Reentrant Solid-Liquid Transition in Ionic Colloidal Dispersions by Varying Particle Charge Density

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The influence of the particle surface charge density on the solid-liquid phase transition in electrostatically stabilized colloidal silica and polymer latex dispersions is examined. Both systems show a reentrant transition with increasing charge density. This is not explainable in terms of the Yukawa potential and the charge-renormalization model.   [S0031-9007(98)06414-X]

The ionic colloidal systems have substantial experimental advantages to study the solid-liquid phase transition, since the interparticle interaction can be tuned in a wide range by varying experimental variables such as the effective surface charge density of the particles σ_e, the particle volume fraction ϕ, and the salt concentration C_s [1]. The phase diagram of the transition has extensively been studied [1–4]. ϕ and C_s have usually been adopted as variables, and, as far as we know, the charge dependence was examined only in recent studies by Palberg *et al.* [3] and by ourselves [4]. In both studies, the C_s value at the transition point, which was determined at a fixed ϕ and at relatively small σ_e's, increased with σ_e.

In the present Letter, we report for the first time a three dimensional phase diagram of the solid-liquid transition as a function of σ_e, ϕ, and C_s. Here, we investigated much broader charge conditions than in the previous studies, and found that the liquid state became ordered to give the solid state and thereafter reentered into the liquid state with increasing σ_e. Aqueous dispersions of colloidal silica particles were used, whose σ_e value could be varied continuously by changing the amount of added NaOH [4,5]. The phase diagram was determined by observing iridescence due to a Bragg diffraction from the solid structure, and further by applying an ultra-small-angle x-ray scattering (USAXS) method. The reentrant transition was also confirmed for ionic polymer latex systems having various charge densities by direct observations of their internal structures with a laser scanning confocal microscope (LSCM).

Colloidal silica samples, KE-P10W (Nippon Shokubai Co., Ltd., Tokyo, Japan; diameter = 0.12 ± 0.01 μm) and SI-80P (Catalyst and Chemicals Co., Ltd., Osaka, Japan; 0.11 ± 0.01 μm), were purified by dialysis and the ion-exchange method. They had σ_e's of 0.07 and 0.23 μC cm^{-2} due to partial dissociation of weakly acidic silanol groups on their surfaces. The degree of dissociation of the silanol groups, and thus the σ_e value, was increased by adding NaOH at pH < 8, that is, under conditions where the concentrations of excess NaOH were less than 1 μM.

The particles thus prepared (hereafter designated as Na$^+$-type silica) had Na ions as counterions, which are partly condensed near the particle surface, reducing the charge number [1]. Consequently, σ_e is quite different from the *analytical* (*bare*) charge density σ_a, which could be calculated from a concentration of added NaOH. We determined σ_e at various σ_a's from the conductometry. The electrical conductivity of the silica dispersion, K, is given by $K = 10^{-3}(\lambda_C C_C + \lambda_p \phi) + K_b$, where C_C is the concentration of free counterions, λ_C and λ_p are the equivalent conductivities of the counterions and the particles, and K_b is the background conductivity. The λ_p value was determined by comparing conductivities of Na$^+$- and K$^+$-type silica dispersions, assuming that the C_C values were the same in both cases. The transport number of the particle, t_p [$\equiv \lambda_p \phi/(\lambda_C C_C + \lambda_p \phi)$], did not significantly vary with ϕ at $\phi = (1$–$3) \times 10^{-2}$, and was 0.51–0.48 for Na$^+$-type silica. A relationship between σ_e and σ_a will be discussed later [Fig. 4(A) (below)].

