

# Gathering of Charged Colloidal Particles near a Like-Charged Glass Plate

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**Abstract:** The distribution of negatively charged colloidal particles near a like-charged glass plate was investigated using a confocal laser scanning microscope and video imagery. It was found that the number of particles about 5  $\mu\text{m}$  from the glass surface was higher than that inside the dispersion and decreased gradually with distance. At shorter distances, such as 1  $\mu\text{m}$ , there were no particles due to an electrostatic repulsion between the glass plate and the particles. The “condensation” near the glass surface was observed at low ionic strengths in the dispersion, such as NaCl concentrations of  $10^{-5}$  M or lower, and the peak in the particle distribution profile as a function of distance from the glass surface disappeared at  $10^{-4}$  M. The peak height increased with the number of surface charges on the particles and with the surface  $\zeta$ -potential of the plate. The greater the number of charges on the plate and particles, the more pronounced became the condensation. The dependencies of the peak height indicated that the driving force for the condensation was an electrostatic attractive interaction between the like-charged plate and particles, though such an interaction is not predicted by the conventional DLVO theory.

## Introduction

It is well known that charged polymer latex particles form an ordered structure in deionized dispersion,<sup>1–4</sup> and several types of inhomogeneous particle distributions have been observed at relatively low particle concentration. For example, the “two-state structure”<sup>5–7</sup> is the coexistence of ordered (solid-like) and disordered (liquid-like) particle distributions in deionized dispersions, the “void structure”<sup>8–12</sup> is a liquid-like distribution coexisting with spherical gas-like regions which contain almost no particles, and the “vapor–liquid condensation phenomenon”<sup>13–16</sup> is the macroscopic separation of a dispersion into a transparent vapor layer and a condensed liquid layer. Recently, the relation of the “void formation” to the “vapor–liquid separation” was systematically studied by Yoshida et al.,<sup>12</sup> who claimed that these inhomogeneous particle distributions were formed by an electrostatic attractive interaction between like-charged particles,<sup>17</sup> though such an interaction is not explicable in terms of the conventional DLVO theory.<sup>18</sup> As

the examples show, the particle distribution is not homogeneous when the electrostatic interaction is strong enough.

We reported previously preliminary experimental results on another type of inhomogeneous particle distribution, that of a condensation of charged particles near a like-charged glass plate. The dependence of the particle distribution on the ionic strength of the dispersion and on the density difference between the particles and the dispersion medium were examined.<sup>19</sup> We suggested that the driving force for the condensation was an electrostatic interaction between the plate and the particles because the particle condensation was observed at low ionic strengths, in other words, under the conditions for strong electrostatic interaction. However, the problem with this suggestion was that the electrostatic interaction seemed to be attractive even though the signs of the charges on the plate and particles were identical. To confirm the suggestion, we have investigated the charged particle distributions near like-charged plates, changing the number of charges on the particles and the surface potential of the plate. The results are shown in this paper together with the consequences of precise reexaminations of the ionic strength and density dependencies.

## Experimental Section<sup>20</sup>

The latex dispersions used in this study were synthesized in our laboratory by copolymerization of styrene and *p*-styrenesulfonate, with divinylbenzene as the cross-linking agent. The reaction was initiated with potassium persulfate in a water–methanol mixture without any emulsifier. The dispersions obtained were dialyzed against distilled and deionized water. Before use in the measurements, the dispersions were thoroughly purified by ultrafiltration (model 202, Amicon, with Millipore membrane, pore size 0.22  $\mu\text{m}$ ) and mixed-bed exchange resin

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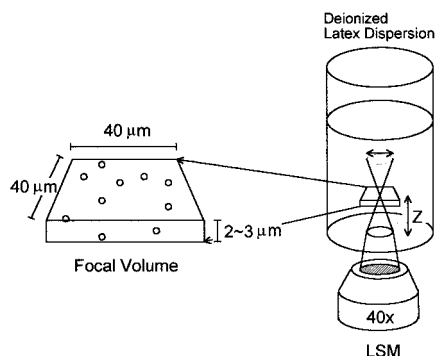


Figure 1. Schematic representation of the observation system.

beads (AG501-X(8)D, BioRad). The number of sulfonic acid groups on the particles was determined by conductometric titration, and the diameter was measured with a dynamic light scattering apparatus (DLS-7000, Otsuka Electric). The number of sulfonic acid groups and diameters were in the range of  $10^4$ – $10^5$  and 0.3–0.6  $\mu\text{m}$ , respectively. Effective charge numbers of the particles were estimated by conductance measurements on the dispersions, assuming that the measured conductance was the sum of contributions from hydrogen ions dissociated from the sulfonic acid groups on the particles and  $\text{H}_2\text{O}$ . Using the number of hydrogen ions coming out from the effectively dissociated sulfonic acid groups, the ratio of the effective charge number to the analytical charge number was calculated. It was about 0.2 for all the particles used in this study.

