

Reversible flocculation of silica colloids in liquid mixtures

T. Narayanan, A. Kumar, and E. S. R. Gopal*

Department of Physics, Indian Institute of Science, Bangalore, 560 012 India

D. Beysens and P. Guenoun

*Service de Physique de l'Etat Condensé, Département de Recherche sur l'Etat Condensé
les Atomes et les Molécules, Centre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette CEDEX, France*

G. Zalczer

*Service de Recherches sur les Surfaces et l'Irradiation de la Matière,
Département de Recherche sur l'Etat Condensé les Atomes et les Molécules,
Centre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette CEDEX, France*

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We report some observations concerning the reversible flocculation of silica colloids in reentrant liquid mixtures of 3-methylpyridine plus water plus heavy water and 2,6-lutidine plus water. Our research involved a detailed determination of the line of flocculation temperatures for phase-separating as well as non-phase-separating mixtures. We find that the flocculation temperature is more influenced by the impurities in the suspension rather than the concentration and size of the spheres. For a fixed volume fraction and diameter of the colloids, we notice a close similarity between the dome of flocculation temperatures and the bulk-coexistence surface but with different amplitudes and exponents in each case.

INTRODUCTION

The phenomenon of flocculation of silica colloids in the one-phase region of a 2,6-lutidine plus water mixture near its bulk coexistence has received considerable attention in the recent past [1–4]. This flocculation occurs at a well-defined temperature and is reversible with respect to temperature. The precise origin of this phenomenon is still not known. It was first observed as a sequel to the strong adsorption of lutidine while exploring the prewetting transition [1]. It has been shown that lutidine adsorbs onto Stöber silica particles whereas water adsorbs on fused quartz [2,5]. Flocculation appears in the region of phase diagram which is poor in the adsorbed component. A similar observation has been reported using polystyrene latex [4]. The adsorption of lutidine on Stöber silica can be suppressed (resulting in the disappearance of flocculation) and eventually caused to revert to water adsorption by the addition of small amounts of $\text{Mg}(\text{NO}_3)_2$ [3].

The exact mechanism for this flocculation necessarily involves the preferential adsorption of one of the components leading to a concentration profile around the spheres. This profile introduces attractive interactions (London–van der Waals type) between two spheres, which at one stage overcomes the repulsive electrostatic interaction stabilizing the suspension. Near an isolated sphere (wall), this profile can evolve into a thick layer (prewetting transition) discontinuously [6]. However, this transition should be smoothed out as a result of the finite size of the spheres [7,8]. The problem is further complicated when two spheres come closer due to Brownian motion. The wetting layer can form a bridge

between two adjacent spheres (capillary condensation) [9–11]. When the gap between the spheres becomes comparable with the bulk correlation length, the dimensionality experienced by the intervening fluid may be reduced [12,13]. These interesting scenarios have been the topic of recent reviews [14,15].

In this article we report some systematic studies concerning the behavior of silica colloids in 2,6-lutidine (L) plus water (W) and 3-methylpyridine (MP) plus water plus heavy water (HW) mixtures, henceforth referred to as LW and MW , respectively. We studied the effect of size (d) and concentration (c_b) of the spheres on the flocculation temperature (T_F) and find that their influence is somewhat camouflaged by the dissolved impurities. These impurities, that are evolved as a result of leaching or dissolution of silica spheres by the mixture, widen the gap $\Delta T_F (= T_{cx} - T_F$, where T_{cx} is the bulk coexistence temperature) with time. For a fixed d , c_b , and impurity concentration, we measured the flocculation line (loci of T_F 's) in the neighborhood of the bulk-coexistence surface.

EXPERIMENT

Though LW mixture has a closed loop phase diagram with upper and lower consolute points (T_U and T_L , respectively), this system is widely studied only near T_L ($= 34.108^\circ\text{C}$) as T_U ($= 230.7^\circ\text{C}$) is somewhat inaccessible [16]. On the other hand, the MW system permits the approach to T_U and T_L rather easily [17]. MP and L (2,6-dimethylpyridine) both being methylpyridines, their wetting properties are expected to be similar. Thus LW can

be considered as a very wide loop of the MW system.

