

## Adsorption Phenomena at the Surface of Silica Spheres in a Binary Liquid Mixture

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Silica spheres of 1600-Å diameter immersed in the binary fluid water+2-6-lutidine have been studied by light-scattering techniques. The scattered light was seen to be strongly dependent on temperature and concentration. This effect is due to the appearance of a lutidine layer on the spheres. The layer thickness dramatically increases near a transition line where the spheres aggregate as a result of attractive interactions. This transition exhibits all the features predicted for the prewetting transition between high and low adsorption of a fluid on a surface.

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Wetting phenomena on a wall appear in multicomponent systems when the components exhibit different interactions with the wall. Even in the simplest case of a binary fluid, a rich behavior is expected.<sup>1-2</sup> In the region where the system exhibits two phases, i.e., on the coexistence curve (Fig. 1), a first-order transition between partial wetting (finite contact angle between the wall and the two phases) and complete wetting (one phase wets the wall and surrounds the other phase) has already been observed.<sup>3</sup> In the case of the water-lutidine (W-L) mixture, which presents a lower critical point at the L mass fraction  $C = 0.286$  and at the temperature  $T = 34^\circ\text{C}$ ,<sup>4</sup> this "wetting transition" takes place for a silica wall at  $C_W \approx 0.07$  and  $T_W \approx 50^\circ\text{C}$ ,<sup>5</sup> with the L-rich phase wetting the silica. In the one-phase region of a binary mixture one expects a line of first-order "prewetting" transition which should separate a region of weak chemical adsorption from a region of large adsorption. This line (Fig. 1) should begin at the wetting transition  $(C_W, T_W)$  and end with a prewetting critical point  $(C_A^c, T_A^c)$ —which should not be confused with the liquid-liquid critical point  $(C_c, T_c)$ . Up to now, prewetting has remained undetected. However, the behavior of small silica spheres immersed in the W-L mixture provides, as we shall see, some evidence of the existence of such a prewetting line in the one-phase region. (The anomalous adsorption which has already been detected near the bulk critical point<sup>6,7</sup> is related to the bulk critical region and is not connected to the prewetting transition.)

Small spheres immersed in binary fluids have already been studied near the liquid-liquid critical point by microscopy<sup>8</sup> or dynamic light scattering.<sup>9,10</sup> In all cases anomalous mobilities have been observed, attributed to correlated layers<sup>8,10</sup> or to surface interactions.<sup>9</sup> Finally, interferometric measurements in the W-L mixture have already proved the existence of a L-adsorption layer on silica spheres.<sup>11</sup>

*Experiments.*—Our initial aim was to deduce the thickness of the L layer sticking on silica by measuring the optical cross section of small silica spheres (diameter  $2a = 1600 \text{ \AA}$ ) immersed in the W-L mixture. For that purpose, we prepared W-L samples with water incorporating a small mass fraction  $C_0$  (0.004 or 0.009) of monodisperse silica spheres prepared with use of the Störber method.<sup>12</sup> No shift of the bulk critical point due to the addition of spheres was observed. We measured, at different temperatures, the turbidity  $\tau = -(1/l)\ln I$  [ $l$  is the path of light (0.2 or 2 cm) and  $I$  is the light transmittance] while detecting the forward scattered light on a screen in order to evaluate the

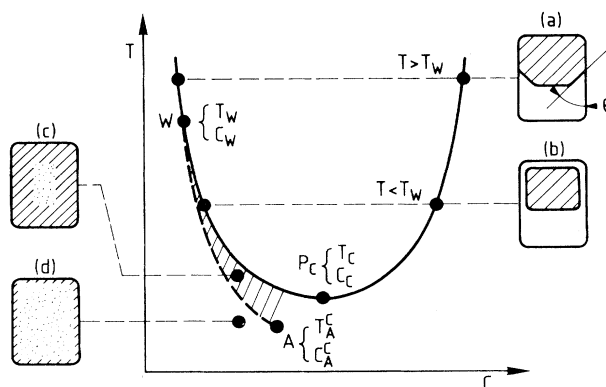


FIG. 1. Phase diagram of a binary fluid with a lower consolute point. Solid curve, coexistence curve with  $P_c(C_c, T_c)$  the liquid-liquid critical point. Dotted curve, first-order prewetting line, which separates a region of large adsorption (hatched region) from a region of small adsorption. The overall aspect of the mixture is represented by (c) and (d), with an excess concentration of one component near the sample walls.  $A(C_A^c, T_A^c)$  is a critical adsorption point, and  $W$  is the wetting point which separates, when two phases are in coexistence, a region of partial wetting (a), with a finite contact angle  $\theta$ , from a region of complete wetting (b), where  $\theta = 0$ .

mean size of the scattering objects.

We observe that besides the expected changes in the turbidity due to changes in the L-layer thickness, a phenomenon of sphere aggregation systematically occurred in the one-phase region on approaching the coexistence curve.