The solid-liquid phase transition was examined under various σ_e, ϕ, and C_s conditions. Figure 1 is the phase diagram for KE-P10W silica [6], which was constructed by observing iridescence. C_s values were estimated from the sum of concentrations of coexisting NaCl, ionic species in the water used (2 μM), and excess NaOH, if any. The region whose C_s is smaller than that at the phase boundary (shown by rectangles) corresponds to the solid state. With increasing ϕ at fixed σ_e's, the C_s at the boundary increased monotonously as reported previously [1,2]. On the other hand, a characteristic behavior was observed for σ_e dependence: On increasing σ_e for $\phi \geqq 2 \times 10^{-2}$, the phase boundary first shifted towards higher C_s due to an augmented electrostatic interaction. However, with a further increase in σ_e, a maximum was observed at around $\sigma_e = 0.4$–0.5 μC cm^{-2}, after which the C_s value at the boundary decreased. Namely, there existed a reentrant liquid state in the high σ_e region.
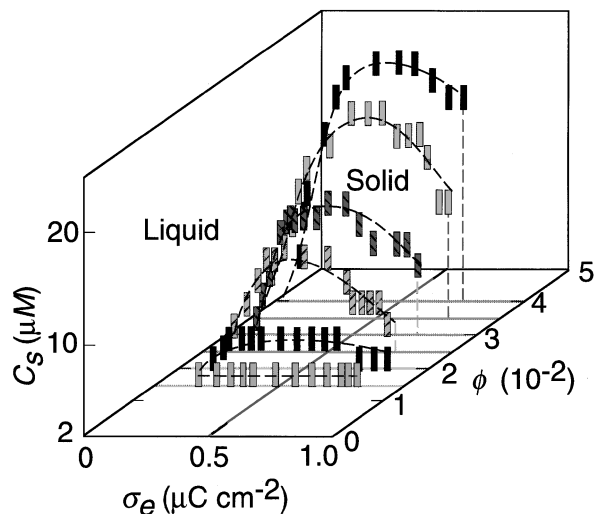
FIG. 1. A phase diagram for the solid-liquid transition of aqueous dispersion of KE-P10W silica particles (diameter = 0.12 μm) as a function of the effective charge density σ_e, the particle volume fraction ϕ, and the salt concentration C_s. The solid-liquid phase boundary was shown by rectangles. Dashed lines are guides for the eye.

The phase diagram was further examined by applying the USAXS method [4]. Figure 2 shows the scattering intensity versus scattering vector q at $\phi = 3 \times 10^{-2}$, $C_s = 10$ μM, and at three σ_e's, which corresponded to the liquid, solid, and the reentrant liquid states in the phase diagram (Fig. 1). In the liquid state ($\sigma_e = 0.07$ μC cm^{-2}),

a broad peak due to interparticle interference, resulting from an electrostatic interaction, was observed in addition to the form factor of an isolated particle. In the solid state ($\sigma_e = 0.36$ μC cm^{-2}, taken from Fig. 3 of Ref. [4]), sharp peaks were observed, which were attributable to the Bragg diffractions from the (110) plane of a bcc lattice [7]. At $\sigma_e = 0.72$ μC cm^{-2}, again a profile due to the liquidlike particle arrangement was observed, which confirmed the presence of the reentrant liquid state.

We further examined ionic polymer latex particles having strongly acidic groups (diameters = 0.12–0.13 μm). SS-10, SS-16, and SS-19 ($\sigma_e = 0.28$, 0.42, and 0.70 μC cm^{-2}) were synthesized by an emulsifier-free polymerization method, and N-100 (0.50 μC cm^{-2}) was purchased from Sekisui Chemicals Co., Ltd., Osaka, Japan. They were purified as described earlier [8], and the dispersion structures were observed by LSCM as reported before [8]. Figure 3 is a phase diagram determined at $C_s = 2$ μM and at relatively dilute conditions. The data for the two kinds of silica in the absence of NaOH ($\sigma_e = 0.07$ and 0.23 μC cm^{-2}) were also shown. Coexistence of the solid and liquid states was observed in the solid state near the phase boundary. Clearly, there exists the liquid state at high σ_e's, not only when ϕ and/or σ_e are small.

We compare now the effective charge and the phase diagram determined here with theoretical studies. The interaction between charged colloidal particles has often been claimed to be explainable in terms of a pair potential of the Yukawa form $U_Y(r) = A[(Ze)^2/4\pi\varepsilon]\exp(-\kappa r)/r$, where r is the interparticle distance, Z is the charge number, e is the elementary charge, $1/\kappa$ is the Debye screening length defined as $\kappa^2 = 4\pi e^2[C_C + 2C_s]/\varepsilon k_B T$, $A = [\exp(\kappa a)/(1 + \kappa a)]^2$ (a geometrical factor), and a is the particle radius [1]. A numerical simulation study on the phase diagram for the Yukawa system has been reported by Robbins et al. [9].
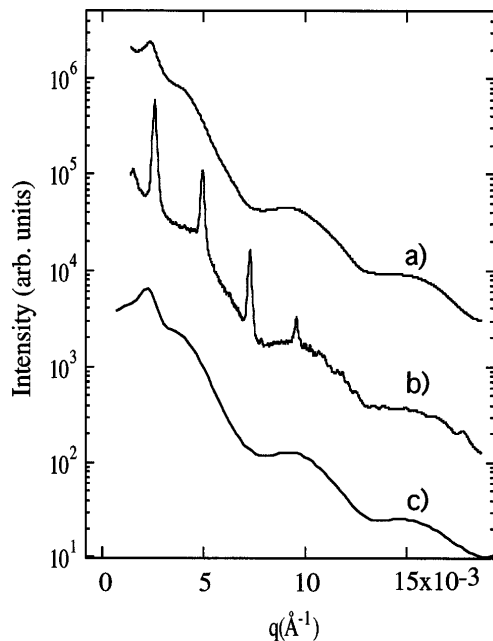