The reentrant miscibility in MW has been studied extensively [17], the reason being the delicate but possible tunability of the loop size ($\Delta T_X = T_U - T_L$) by adjusting the weight fraction (X) of HW in $W+HW$. A double critical point (DCP) is realized when $\Delta T = 0$. The quantity X simulates the condition of a thermodynamic field similar to pressure. The bulk-coexistence surface is a paraboloid in the $C_{MP}-T-X$ space (where C_{MP} is the weight fraction of MP in the mixture) whose apex (coordinates C_{MP}^c, T_D, X_D) is the DCP. There is no bulk phase separation for $X < X_D$ [17].

The colloids were synthesized by the Stöber method [18] which involves the hydrolysis of tetraethyl orthosilicate in an aqueous ethanol solution containing ammonia. The resulting particles were repeatedly rinsed with water by removing and diluting the supernatant after allowing the spheres to sediment. The radius and polydispersity of the spheres were determined using electron microscopy. Some of the dispersions were also characterized by static light scattering. The properties of the different batches of colloids used for the present work are listed in Table I. Batch IV colloids were prepared using the modified method (for higher monodispersity) given by Bogush, Tracy, and Zukoski [19].

Samples were prepared using 3-methylpyridine (Aldrich gold label 99.50%), heavy water (Sigma 99.96%), and 2,6-lutidine (Merck >99%) as purchased. Water used was either quadruply distilled in an all quartz distiller (MW) or obtained from a Milli-Q system (LW). For MW samples, the silica spheres used were rinsed 15 times with quadruply distilled water. This procedure was essential as the coexistence surface of MW is extremely steep (especially in the limit $\Delta T \rightarrow 0$), and unlike in the case of LW (where $\Delta T_X = 197^\circ\text{C}$), any small changes in impurity concentration not only affect T_F but T_{cx} also. After thorough rinsing the resulting suspension in W was diluted to (volume fraction of the colloids) $c_b = 0.01$. In each case, a small portion of this suspension was further diluted to $c_b = 0.003$ by adding the appropriate amounts of MP, W , and HW to obtain the desired C_{MP} and X .

The initial set of experiments for MW samples was carried out using flame-sealed containers (cells). These samples yielded unusually large ΔT_F . In addition, the flocculation was observed over a wide range of C_{MP} and X and had poor reproducibility. We also noticed that the flocculation boundary could drift away from the coexistence

surface with increase in the exposure time of the flame, while sealing the cells. This led us to the conclusion that during the course of flame sealing some impurities are evolved which mainly affect T_F and not T_{cx} significantly. As we were not in a position to standardize these impurities, we completely avoided using flame-sealed cells. All the measurements reported here were performed using cells with Teflon high-vacuum stopcocks (Rotaflo).

Another potential source of impurities is the leaching of the silica spheres and walls of the container by L-MP. The LW mixtures were studied in quartz containers, whereas for MW mixtures a switch from a Pyrex to a quartz container did not yield an appreciable difference in ΔT_F . This indicates that the role of impurities which are leached out from the walls of the container is insignificant in shifting ΔT_F with time. For MW samples, containers were initially soaked with the ternary mixture. The drifts in T_F in such cells were about 10–20 mK/day (near C_{MP}^c for $X = 0.2$) which further reduced to 5 mK/day after a week. Each flocculation line was generated using the same parent solution in order to maintain the constancy of X as well as the unknown impurities. In all the cases T_F decreased and T_{cx} increased with time near T_L and vice versa near T_U . Hence ΔT_F increased with the age of the sample.

The flocculation and phase separation temperatures were observed in either water (LW) or liquid paraffin (MW) thermostated baths with temperature stability better than ± 1 mK. The temperature of the water bath was measured by a quartz thermometer (HP2804A) and that of the liquid paraffin bath using a platinum resistance thermometer (ASL,F17). The absolute accuracy of temperature measurement in each case was better than 20 mK. The onset of flocculation was detected by a sudden increase in sample turbidity. The temperature of the water bath was changed continuously at a sufficiently slow rate (50 mK/h) to ensure thermal equilibrium and the transmitted light intensity was recorded. The experimental setup is similar to the one described previously [3].

In the case of MW samples, the temperature of the liquid paraffin bath was varied in steps, and flocculation and phase separation were observed visually. Prior to T_F the cells were gently tumbled down at regular intervals to eliminate the vertical concentration gradient of silica spheres. The visual observations indicated a finite temperature gap (≈ 20 mK) between the onset of flocculation and sedimentation of aggregates. This feature ought to be related to the kinetics of aggregation [20].

