscus and then proceed to redissolve into the lower, preferred phase. The resulting cloudy rain of colloidal particles re-entering the preferred phase lasts for many hours, but eventually results in a uniform dispersion of PLS in the water-rich phase. If the PLS population on the interface is high enough, the rate of droplet coalescence becomes very small and we observe the formation of metastable foams embedded in the upper phase. These foams consist of many (presumably water-rich) films with high concentrations of colloidal spheres, easily determined from both the milky white appearance and from the resulting diffraction pattern when they are illuminated (indicating crystalline order). They have remained for many hours and even days in some samples if left undisturbed but have always eventually reached the relevant equilibrium state described above for their temperature. We speculate that the slow rate of coalescence and the eventual formation of foams result from the very low effective α/β surface tension caused by the presence of many colloidal particles on the interface. For low surface-charge-density particles (i.e., type *E*) which prefer the lutidine-rich phase, we have observed the same repopulation of the wetting phase at equilibrium after stirring, but have not observed significant formation of these metastable foams in the interim.

If the temperature of the sample is moved too far from the critical temperature (i.e., typically > 10 K) we observe irreversible aggregation of the PLS particles. These aggregates are quite large (several millimeters) in size, irregular in shape, and fairly dense, usually settling at the bottom of the sample tube. We have been unable to redisperse these aggregates even after lowering the temperature closer to T_c , or even into the one-phase region, and vigorously stirring or sonicating in an ultrasonic bath. Consequently, once this problem was discovered, we made new samples and protected them by

avoiding large temperature differences from T_c in the two-phase region of the liquid mixture. Irreversible aggregation is known to occur [4, 22] in PLS colloids at large solvent ion concentrations and is believed to result from particle/particle contact at distances small enough that van der Waals interactions become important. We do not know what leads to this irreversible aggregation at high temperatures in our system, but we speculate that the larger ion concentrations and the larger shift in the pH value of the disfavored phase at higher temperatures could be responsible.

IV. CONCLUSION

We have made a systematic study of the behavior of polystyrene latex spheres in critical LW mixtures in a temperature region where the mixture consists of two immiscible phases. We find a robust and reversible set of phenomena which occur in all of our samples regardless of variations in the surface charge density, size, or concentration of PLS particles. Replacing the LW solvent mixture with IBW results, at least qualitatively, in the same set of observed phenomena. These phenomena can be broadly categorized into three temperature regimes: (1) partition of a majority of the PLS particles into a preferred bulk phase at temperatures closest to T_c , (2) the onset of preferential adsorption of the PLS onto the interface between the two liquid phases at a temperature T_w , and (3) at temperatures still farther from T_c , the appearance of very concentrated populations of PLS on the liquid interface. In this final temperature region, PLS interactions and the low effective liquid surface tension result in a variety of phenomena including the formation of ordered (crystalline) arrays of PLS on the equilibrium interface and interesting kinetic effects which can (at some temperatures) result in the formation of metastable foams following stirring. Only at very

large temperature differences from T_c have we observed irreversible aggregation of the colloidal suspension.

We have extended existing thermodynamic models [1–3] describing the behavior of movable macromolecules in an immiscible liquid mixture to include the power-law temperature dependence of the important energetics near the critical point of the liquid mixture. We find that these models predict a necessary crossover from partition into a preferred bulk phase near T_c to a preferential adsorption on the interface between the phases farther from T_c at a temperature T_w , in analogy with standard arguments for a necessary crossover from complete to partial wetting of a flat wall [6]. These extended models are in excellent qualitative agreement with our observations. We point out that the movability of the colloidal particles means that the configuration of the liquid mixture (i.e., the location of the liquid interface relative to the wetting “walls”) remains unchanged in these systems, unlike the standard wetting of a macroscopic wall. Since a wetting layer does not appear to form on the particles, many curvature effects which have been suggested [23, 24] for wetting in colloidal systems may not play an important role in the behavior of the system. However, the crossover to population of the interface is related to the same energetics as those that govern the wetting transitions, and should be able to provide useful information regarding the location of surface transitions.

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* Present address: Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215.

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