*The L-layer below the aggregation line.*—The turbidity due to the layered spheres is related by diffraction theory to the index profile of the layer. Since a detailed expression for this profile in W-L is lacking, we have assumed it to arise from a layer of pure L of thickness  $e$  and refractive index  $n_L$  [ $n_L = 1.48855 - 5.024 \times 10^{-4}(T - 34)$  at  $\lambda = 6328 \text{ \AA}$ ]. This index lies close to the index of silica,  $n_S = 1.4571$ , and thus a layered sphere exhibits, within a good approximation, the same optical cross section  $s$  as a silica sphere of radius  $a + e$ . For the small spheres that we consider here, the Rayleigh formula<sup>13</sup> holds and one gets

$$s = s_0 n^4 [(n_S/n) - 1]^2 (a + e)^6, \quad (1)$$

where  $n$  is the refractive index of the mixture, which was assumed to vary with  $C$  according to the Lorentz-Lorenz formula, and

$$s_0 = 2^4 (32/27) \pi^5 / \lambda^4 = 3.62 \times 10^{20} \text{ cm}^{-4}. \quad (2)$$

The turbidity due to the layered spheres is then

$$\tau = \frac{3C_0}{4\pi a^3} \frac{\rho_W}{\rho_S} \left( 1 + \frac{\rho_W}{\rho_L} \frac{C}{1-C} \right)^{-1} s, \quad (3)$$

where  $\rho_{W,L,S}$  denotes the density of W, L, or silica. Once the small contribution to the observed turbidity  $\tau$  due to bulk concentration fluctuations has been removed, one can deduce an estimate of  $e$  using the above relations.

We first checked our method by determining the diameter of the spheres in pure water. We found  $2a = 1560 \pm 20 \text{ \AA}$ , in reasonable agreement with the value obtained from electron microscopy and photon-beating experiments,  $2a = 1600 \text{ \AA}$ . As can be seen in Fig. 2(a), the L-layer thickness increases with  $C$  at constant  $T$  up to a concentration  $C_A^c$  and then drops to much smaller values. This concentration  $C_A^c = 0.275 \pm 0.03$  is actually lower than  $C_c = 0.286$  and clearly delimits two L-adsorption regimes. The growth of  $e$  at constant  $C$  as  $T$  increases up to the aggregation line is shown in Fig. 2(b) for two values of  $C$  around  $C_A^c$ . The layer thickness increases in both cases as the temperature approaches the aggregation temperature, but the effect is always stronger below  $C_A^c$ .

*Aggregation line.*—This line (Fig. 3) is determined by a large increase in the turbidity together with an intense small-angle diffraction pattern. This pattern corresponds to aggregates of a few microns which increase in size while undergoing sedimentation. The turbidity and the scattered light then decrease until all the spheres lie at the bottom of the cell. Then the mixture

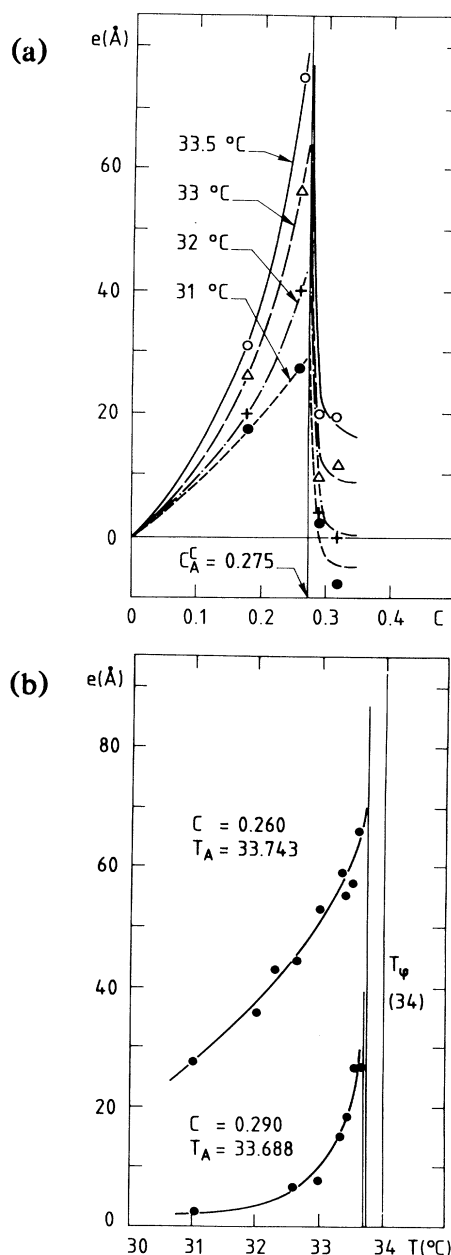


FIG. 2. Thickness of the adsorbed 2-6-lutidine layer before aggregation: (a) At given temperatures vs concentration. Note the lowering when  $C > C_A^c$ . (b) At two concentrations around  $C_A^c$  vs temperature.  $T_\phi$  and  $T_A$  are the phase separation and aggregation temperatures. Note the reduction of the layer thickness when  $C > C_A^c$ .

looks homogeneous and the turbidity is that of the mixture without spheres. If  $T$  is then increased the mixture is seen to phase separate at the expected temperature.