RESULTS

In a first series of experiments LW samples of varying c_b 's [for constant weight fraction of L (C_L) = 0.2] were prepared by diluting the original silica dispersion in water with fresh L and W . Three different sizes of the spheres (d) were used (batches I–III in Table I). The observed variation of ΔT_F is displayed in Fig. 1. In each case the ΔT_F 's lie on a straight line as a function of c_b . However, the slopes of these straight lines or the intercepts cannot be related to d in any simple manner. The MW samples prepared in an identical way (using batch

TABLE I. The details of silica colloids used in the present investigations. The colloids were suspended in water. The average diameter (d) and its variance ($\Delta d/d$) were determined using electron microscopy. The numbers in parentheses are deduced from static light-scattering measurements. c_b is the volume fraction of the colloid.

Batch	d (nm)	$\Delta d/d$	$10^3 c_b$
I	130(136)	0.13	5.4
II	346	0.25	8.9
III	510(626)	0.07	9.5
IV	330	0.09	10.1

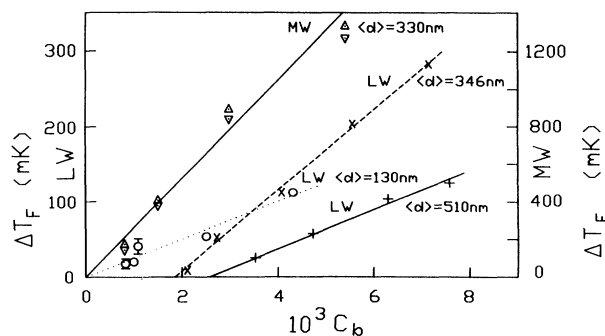


FIG. 1. Variation of ΔT_F as a function of the volume fraction of the silica spheres (c_b) for different sizes (d) of the colloids in LW ($C_L=0.20$) and MW ($C_{MP}=0.30$) mixtures. The samples were prepared using proportional amounts of the stock suspension.

IV colloids) yielded a similar behavior near both T_U and T_L (Fig. 1).

In order to reexamine the effect of c_b and d on ΔT_F , we prepared samples of differing c_b 's (for $d = 346$ nm) by isolating different parts of a heterogeneous suspension. The resulting c_b was determined by turbidity. The observed variation in ΔT_F as a function of c_b in this case was much less systematic than that represented in Fig. 1. Thus we suspect that small amounts of uncontrollable impurities present in the original suspension are responsible for the systematic variation of ΔT_F with c_b shown in Fig. 1. These impurities could be evolved either by the leaching of trapped remnants of colloid synthesis from the pores of the silica spheres or by a slow dissolution of colloidal silica by the mixture (note that the surface chemistry of charge-stabilized silica colloids is extremely complex) [21]. To probe this impurity effect further, we replaced part of the solvent by fresh LW mixture or by LW mixture prepared using water that has been possibly deteriorated as a result of prolonged contact with either silica colloids or quartz powder. In the former case we found a decrease of ΔT_F and vice versa for the latter. The above findings as well as the observed drift in ΔT_F (widening) with time confirmed our doubts regarding the role of impurities.

Figure 2 illustrates the temporal shift of flocculation line (loci of T_F 's) in the neighborhood of closed loop phase diagram of MW mixture (for $X=0.2$, $\Delta T_X=18.46$ K). The ΔT_F 's of samples denoted as fresh were determined within 6 to 8 h after their preparation. For the four aged samples, the silica spheres were in the MW mixture for about ten days. In all the cases the flocculation line terminated on the coexistence curve at the MP-rich side which further drifted away from C_{MP}^c with time.

The variation of ΔT_F with C_L for a fixed volume fraction of the colloids is pictorially represented in Fig. 3. The flocculation line, which terminates on the bulk coexistence curve, clearly extends beyond C_L^c (critical concentration corresponding to L).