An ordinary microscope cover glass was used as the charged plate. It was cleaned by dipping in concentrated sulfuric acid and rinsed repeatedly with pure water. The surface electric potential was estimated by measuring the  $\zeta$ -potential with an electrophoretic dynamic light scattering apparatus (ELS-800, Otsuka Electric, courtesy of Dr. Nakamura at Otsuka Electric, Osaka). The values were  $-24$  mV in a  $10^{-2}$  M NaCl solution and about  $-90$  mV in deionized water (the value in deionized water was measured in our laboratory by the microelectrophoresis method<sup>21</sup> with a PenKem Model 501). In order to change the surface potential of the glass plates, the surfaces were modified by polymerizing charged or uncharged monomers to reactive end groups of silane coupling agents bound to SiOH groups on the glass surface. Bound (3-methacryloxypropyl)trimethoxysilane was used to polymerize acrylamide monomers to obtain polyacrylamide (PAA) chains which are soluble in water but uncharged. The polymer chains were expected to cover the glass surface and decrease the effective surface potential of the glass surface.<sup>22</sup> The  $\zeta$ -potential of the PAA-modified glass surface was  $-4$  mV in a  $10^{-2}$  M NaCl solution. *p*-Styrenesulfonate monomers were polymerized to (3-methacryloxypropyl)trimethoxysilane bound to the glass surface to increase the surface potential, due to dissociation of the sulfonic acid groups. The  $\zeta$ -potential of the polystyrenesulfonate (PSS) modified glass surface was  $-94$  mV in a  $10^{-4}$  M NaCl solution whereas the  $\zeta$ -potential of the uncoated glass surface was  $-70$  mV at the same NaCl concentration. The  $\zeta$ -potentials were measured at relatively high concentrations of NaCl, compared with those under the conditions of microscopic observation, due to an experimental limitation. Accordingly, the values of  $\zeta$ -potentials are expected to be more negative under the conditions of microscopic observation. The observation cell was made of Pyrex glass tube, with the cover glasses glued to the bottom.

The particles were observed with a reversed-type confocal laser scanning microscope (LSM410, Carl Zeiss) using an objective lens of 40 $\times$  and a working distance of 330  $\mu\text{m}$ . The microscope scans an object with a focused Ar laser, and the reflected light is detected through a pinhole placed at the confocal point of the objective lens and detector lens. The reflected light intensity in the scanned rectangular area is displayed on a TV monitor to obtain a microscopic image of the object. The pinhole eliminates the light reflected from out-of-focus points, so the images obtained are free from background scattering and the

particles in the image are clear and highly contrasted.<sup>23</sup> Using this optical system, latex particles far inside the glass cell ( $\sim 300$   $\mu\text{m}$ ) could be observed. A schematic representation of the optical system is shown in Figure 1. Particle distribution profiles were obtained by counting the number of particles in an observation area ( $40 \times 40$   $\mu\text{m}^2$ ) using a digital image processing computer (IBAS, Carl Zeiss) and plotting the numbers against distance from the glass surface ( $Z$ ). The particle numbers of 20–25 different images obtained from different places in the same sample were averaged. The effective depth of the observation volume was determined by measuring the reflected light intensity profile as a function of distance from the glass surface. It was about 2–3  $\mu\text{m}$  depending on the pinhole size, contrast, and brightness value of the monitor.

## Results and Discussion

In our previous report,<sup>19</sup> we showed that charged colloidal particles gather near a like-charged glass plate in deionized water. There was a peak in the particle distribution profiles, and the peak height decreased with increasing added NaCl concentration. Accordingly, the phenomenon could not be observed at  $10^{-4}$  M or higher. We suggested that the condensation was an electrostatic phenomenon because it seemed reasonable to understand the decrease of the peak height on the addition of NaCl as being due to shielding of the electrostatic interaction between the plate and particles, and between particle and particle. Concerning the effect of added NaCl, one may be reminded of polyelectrolyte bridging. However, we did not think that it was appropriate to explain the condensation phenomenon, because the interparticle distance between neighboring particles in the condensed region was about 4  $\mu\text{m}$ . The effect of sedimentation of the particles on the condensation was also examined using a  $\text{H}_2\text{O}$ – $\text{D}_2\text{O}$  mixture as the dispersion medium to match the density of the particles at about 1.05  $\text{g}/\text{cm}^3$ . It was found that the sedimentation effect was negligible, the condensation being observed even in a density-matched dispersion. However, there remained a slight possibility that sedimentation was the driving force because a small difference in the densities, brought about by experimental error in mixing  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , might cause the condensation. The reason why we were so cautious about this sedimentation effect is that the effect could become pronounced in deionized dispersions when the particles' Brownian motion is depressed by the strong electrostatic interaction between the particles and/or between the particles and counterions.<sup>24</sup> To rule out this possibility, we repeated the experiments at several values of dispersion medium density. The results are shown in Figure 2. At all dispersion medium densities, the condensation was observed and only small differences in the peak heights could be detected. It was therefore reconfirmed that the density difference between the particle and the dispersion medium is not the driving force for the condensation.