The aggregation process is *reversible* with respect to temperature: When  $T$  is lowered from  $T > T_A$  to

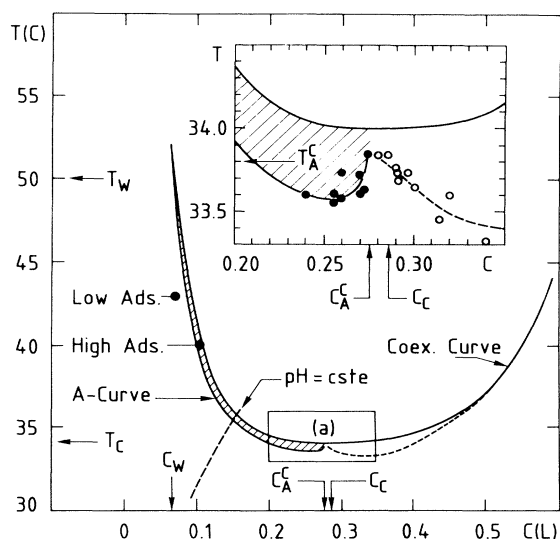


FIG. 3. Coexistence curve of the water+2-6-lutidine system (solid curve) and aggregation curve (hatched curve), upon addition of silica spheres. The notations are the same as in Fig. 1. The aggregation line exhibits the same features as expected for the first-order prewetting line. The dotted line corresponds to a much weaker aggregation process (see text). For clarity only the smooth curves are shown (34 data points have been obtained). The critical region (a) is magnified in the inset. Solid (open) circles correspond to a high (low) aggregation process. A line of constant  $pH$  has been reported for comparison.

$T < T_A$  and the mixture is stirred, the optical cross section before aggregation is strictly recovered. Also, photon-beating experiments show that the diffusion coefficient is the same as before aggregation.

The concentration  $C_A^c$  also delimits two aggregation regimes: (1) the time constant of the aggregation process is roughly 2 h below  $C_A^c$  and 24 h or more above; (2) both the turbidity and the light scattered by the aggregates are large below  $C_A^c$  and small above. One distinguishes clearly a strong aggregation process for  $C < C_A^c$  and a much weaker one for  $C > C_A^c$ . The two corresponding aggregation lines meet with an angular point at  $C_A^c = 0.275$  and  $T_A^c = 33.8^\circ\text{C}$ .

When  $C \leq 0.1$  it becomes impossible to distinguish between the aggregation phenomenon and the mixture phase transition. This indicates that the strong aggregation line and the coexistence curve meet near the wetting transition ( $C_W \sim 0.07$ ). On the other hand, the weak aggregation line joins the coexistence curve for  $C \sim 0.5$ .

*The aggregation process.*—Similar aggregation phenomena occur in many colloids<sup>14</sup> when the van der Waals forces between particles overcome the electrostatic repulsion. The aggregation process is then controlled by the  $pH$  or by the concentration of ions in solution.

We have deduced from electrophoresis experiments that the silica spheres are negatively charged in water with a typical charge of 140e. Lutidine is a weak base and it is known<sup>11</sup> that L cations are adsorbed on the surface of silica spheres, thereby reducing the repulsive interactions. Aggregation by this mechanism, however, is ruled out in W-L mixtures since the aggregation line does not follow at all an iso- $pH$  curve (see Fig. 3). More probably, the aggregation process results from attractive interactions between spheres due to the presence of a L layer. Indeed, such interactions have been proposed by de Gennes<sup>15</sup> and evaluated in the vicinity of the critical point ( $C_c, T_c$ ). It is also clear that the decrease of the surface-tension energy when the layers of different spheres overlap leads to attractive interactions. The aggregation is expected to occur when the layer is wide enough; if a first-order transition towards a large layer occurs before this critical width has been reached, one expects a strong aggregation process. We tentatively propose that this happens for the strong aggregation line which goes from ( $C_W, T_W$ ) up to ( $C_A^c, T_A^c$ ); this line would be the prewetting line, with its critical end point. It must be noted, however, that all theoretical calculations were performed for a semi-infinite medium limited by a plane surface. On a small sphere, the surface tension tends to limit the growth of the layer and a rounding off of the transition could occur.

We have also studied the behavior of spheres twice as large and observed that the same phenomena occurred at nearly the same temperatures. Such phenomena seem, therefore, to be a general feature of silica spheres. A systematical study will be given in a future article.

*Conclusion and perspectives.*—Silica spheres immersed in the W-L mixture display a rich behavior and present in particular a strong aggregation line that we interpret as a prewetting line. Colloids clearly provide a very sensitive tool for studying adsorption phenomena, and this could open a new field for both experimentalists and theorists. Finally, an interesting by-product of this study concerns the capability of reversible aggregation of colloids simply by change of the temperature. Fractal structures are usually obtained in such an aggregation.<sup>16</sup>

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