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Stability of colloids and wetting phenomena

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Light scattering and interferometry techniques are used to demonstrate the influence of wetting phenomena on the stability of silica colloids when immersed in a homogeneous two-component fluid (2,6-lutidine and water). A reversible flocculation is observed for both fused quartz and Stöber silica particles. Its location in the fluid phase diagram is different according to the origin of the particles and corresponds only to the "wetting" side of the coexistence curve. The flocculation is preceded by the growth of adsorption layers whose composition is that of the expected wetting phase. A number of mechanisms, related to wetting transitions, that can explain these observations are discussed.

Wetting transitions, because of their expected universal aspects and their practical importance, have recently received a great deal of attention.[1] When compared with the sophisticated state of the theory, the experimental situation is rather poor; in particular, the case of the nonflat substrate has been the object of only a few investigations.[2] In this paper we present an experimental study of the wetting properties of a binary mixture with colloids used as a substrate. The strange behavior of silica colloids immersed in a 2:6 lutidine-water (LW) mixture was first reported by Beysens and Esteve (BE).[3] They observed a reversible flocculation of the colloidal particles in the one-phase region of the binary fluid when the temperature was increased close to the coexistence curve (the LW system has an inverted coexistence curve) that might be connected to wetting transitions. The aim of the present work is to determine to what extent this flocculation is related to wetting phenomena. For this purpose a new, more complete, investigation of the phenomenon involving a number of different techniques and using colloids with different origins is reported. The result of our study is that flocculation is actually connected to universal aspects of adsorption and wetting phenomena. However, we have been unable to demonstrate unambiguously that this phenomenon is the signature of a surface transition.

EXPERIMENT

We have studied two types of silica colloids, whose characteristics (average radius $\bar{R}$, polydispersity δ) as determined by electron microscopy are reported in Table I. The first aqueous sols that we used were prepared in two different laboratories by means of the Stöber method.[4] Experiments have been also carried out with silica particles (dry powder of fused quartz) provided by Quartex (Q-silica). The sol is prepared by immersion of the dry particles in deionized water, and the largest particles are removed by sedimentation. Observation of the remaining particles with an electron microscope shows a larger polydispersity and a weaker sphericity than silica prepared by the Stöber method (Table I). The colloid concentrations in the samples (density number c_B) were in the range $1\times10^{11}-5\times10^{12}$ cm^{-3} which corresponds to the range $1\times10^{-3}-7\times10^{-3}$ in volume fraction.

The coexistence curve of the LW mixture (Fig. 1) exhibits a lower critical point at the L-mass fraction $c_L=c_c=0.29$ and at the critical temperature $T=T_c=34\,^\circ\mathrm{C}$.[3] The refractive indices of the components at 6328 Å are $n_W=1.33$, $n_L=1.48$, which is close to the refractive index of silica $n_S=1.46$. Details can be found in Refs. 3 and 5. Systematic measurements as a function of T and c_L have shown[5] that the Lorentz-Lorenz formula is indeed a good approximation for determining the refractive index (n_B) of the bulk LW system. Here we have mainly studied two typical L concentrations which are symmetric with respect to c_c ($c_L^-=0.23$ and $c_L^+=0.35$).

When the colloids are not flocculated, optical methods of investigation have been used. In order to prevent sedimentation-induced gradients, the colloids were gently stirred (magnetic stirrer). Light transmission (I_T/I_0), with I_T and I_0 the transmitted and incident light intensities, and scattered light intensity (I_q) at various transfer

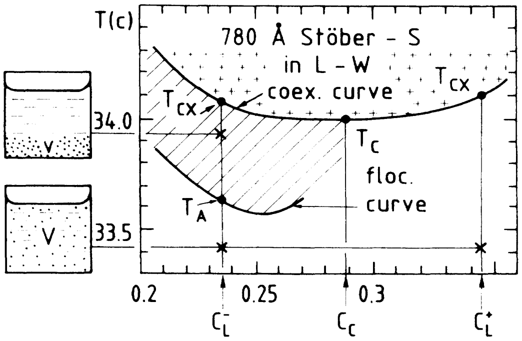

FIG. 1. Schematic diagram of the observations. T is temperature and c_L the mass fraction of lutidine.