Figure 4 depicts the flocculation line in the neighborhood of a closed loop phase diagram with $\Delta T_X = 18.46$ K

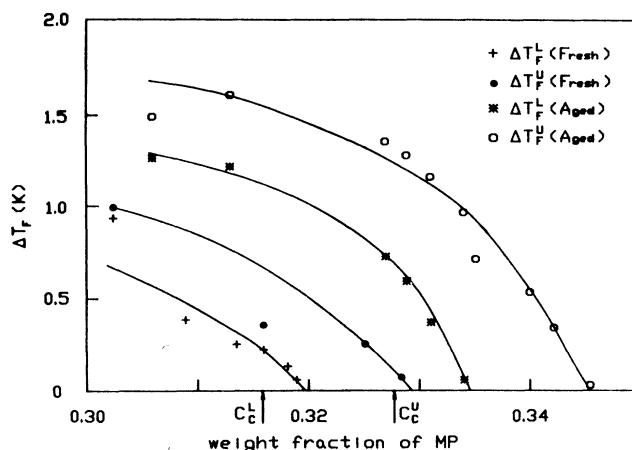


FIG. 2. The behavior of flocculation line in the vicinity of C_{MP}^c (critical concentration) both near T_U (ΔT_{FU}) and T_L (ΔT_{FL}) in the MW system ($X=0.2$, $\Delta T_X=18.46$ K, $c_b=0.003$, and $d=330$ nm) for fresh and aged samples. For this system C_{MP}^c 's differ distinctly near T_U and T_L . The continuous lines are only a guide to the eye.

($X=0.2$) of MW. The c_b and d of silica colloids used were 0.003 and 346 nm, respectively. Two striking features of this curve are (a) the flocculation line does not originate from the coexistence curve, rather it envelops the coexistence curve on the MP-poor branch; (b) it terminates near T_L and T_U corresponding to different values of C_{MP} . Such a mismatch of C_{MP} occurs even for the bulk-coexistence curve [22]. For example, C_{MP}^c for this ΔT_X (deduced from equal volume coexistence) corresponding to T_U and T_L are 0.328 and 0.316, respectively. The true C_{MP}^c differs appreciably from the extrema of the coexistence curve [17]. This factor stems from the ter-

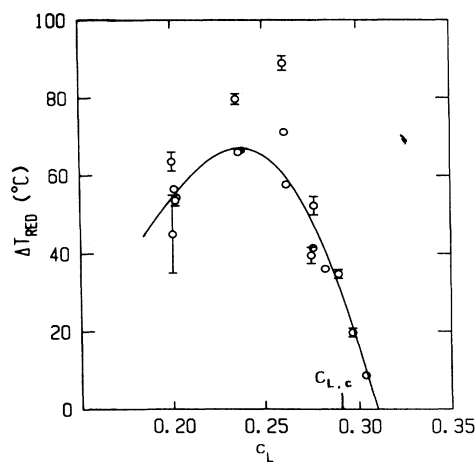


FIG. 3. The reduced difference between flocculation and coexistence temperature ($\Delta T_{RED} = T_{cx} - T_F$) vs lutidine weight fraction C_L . "Reduced" means corrected for a constant impurity concentration ($=1$) according to Fig. 1. (The line drawn through the points is for visual aid only.)

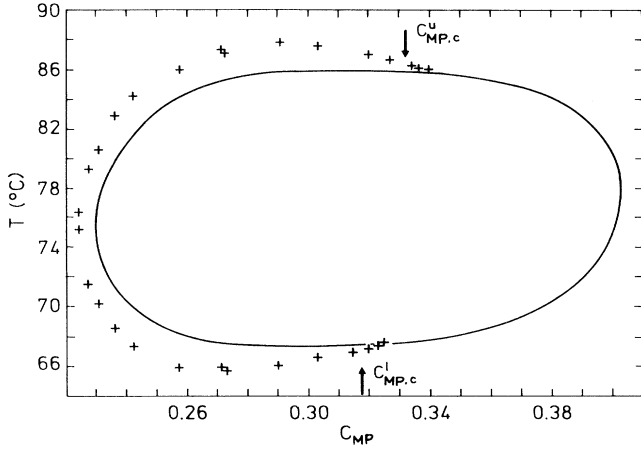


FIG. 4. The measured flocculation line for $X=0.2$, $c_b=0.003$, and $d=346$ nm. The continuous curve corresponds to the fitted coexistence curve. The error bars for the T_F 's are smaller than the size of the symbols.

nary nature of the system, the coexistence curve (for any $X < 1$) being an oblique section of the actual coexistence dome (to be visualized in a triangular base prism). However, the flocculation line terminates on the coexistence curve at a point (C_{MP}^f) in the vicinity of C_{MP}^c with $C_{MP}^f - C_{MP}^c \approx 0.003$, if the sample is fresh and C_{MP}^f shifts away (to the W -rich side) from C_{MP}^c with aging of the sample (see Fig. 2).