FIG. 2. The USAXS profiles showing the reentrant solid-liquid transition for KE-P10W silica dispersions with varying σ_e. (a) $\sigma_e = 0.07$, (b) 0.36, and (c) 0.72 μC cm^{-2}; $C_s = 10$ μM; $\phi = 3 \times 10^{-2}$.
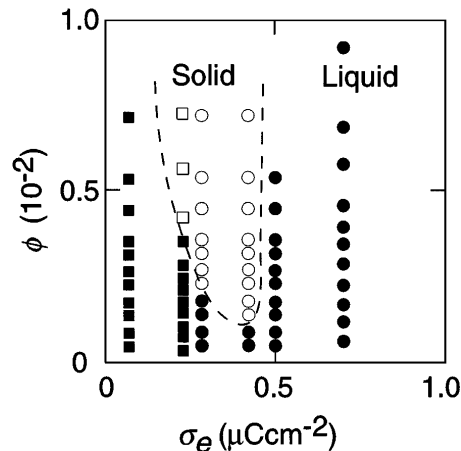

FIG. 3. A phase diagram determined by confocal laser scanning microscopy for polymer latex (circle) and colloidal silica (square) dispersions. $C_s = 2$ μM. Open symbols, solid state; filled symbols, liquid state.

$U_Y(r)$ is derived from the linearized Poisson-Boltzmann (P-B) equation assuming the potential energy at the surface $Ze^2/[a\varepsilon(1 + \kappa a)] < k_BT$ (Debye-Hückel (D-H) approximation) [1]. In practice, especially at low-salt conditions, the D-H approximation is not valid. Even then, however, the use of $U_Y(r)$ was considered to be justified, if one introduces a renormalized charge density σ^*, which is obtained by solving the full P-B equation in a spherical Wigner-Seitz cell and matching the resulting electrostatic potential to the solution of the linearized P-B equation at the cell boundary [10,11]. Several authors [2,3] have reported that the experimental phase diagrams showed close agreement with that by Robbins $et~al.$ by using σ^*. Furthermore, Palberg $et~al.$ [3] reported that the renormalized charge was close to the effective charge determined by their conductivity measurements. It should be noted that these conclusions have been drawn for relatively small charge particles ($\sigma_a < 0.63~\mu$C cm^{-2} in Ref. [3]).

In Fig. 4(A), σ_e obtained in the present study (KE-P10W silica, $\phi = 2 \times 10^{-2}$) and σ^* calculated by the method in Ref. [8] (broken curve) are shown as a function of σ_a. The data for the polymer latices [5] were
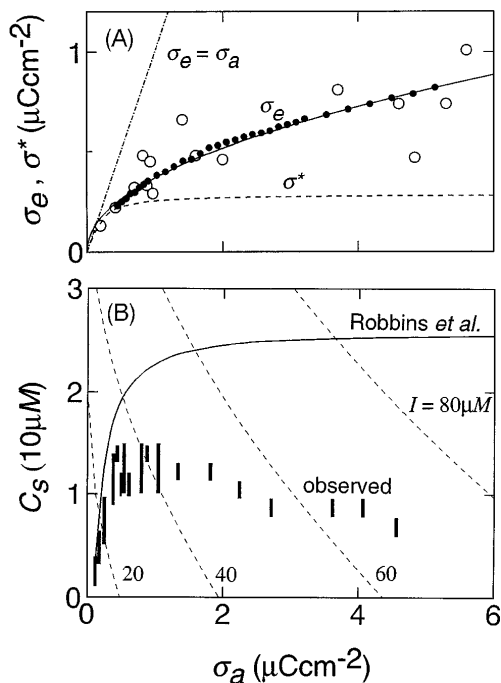