TABLE I. Characteristics of colloids.

Origin	Stöber D^{a}	Stöber S^{b}		Silica
Mean radius $\bar{R}$ (Å)	650	780	2000	~ 1000
Polydispersity $\delta = \frac{\Delta R}{\bar{R}}$	0.22	0.225	~ 0.1	~ 1
$d/\bar{R}$	3.0	2.7	3.3	

[a] Prepared by M. Dubois, Departement de Physico-Chimie at Saclay.

[b] Prepared by L. Strzelecki, Laboratoire de Physique du Solide at Orsay.

wave vectors (q) have been recorded. The typical relative accuracy is of order 10^{-2}. The range in q (3×10^{4}–3×10^{5} cm^{-1}) allows the study of (i) the structure factor at small q, and through it the possible modification of the correlations between particles including a progressive flocculation, and (ii) the form factor at larger q.

For a dilute suspension of N spheres with the same radius R and index of refraction n, dispersed in a fluid of index n_0, when the Rayleigh-Debye condition $2qR(m-1) \ll 1$ is satisfied with $m = n/n_0$ sufficiently close to unity, the scattering intensity is given by[6]

$$I_q = AI_0NR^6(m-1)^2P(qR) \ . \tag{1}$$

Here I_0 is the incident intensity and

$$P(qR) = \left[\frac{3}{(qR)^3}(\sin qR - qR \cos qR) \right]^2 \ . \tag{2}$$

In the Guinier regime ($qR \ll 1$) one can easily show that

$$P(qR) \simeq \exp(-q^2R^2/5) \ . \tag{3}$$

For a polydisperse system (1) can be rewritten in terms of a function of the average radius $\bar{R}$ and of a parameter Z (Refs. 7 and 8) related to the width of the spheres' size distribution through

$$\delta^2 = \overline{(R-\bar{R})^2} = \frac{\bar{R}^2}{Z+1} \ . \tag{4}$$

Equation (1) is replaced by

$$I_q = AI_0N\rho^6(m-1)^2P(qR_s) \ . \tag{5}$$

Here

$$\rho^6 = \bar{R}^6 \frac{(Z+6)!}{(Z+1)^6 Z!} \tag{6}$$

and

$$R_s = \left[\frac{(Z+8)(Z+7)}{(Z+1)^2} \right]^{1/2} \bar{R} \ . \tag{7}$$

A plot of $\ln(I_q)$ as a function of q^2 is given in Fig. 2. If an adsorbed layer forms on the colloids, the intensity and shape of the $\ln I$-q^2 plot will change; the nature and the thickness of the adsorbed phase can be determined from this variation.

From the transmission measurements one gets the turbidity $\tau = (1/e)\ln(I_T/I_0)$ which is the integral over all angles of the scattered intensity. Note that measurement of turbidity was the technique used in Ref. 3, and although useful information on the colloids can be given by this quantity, it is a much more averaged quantity than the scattered intensity. In particular it is not possible with this technique to differentiate between a modification at the surface of the colloids such as adsorption, and a change in particle interactions such as the formation of a few aggregates.

Intensity and transmission measurements were carried out at different colloid concentrations. The temperature (controlled within a few mK) was increased by steps until either flocculation or bulk phase separation took place. Measurements at the same L concentration were also made in the fluid free of colloidal particles in order to accurately estimate the bulk contributions, mainly due to the local concentration fluctuations; in particular the correlation length behavior has been determined. The raw intensity data I_q^{expt} have been corrected for the bulk contribution I_q^{bulk} and normalized before being compared to (5) according to $I_q = (I_q^{\text{expt}} - I_q^{\text{bulk}})(I_T/I_0)^{-1}$.