Figure 5(a) illustrates the stability of silica colloids in a non-phase-separating mixture ($X=0.1475$, slightly less than $X_D=0.1485$, $c_b=0.003$, and $d=346$ nm). The area within the curve marks the aggregated state of the suspension and hence the reentrant character of the stability of colloids. An important feature of the curve is its extension up to $C_{MP}=0.325$. This factor coupled with the fact that the extrema of the loop in the limit $\Delta T_X \rightarrow 0$ lie between $C_{MP}=0.3$ and 0.305 suggests that the flocculation line completely encircles the coexistence curve for very small ΔT_X 's ($\leq 1^\circ\text{C}$). Unfortunately such small loops are very difficult to stabilize in the presence of silica spheres.

The close resemblance of the flocculation line in Fig. 5(a) with the bulk-coexistence curve [22] stimulated us to describe it by the following function:

$$C_{MP}^+ - C_{MP}^- = B_1 t_F^{\beta'}$$

where $t_F = \{(T_{FU} - T)(T - T_{FL}) / T_{FU} T_{FL}\}$, T_{FU} ($= 354.35$ K) and T_{FL} ($= 344.95$ K) are the temperatures (T) corresponding to the upper and lower extrema of the flocculation curve, respectively. Motivation for employing t_F to describe the flocculation loop emanates from the fact that an analogous field variable $t_{UL} = \{(T_U - T)(T_L - T) / T_U T_L\}$ fits closed loop phase diagrams of any ΔT_X with β' equal to its Ising value ($= 0.325$) [22]. However, in the present case the shape of the line is much more susceptible to the effect of various perturbations such as impurities, in contrast to the bulk phase diagram. The choice of the composition variable

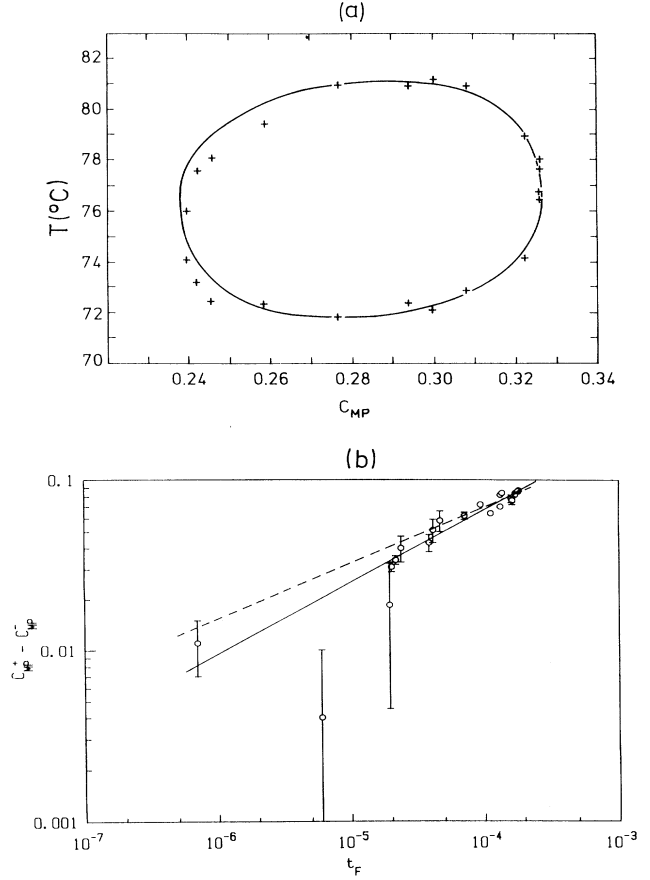


FIG. 5. (a) Flocculation temperatures determined for a non-phase-separating mixture ($X=0.1475 < X_D$, $c_b=0.003$, and $d=346$ nm). The continuous curve is generated by Eq. (1) using the best-fit parameters with a linear diameter. (b) A log-log plot of t_F vs the concentration difference ($C_{MP}^+ - C_{MP}^-$) for the flocculation curve in (a). The continuous and dashed lines refer to β' equal to 0.43 and 0.325, respectively.

in such a complicated case is again debatable.