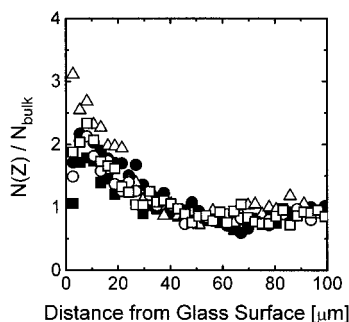
If it were an electrostatic interaction, the peak height would depend on the number of charges on the particles. We used six different samples with different charge numbers and measured the peak height for each sample. Figure 3 shows how the peak height depends on the number of charges on the particles. It is clear that the peak height increases with the number of charges and decreases to unity in the zero charge limit,<sup>25</sup> confirming again that the condensation is an electrostatic phenomenon. The increase of the peak height with charge number suggests that the electrostatic force between the like-charged plate and particles is attractive because the more charges the particles bear, the more particles gather near the glass plate.

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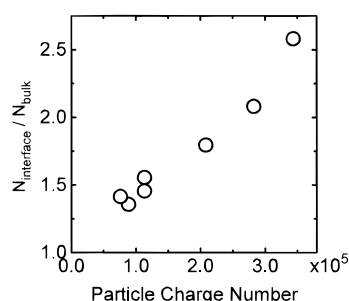
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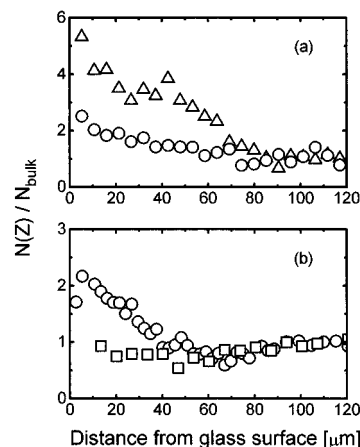
**Figure 2.** Particle distributions in dispersions with different densities. The density of the dispersion medium was varied by mixing H<sub>2</sub>O and D<sub>2</sub>O. The ratio of the number of particles observed at distance  $Z$  [ $N(Z)$ ] and the averaged number of particles in the region of 100–120  $\mu\text{m}$  [ $N_{\text{bulk}}$ ] was plotted against distance from the glass surface.  $N_{\text{bulk}}$  was confirmed to agree with the calculated value using the particle diameter, particle concentration, and focal volume. Key: latex MSS-17, diameter 0.56  $\mu\text{m}$ , charge number  $3.4 \times 10^5$ , particle concentration 0.07 vol %; dispersion medium densities [ $\text{g}/\text{cm}^3$ ], (●) 1.00, (■) 1.02, (△) 1.03, (○) 1.05, (□) 1.06; particle density [ $\text{g}/\text{cm}^3$ ] 1.05. The plate was bare glass.



**Figure 3.** Particle charge number dependence of the peak height.  $N_{\text{interface}}$  was the number of particles in the region of 5–25  $\mu\text{m}$ . The latexes used and charge numbers and diameters are MSS-16,  $2.8 \times 10^5$ , 0.62  $\mu\text{m}$ ; MSS-17,  $3.4 \times 10^5$ , 0.56  $\mu\text{m}$ ; MSS-18,  $2.1 \times 10^5$ , 0.51  $\mu\text{m}$ ; MSS-19,  $7.6 \times 10^4$ , 0.45  $\mu\text{m}$ ; MSS-20,  $1.2 \times 10^5$ , 0.41  $\mu\text{m}$ ; and MSS-21,  $9.1 \times 10^4$ , 0.21  $\mu\text{m}$ . The measurement for MSS-20 was repeated twice to confirm experimental reproducibility. Both results were plotted. The plate was bare glass.