FIG. 4.   (A) Relationship between σ_e and σ_a for KE-P10W silica dispersions ($\phi = 2 \times 10^{-2}$, filled circles). The full curve is an empirical relationship, $\ln \sigma_e = 0.49 \ln \sigma_a - 1.0$, determined from the data for latices (open circles; extrapolated value to $\phi = 0$) [5]. The renormalized charge density, σ^* (broken curve) was shown for comparison. The dot-dashed curve represents $\sigma_e = \sigma_a$. (B) Comparison between observed phase boundary (rectangles) and the numerical simulation results by Robbins $et~al.$ with σ^*. $\phi = 3 \times 10^{-2}$. Conditions where the ionic strength of the dispersion, $I~(\equiv C_s + \frac{1}{2}C_C)$, were 20, 40, 60, and 80 μM are also shown.

also demonstrated. At small σ_a's, σ_e was close to σ^*. However, at higher σ_a's, the σ^* value tended to level off, while σ_e kept increasing. The observed σ_e was well described by an empirical relationship determined for latices, $\ln \sigma_e = 0.49 \ln \sigma_a - 1.0$ (full curve) [5]. Figure 4(B) shows a comparison between the experimental phase boundary and that determined by the method of Robbins $et~al.$ by using σ^* ($\phi = 3 \times 10^{-2}$). For all of the data points, the D-H approximation was not valid. At small σ_a's, the predicted boundary (full curve) was close to the observed one, as reported previously [12]. At higher σ_a's, however, C_s at the boundary became constant, because of the saturation of σ^*. Thus the reentrant transition was not in accord with the theoretical treatment based on the Yukawa potential and the charge-renormalization concept.

When σ_e was used instead of σ^*, C_s of the boundary increased with σ_a under the conditions examined here, and showed a maximum at around $\sigma_a = 6~\mu$C cm^{-2}, as a result of increases in both σ_e and C_C with increasing σ_a: The ionic strength of the dispersion, $I~(\equiv C_s + \frac{1}{2}C_C$ for monovalent extraneous ions and counterions [13]), increases with σ_a. Since κ is proportional to $I^{1/2}$, the screening effect becomes more pronounced at higher σ_a's, resulting in a reentrant solid to liquid transition. Conditions where I values were constant ($isoionic~lines$), which are measures of the screening effect, are also shown in Fig. 4(B) for reference. Thus, when σ_e was coupled with $U_Y(r)$, the reentrant transition is expected because of the screening effect. However, the predicted maximum position was much higher than the observed one ($\sigma_a \sim 1~\mu$C cm^{-2}).

The above-mentioned discrepancy might be partly attributed to, e.g., neglect of the many-particle interaction in the theory, which appears to be more significant in strongly interacting systems such as the present one. In our opinion, the Yukawa potential, in which only Coulombic repulsion between two particles is assumed, does not duly account for the phase behavior in low-salt dispersions: Recent experimental results suggest the presence of interparticle net attraction in ionic colloidal systems in low-salt conditions [1]. For example, spontaneous formation of void structures [14], where vapor and liquid states are coexisting, seems to be difficult to explain without assuming a net attraction. We point out that the void structure was favored for highly charged particles [15], for which the reentrant disordered states were observed here. In order to describe the interparticle attraction, the Sogami potential $U_s(r) = [\sinh(\kappa a)/\kappa a]^2 [1 + \kappa a \coth(\kappa a) - \kappa r/2] \times [(Ze)^2/4\pi e] \exp(-\kappa r)/r$, which has both electrostatic attractive and repulsive terms, has been used [1]. Although performed under limited conditions, simulation studies with $U_s(r)$ [16,17] predicted the reentrant behavior.

Further studies are in progress to discuss the reentrant transition in more detail. However, in the present stage, we may reasonably conclude that the argument in terms of the

Yukawa potential and the charge-renormalization concept is not applicable for highly charged colloidal systems.

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[12] The boundary predicted by the Sogami potential also showed a good agreement with the experiment at low σ_a, because of the repulsive term dominating when σ_a is small (see Ref. [16]). At higher σ_a conditions, however, several experimental results suggest the presence of *net* attraction. For example, the USAXS study showed the closest interparticle distance of the present system ($\sigma_a = 0.64$ μC cm^{-2}, $C_s = 2$ μM, and $\phi = 3 \times 10^{-2}$) was smaller than the average interparticle distance, estimated by assuming homogeneous distribution of the particles [4]. This appears to imply that the solid structure was non-space-filling, which could be explained in terms of net attraction.

[13] In our previous paper [4], we followed the definition $I \equiv C_s + C_C$, which implies that a contribution of particles, which are polyions, is considered in the same manner as that for a monovalent small ion. However, this does not appear to be adequate. The definition of I (or, equivalently, κ) is still controversial. See, e.g., K. S. Schmitz, Langmuir **12**, 3828 (1996).

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