The best-fit value of parameter B_1 is 3.59 ± 0.36 , corresponding to $\beta' = 0.43$. The uncertainty (corresponding to three standard deviations) of β' is as high as 0.1 due to the large scatter in the data [see Fig. 5(b)] which could not be eliminated despite our best efforts. The continuous line in Fig. 5(a) is generated using the best-fit values. Though β' is equal to the Ising value of critical exponent β ($= 0.325$) in the lower limit of error bar, there is no compelling reason to believe that β' should be Ising-like. A possible explanation for the apparent increase in β could be a crossover from bulk (0.325) to surface (0.8) critical behavior [23]. However, this inference has to be corroborated further both experimentally and theoretically.

The system MW provides an instance to examine the stability of colloids in a field space (in this case the X, T plane) for a fixed C_{MP} . Figure 6 shows the behavior of silica colloids for $C_{MP}=0.27$ (guided by the fact that it is nearly the extremum of the lower half of the flocculation

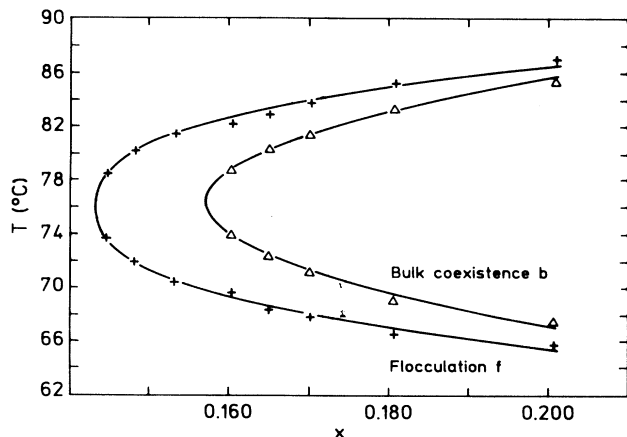


FIG. 6. The reentrant flocculation (f) and bulk coexistence (b) boundaries for $C_{MP}=0.27$, $c_b=0.003$, and $d=346$ nm. The continuous lines are generated using the best-fit parameters in Eq. (2).

line as is evident from Figs. 4 and 5) and $c_b=0.003$ ($d=346$ nm) in the X, T plane. As in the case of the bulk-coexistence phase boundary, the flocculation boundary does terminate in a similar fashion marked by a double flocculation point (DFP). DFP defines the limit of flocculation of colloids in this mixture.

In order to deduce the actual shape of the bulk-coexistence (curve b) and flocculation (curve f) boundaries, the measured T_F 's and T_{cx} 's corresponding to the upper and lower halves (superfixed as U and L) for different X 's were fitted to the equation

$$T_Y^U - T_Y^L = A_{1Y}(X - X_Y^D)^{A_{2Y}} \quad (2)$$

The suffix Y is F in the case of flocculation (f) and cx for coexistence (b) boundaries, A_1 and A_2 are their amplitude and exponent, and X^D denotes the limiting value of X (0.1435 and 0.157 for flocculation and bulk coexistence, respectively).

The best-fit values of the parameters for the bulk-coexistence boundary are $A_1=91.8 \pm 1.6$ and $A_2=0.508 \pm 0.040$, demonstrating its true parabolic ($=0.5$) shape. The continuous line b in Fig. 6 is generated using these parameter values. In the case of flocculation boundary, the best fit yielded $A_1=60.7 \pm 0.9$ and $A_2=0.368 \pm 0.016$. This indicates a clear deviation from that of the bulk phase boundary. The continuous line f is generated by these best-fit parameters.

DISCUSSION

Figures 4–6, coupled with Fig. 3 build a vivid picture of the existence of a flocculation surface covering the

MP- (L) poor section of the coexistence surface. In the case of MW the flocculation line is not meeting the MP-poor side of the coexistence curve. In an attempt to rationalize this observation, we examined the behavior of the colloids in the two-phase region for $\Delta T_X=18.46$ K and $c_b=0.003$. We observed that the silica spheres were nearly confined to the MP-rich phase at all temperatures in the two-phase coexistence region. Such a behavior is expected only when the system is in the complete wetting regime [4]. This suggests that the entire closed loop coexistence region for this ΔT_X refers to complete wetting.