The study of the flocculated phase of colloids was performed first through the determination of the volume (v) of the condensed phase formed. With the knowledge of the total volume (V) of the sample, the mean distance (d) between the particle centers can be estimated through the relation

$$d = \left[\frac{v}{c_B V} \right]^{1/3} \ . \tag{8}$$

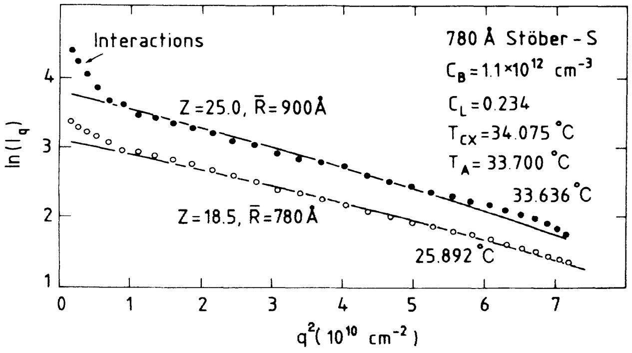

FIG. 2. Logarithm of the scattered light intensity (I_q) in arbitrary units vs the transfer wave vector (q). The crosses are data, and solid lines a fit to Eqs. (4)–(7).

The difference in L concentration of the flocculated phase can be estimated by measuring the refractive index change of the bulk after a quench from $T > T_A$ to $T < T_A$. An interferometric method, where the sample itself is the interferometer,[9] enables us to detect a front of desorption and to estimate the change in concentration of the liquid phase around the spheres before and after flocculation. The sensitivity is of order of 10^{-4}. Details of this method will be given elsewhere.[10]

FLOCCULATION

We have first studied the Stöber colloids, which all exhibit the same behavior whatever their laboratory of origin. The use of gentle stirring during light scattering and turbidity measurements enabled us to prevent sedimentation and to preserve a constant and uniform colloid concentration in the sample. Thus we have been able to characterize what BE called "weak" or "strong" flocculation. In fact the "weak" flocculation, previously observed for concentrations $c_L > c_c$, was found to be simply the sedimentation of particles under the gravity field. It does not depend on a special location in the phase diagram, but on the precise history of the experiment. In contrast, the flocculation phenomenon can be seen only for $c_L < c_c$ and at a specific temperature (T_A) defined within a few mK. It is typically 100 times more rapid than sedimentation. At T_A the whole sample becomes so turbid that light scattering measurements are no longer possible. The aggregated particles fall and a colloid condensed phase is formed at the bottom of the cell. If T is increased further, the fluid phase above the floc remains homogeneous until phase separation occurs (at $T = T_{cx}$). The temperature difference ($T_{cx} - T_A$) varies between a few 10 mK and 1 K according to the radius and the concentration of the colloids. Some trends are visible, but a systematic study of the ($T_{cx} - T_A$) variations has not been performed.

A flocculated phase is finally formed in the bottom of the cell, with an interparticle distance which remains nearly constant for $\bar{R}$ ranging from 650 to 2000 Å (Table I):

$$d/\bar{R} = 3.0 \pm 0.3 \ .$$

This phenomenon is reversible and the dispersed colloid phase can be recovered by lowering the temperature so that $T < T_A$ and by gently shaking. Note that in the final state of simple sedimentation, also reversible, the mean interparticle distance is slightly less than d.

The remarkable dissymmetry, and the reversible character of the flocculation phenomenon seem to indicate that this transition is connected to wetting. The following results will be devoted to the detection and characterization of the adsorption layers.

ADSORBED PHASE

The presence in the floc of a slightly L-enriched liquid phase has been detected by observing a desorption front as described above. A systematic increase of refractive index after a quench from $T > T_A$ to $T < T_A$ shows that the Stöber spheres in the floc are surrounded by a liquid phase which is on average richer in L than the phase above the floc. The concentration difference for a bulk sample at $c_L = 0.23$ can be estimated to be of order of 10^{-4}.