However, in colloid science, it is believed that the electrostatic force between like-charged entities is repulsive, and it has been suggested that the condensation is due to the particles near the glass plate being pushed toward the plate by electrostatic repulsion from the other particles inside the dispersion. In such a case, however, particles would gather near the plate even when the plate has no charges on its surface, and in addition, the particles would be repelled more strongly by the plate when the plate charge is increased. Consequently, the peak position of the distribution profile would move toward the interior of the dispersion. On the contrary, if the force is attractive, the particles will never gather near an uncharged plate, and the peak in the distribution will move closer to the glass plate and become more pronounced when the plate charges are increased. To give an answer to the question as to whether the electrostatic force is an attractive or a repulsive one, we examined the particle distribution near the glass plates with lower and higher charges on the plate. Figure 4 shows the particle distributions near the PSS- and PAA-modified glass plate compared with the distribution near the bare glass plate. The peak for the PSS-modified glass is higher than that for the bare glass, and its position is

(25) Generally, the number of charges tends to increase with the size of a particle, so one may take the peak height dependence as a result of sedimentation of the particles. However, it is not the case for the data in Figure 3, because the peak height for the MSS-17 sample, which carries the highest number of charges, is highest despite the size being the second largest.



**Figure 4.** Effect of the surface potential of the glass plate on particle distribution. (a) PSS-modified and bare glasses.  $\zeta$ -potentials of the glasses are  $-94$  and  $-70$  mV in  $10^{-4}$  M NaCl solution. Key: (△) PSS-modified glass, (○) bare glass; latex MSS-28; diameter 0.60  $\mu\text{m}$ , charge number  $4.6 \times 10^5$ , particle concentration 0.08 vol %. (b) PAA-modified and bare glasses.  $\zeta$ -potentials of the glasses are  $-4$  and  $-24$  mV in  $10^{-2}$  M NaCl solution. Key: (□) PAA-modified glass, (○) bare glass; latex MSS-17, particle concentration 0.07 vol %.

closer to the glass plate (Figure 4a). Furthermore, no gathering is observed near the PAA-modified glass plate (Figure 4b). These results show that the gathering of the negatively charged particles becomes more pronounced on increasing the number of charges of the plate and is reduced by decreasing the charge number. This tendency agrees completely with the case predicted by the electrostatic attraction.

It is important to note that the gathering takes place without any relation to the chemical difference between the ionizable groups on the plate and particle surfaces. Because the origin of the negative charge on the bare glass is dissociation of the weak acid group ( $-\text{SiOH}$ ) and that on the particle is the strong acid group ( $-\text{SO}_3\text{H}$ ), it has been suggested that a decrease of the degree of dissociation of the weak acid due to approach of the particle might be significant for the gathering of particles. However, the particles with strong acid groups gathered near a glass plate with identical ionizable groups.

Another point to be mentioned is the possible effect of cations such as  $\text{Na}^+$  coming out continuously from the glass when it is in contact with pure water. It has also been suggested that a positive atmosphere consisting of such cations might be formed close to the glass surface and the excess cations might contribute to the formation of condensation phenomenon. This suggestion was found to be irrelevant because the condensation was observed near a quartz plate which contains only a negligible amount of cations. Recently we have confirmed this irrelevancy by the observation of the condensation near a Nafion-coated polyethylene surface. Nafion is a fluorinated carbon polymer carrying a sulfonic acid group at the end of the side chain. In this system, no cation comes out from the polyethylene surface, and only strong acid groups exist on its surface. Under such conditions, the particles gathered. On the contrary, the condensation was not observed near a bare polyethylene surface. It can therefore be stated that the continuous solution of cations from the glass into the dispersion is not an essential factor for the condensation and that having charges on the surface is indispensable for the condensation.

We have also to comment on the effect of van der Waals attraction between the glass plate and polystyrene particles, because this attraction is thought to be stronger and of longer range than that between particle and particle. Following the conventional theory for the van der Waals force based on

Lifshitz theory, the distance at which the van der Waals potential between a glass plate and a polystyrene particle in water is comparable to  $-kT$  is on the order of  $0.1 \mu\text{m}$ . Observation of the particle distribution at this distance using a higher magnification objective lens with a lower depth of focus revealed that there was almost no particles in this region, because of electrostatic repulsion between the glass plate and the particles. Hence, the van der Waals attraction can be assumed to be negligible compared with the electrostatic interaction. In addition, this assumption is supported by the experimental results showing the increasing tendency of the condensation with the number of charges on the particles and with the  $\zeta$ -potential of the glass plate, whereas the van der Waals attraction is independent of the surface electric potentials.

In conclusion, it can be stated from the experimental results that charged particles are gathered by like-charged entities in deionized dispersions because of electrostatic attraction. We can refer to many theories<sup>17,26–28</sup> to rationalize the existence of the attraction between like-charged particles. However, the range of the attraction observed in the condensation is too long

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for the theories. Presumably, the charged plate attracts like-charged particles which are moving adjacent to the plate and the attracted particles pull on the other particles inside the dispersion. This might occur sequentially and give rise to an extra-long-range attraction. This assumption is now under investigation.

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**Supporting Information Available:** Text describing the latex preparation, particle charge number evaluation, and plate surface modification and a figure showing the confocal microscope images. (5 pages). See any current masthead page for ordering and Internet access instructions.

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