Apparently, the flocculation process is related to the ability of the bulk mixture to form either a layer of a new phase or a large concentration profile around the spheres. The asymmetry of the flocculation line with respect to the bulk coexistence curve suggests that a mere reduction of the spatial dimensionality of the fluid between the spheres cannot explain the phenomenon. Thus the basic question whether the triggering stage involves a single sphere (prewetting) or more spheres (capillary-condensation-like) remains unanswered. The overall shape of the dome of flocculation temperatures reflects some features of capillary condensation [7–11].

CONCLUSION

A systematic study of the flocculation of silica colloids in 2,6-lutidine plus water and 3-methylpyridine plus water plus heavy water shows that the most relevant parameter which controls the flocculation temperature is the impurities in the mixture. Different tests indicate that these impurities could be the remnants of colloid synthesis or the one generated by the dissolution of the silica in the mixture.

For a fixed characteristic of the colloids (d and c_b), we established the existence of a flocculation dome covering one section (pertaining to the side which is poorer in the component that wets) of the bulk-coexistence surface in a multidimensional field space. The shape of this dome differs distinctly from that of the bulk-coexistence surface. Furthermore, the flocculation of colloids occurs as the coexistence surface is approached by varying any convenient thermodynamic field (X and T in this case).

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*Present address: National Physical Laboratory, New Delhi 110012, India.

[1] D. Beysens and D. Estève, Phys. Rev. Lett. **54**, 2123 (1985).

[2] V. Gurfein, D. Beysens, and F. Perrot, Phys. Rev. A **40**, 2543 (1989).

[3] J. S. van Duijneveldt and D. Beysens, J. Chem. Phys. **94**, 5222 (1991).

- [4] P. D. Gallagher and J. V. Maher, *Phys. Rev. A* **46**, 2012 (1992).
- [5] G. P. Gladden and M. M. Breuer, *J. Colloid Interface Sci.* **53**, 249 (1975).
- [6] M. P. Nightingale and J. O. Indekeu, *Phys. Rev. B* **32**, 3364 (1985).
- [7] M. P. Gelfand and R. Lipowsky, *Phys. Rev. B* **36**, 8725 (1985).
- [8] P. J. Upton, J. O. Indekeu, and J. M. Yeomans, *Phys. Rev. B* **40**, 666 (1989).
- [9] R. Evans, U. M. B. Marconi, and P. Tarazona, *J. Chem. Phys.* **84**, 2376 (1986).
- [10] T. J. Sluckin, *Phys. Rev. A* **41**, 960 (1990).
- [11] H. T. Dobbs, G. A. Darbellay, and J. M. Yeomans, *Europhys. Lett.* **18**, 439 (1992).
- [12] H. Nakanishi and M. E. Fisher, *J. Chem. Phys.* **78**, 3279 (1983).
- [13] M. E. Fisher and P. G. de Gennes, *C. R. Acad. Sci.* **287**, B207 (1978).
- [14] S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1988), Vol. 12.
- [15] *Liquids at Interfaces*, edited by J. Charvolin, J. F. Joanny, and J. Zinn-Justin (Elsevier, Amsterdam, 1989).
- [16] M. A. Handschy, R. C. Mockler, and W. J. O'Sullivan, *Chem. Phys. Lett.* **76**, 172 (1980).
- [17] B. V. Prafulla, T. Narayanan, and A. Kumar, *Phys. Rev. A* **46**, 7456 (1992).
- [18] W. Stöber, A. Fink, and E. Bohn, *J. Colloid Interface Sci.* **26**, 62 (1968).
- [19] G. H. Bogush, M. A. Tracy, and C. F. Zukoski IV, *J. Non-Cryst. Solids* **104**, 95 (1988).
- [20] M. Broide, Y. Garrabos, and D. Beysens, *Phys. Rev. E* **47**, 3768 (1993).
- [21] R. K. Iler, *The Chemistry of Silica* (Wiley, New York, 1979).
- [22] T. Narayanan, A. Kumar, and E. S. R. Gopal, *Phys. Lett. A* **155**, 276 (1991).
- [23] R. Pandit, M. Schick, and M. Wortis, *Phys. Rev. B* **26**, 5112 (1982).