When the colloids are dispersed, light scattering measurements can be used to study adsorption on the spheres. The contributions of aggregates and/or interactions between spheres have been determined from deviations to Eq. (5) at small q in a $\ln(I_q)$-q^2 diagram. As shown in Fig. 2 there are a few aggregates present at room temperature but their proportion does not change significantly until flocculation. This demonstrates, first, that flocculation is a sharp transition, and second, that the increase of turbidity noted by BE was due only to the growth of an L-rich layer at the surface of the spheres. This is confirmed by the increase of the scattered light at large q when T is increased, from which an adsorption layer thickness can be estimated. The results obtained by fitting I_q with Eq. (5) for q larger than 1×10^5 cm^{-3} are drawn in Fig. 3 for $c_L = 0.23$ and 0.34. A simple slab model is used, assuming a pure lutidine layer; as n_L and n_S are very close, the data can be interpreted in terms of an increase of the particle radius. The thickness is assumed to be negligible far from the coexistence curve. At $T = 25\,^\circ\mathrm{C}$ I_q is fitted with values for $\bar{R}$ and δ compatible with micrographies, i.e., $\bar{R} = 780$ Å and $\delta = 0.225$, and thus by a pair [δ, $Z(25)$] according to (4). The fit of I_q as a function of T is carried out with a constant polydispersity δ and considering Z as an adjustable parameter. The thickness (l) is deduced from the relation

$$l(T) = \bar{R}(Z(T)) - \bar{R}(Z(25)) \ . \tag{9}$$

The values for l are in relatively good agreement with the BE results obtained from the turbidity with a simpler model. It is worth noticing that the adsorption layer is

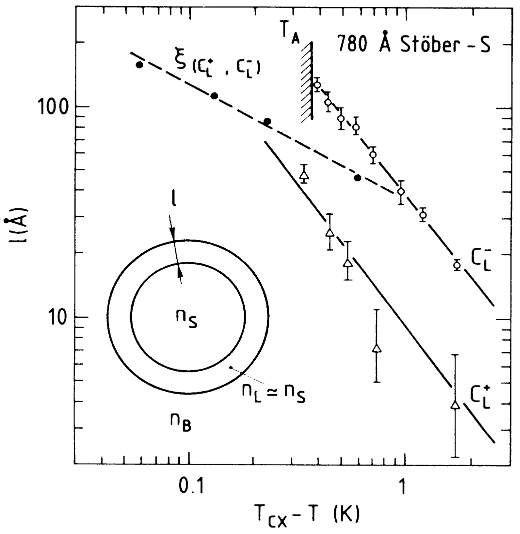

FIG. 3. Thickness (l) of the absorption layer as a function of temperature deduced from Eq. (9) by fitting the light scattering data (see text). For comparison bulk correlation length data (ξ) at the same concentrations are reported. The lines are guides for the eye.

much smaller for $c_L > c_c$.

The same flocculation and desorption phenomena have been observed for smaller spheres ($\bar{R} = 650$ Å, $\delta = 0.22$), at a smaller value of $T_{cx} - T_A$. However, no intensity or turbidity variation could be detected. This suggests a strong $\bar{R}$ dependence of the adsorbed layer.

OTHER SILICA SUBSTRATE

Experiments in which plane walls of Pyrex or silica glass have been immersed in the L-rich phase[11–13] show that the solids are preferentially wet by the W-rich phase. A transition between partial and complete wetting has been observed around 50 °C with Pyrex (its precise location is sensitive to the presence of ions, like $K^+ + Cl^-$, in solution[12]). These results appear to contradict our observations that there is preferential L adsorption on Stöber colloids.

It is obvious that wetting, as defined on a plane surface, cannot be observed on a colloid because the surface energy diverges as the thickness of the adsorption layer goes to infinity.[14] Nevertheless a connection between adsorption and wetting properties is expected. In order to resolve the discrepancy, experiments have been performed with the same type of silica substrate used in the wetting experiment but in colloidal form. We have then used a dry quartz powder (Q-silica) to prepare sols whose characteristics are listed in Table I. The results demonstrated the generality of the flocculation phenomenon and its close connection to wetting phenomena: flocculation occurred on the opposite side of the coexistence curve, that is only for $c_L > c_c$, and the turbidity decreased with increasing temperature, thereby demonstrating the existence of a growing W-rich adsorbed layer. These observations show that the apparent contradiction was due to the different surface properties of the silica substrates. That the wetting properties of silica can be different according to its origin has already been noted;[15] also recent experiments[16] show that smooth and roughened surfaces of Vycor (a porous silica) are preferentially wet by the L-rich phase.

FLOCCULATION MECHANISM

From our results it seems clear that the stability of silica colloids immersed in the LW mixture is closely connected to wetting. A remaining problem then is the origin of the process of the colloid flocculation. At present we are unable to give a definitive answer but we can suggest some mechanisms. The stability of negatively charged silica colloids is due to a balance between repulsive forces (Coulomb) and attractive forces (van der Waals).[17] Flocculation originates in a modification of this balance through the attractive interactions caused by the presence of a thickening adsorbed layer. For a given value of l, the secondary minimum of the potential energy curve may become deep enough to give rise to a (reversible) flocculation. However, the sharpness of the flocculation transition (a few mK) seems more characteristic of a gap in adsorption, although we cannot give an irrefutable demonstration of it. The existence of such a gap can come from two different phenomena: (i) a pure surface transition, e.g., prewetting or (ii) capillary condensation.[18] Prewetting corresponds to a jump of adsorption at the surface of each sphere. Because of spherical geometry, this jump is associated with an increase of surface energy that can be minimized by bringing the spheres into proximity, i.e., by flocculation. Capillary condensation might occur when spheres come to their smallest possible separation distance (by Brownian motion) and that the thermodynamical conditions (c_L, T) are such that a phase transition in the confined fluid can occur. A systematic study of flocculation as a function of the colloid concentration and of the particle radius is in progress. This should give further information about the mechanism.

ACKNOWLEDGMENTS

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[1] See, e.g., S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1988), Vol. 12.

[2] See, e.g., D. Beysens, in *Liquids at Interfaces,* 1988 Les Houches Lectures, edited by J. Charvolin, P. G. de Gennes, W. Helfrich, and J. F. Joanny (Plenum, New York, in press).

[3] D. Beysens and D. Esteve, Phys. Rev. Lett. **54**, 2123 (1985), and references therein.

[4] W. Stöber, A. Fink, and E. Bohn, J. Colloid Interface Sci. **26**, 62 (1968).

[5] C. Houessou, Ph.D. thesis, Universite Paris VII, 1986 (unpublished).

[6] See, e.g., M. Kerker, *The Scattering of Light* (Academic, New York, 1969).

[7] S. R. Aragon and R. Pecora, J. Chem. Phys. **64**, 2395 (1976).

[8] M. Kotlarchyk and S. H. Chen, J. Chem. Phys. **79**, 2461 (1983).

[9] D. Beysens, Rev. Sci. Instrum. **50**, 509 (1979).

[10] V. Gurfein, D. Beysens, and F. Perrot (unpublished).

[11] D. W. Pohl and W. I. Goldburg, Phys. Rev. Lett. **48**, 185 (1982).

[12] L. Sigl and W. Fenzl, Phys. Rev. Lett. **57**, 2191 (1986).

[13] D. Beysens and W. Goldburg (unpublished).

[14] See, e.g., M. P. Gelfand and R. Lipowsky, Phys. Rev. B **36**, 8725 (1987), and references therein.

[15] R. K. Iller, *The Chemistry of Silica* (Wiley, New York, 1979).

[16] D. Bideau, W. I. Goldburg, and E. To (unpublished).

[17] See, e.g, D. J. Shaw, *Introduction to Colloid and Surface Chemistry* (Butterworths, London, 1986).

[18] See, e.g., R. Evans, U. M. B. Marconi, and P. Tarazona, J. Chem. Soc. Faraday Trans. II **82**, 1763 (1986), and references therein.