Positive Adsorption of Charged Particles near a Like Charged Glass Plate

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It is believed that negatively charged entities are repelled by a like charged plate, their concentration being small near the plate and increasing with distance up to the bulk concentration. However, we had noticed in previous work that the concentration of charged colloidal particles near a like charged cover glass became higher when the dispersion was deionized under density-matching conditions, using an H_2O-D_2O mixture as the dispersion medium.[1-3] (See, for example, Figure 14 of ref 3.) Another example of the concentration increase at an interface, which cannot be understood in terms of conventional theory, was observed in a study of void structures in latex dispersions.[3,4] Though the existence of a microscopic vacant space (a region with practically no particles inside) in a macroscopically homogeneous dispersion has been taken as extraordinary, the voids could be easily observed between distances of 10−50 μm from the cover glass. At shorter distances, it was difficult to find voids; in other words, the particles were found to be distributed rather homogeneously. It was therefore inferred that the particle concentration within 10 μm of the cover glass was higher than that in the interior of the dispersion: positive adsorption took place. We have now studied these phenomena more systematically, and we report here our results on the distribution of charged particles near the interface with a like charged glass plate.

The sample used in the present work was styrene−styrenesulfonate copolymer latex (MSS-17, diameter 0.56 μm, charge density −5.5 μC/cm^2), which was synthesized in our laboratory by emulsifier-free emulsion polymerization using potassium persulfate as an initiator. Hence, the sign of the charge on the particle surface was negative due to dissociation of the sulfonate and sulfate groups. The sample was dialyzed with deionized water for about a week, and remaining ionic/oligomeric impurities in the dispersion were removed by mixed-bed ion-exchange resin beads (Amberlite MB-3, Rohm and Haas). Before microscopic observations were begun, the stored dispersion was thoroughly washed with deionized water using an ultrafiltration apparatus (Amicon Model 202 and Millipore cellulose membrane GSWP pore size 0.22 μm). A reversed-type confocal laser scanning microscope LSM410 (Carl Zeiss, Oberkochen, Germany) was used to count the number of particles as a function of the distance (z) from the cover glass. The z value was obtained from the displacement of the microscope stage using a z-correction factor determined experimentally by Dr. H. Yoshida. The magnification of the objective lens used was 40×, and its working distance was 0.33 mm. The observation cell was made of a Pyrex glass tube with a cover glass glued to the bottom. Before being glued, the cover glass was dipped in concentrated sulfuric acid to clean the surface and was rinsed repeatedly with deionized water. It is generally believed that a glass surface treated with acid and water is negative due to SiO^- groups. The ζ-potential of the glass surface thus treated was conveniently determined from the electrophoretic velocity profile of charged latex particles dispersed in a rectangular cell[5] made of the same material as the cover glass, and it was found to be −70 to −90 mV depending on the added NaCl concentration in the range $10^{-4}-10^{-6}$ M. The velocity profiles were measured using a Laser Zee Meter Model 501 (PenKem, Inc., Bedford Hills, NY).

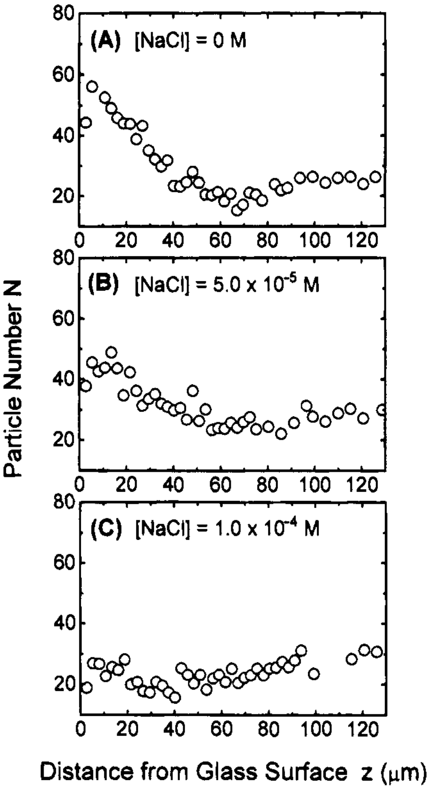

Figure 1. The number of particles as a function of distance from the cover glass: (A) deionized dispersion; (B) [NaCl] = 5.0 × 10^{-5} M; (C) [NaCl] = 1.0 × 10^{-4} M. [Latex]: 0.065 vol %. Diameter: 0.56 μm. Charge density: −5.5 μC/cm^2. Covered area: 37 × 31 μm^2. Attempts were made to attain better particle images by adjusting the contrast so that the effective depth of focus was not fixed but in the range 2−3 μm. By using this value and the area covered (37 × 31 μm^2), the average number in a micrograph (N_{interior}) was estimated to be 20−30.

The number of particles (N) in the observation area (37 × 31 μm^2) near the cover glass is shown as a function of z in Figure 1. In the deionized dispersion (Figure 1A), $N(z)$ in the vicinity of the interface $N_{\text{interface}}$ (say, $N(5-10)$) was larger than that in the interior of the dispersion N_{interior} (say, $N(100-120)$) and decreased with z.[6] The difference ($N_{\text{interface}} - N_{\text{interior}}$) became smaller with the addition of NaCl (Figure 1B) and disappeared at [NaCl] = 1.0 × 10^{-4} M. In the latter case, the particles were distributed homogeneously from the bulk dispersion up to the interface (Figure 1C). It should be noted that $N(z)$ for the homogeneous distribution and N_{interior} in the deionized dispersions were about 20−30, which was consistent with the value calculated from the particle concentration and the focal volume: (observation area) × (depth of focus). It is clear that, in the deionized dispersion, the charged particles were positively adsorbed at z = 5−10 μm by a factor of about 2. The salt concentration dependence of $N(z)$ suggests that the adsorption is caused by electrostatic interaction between the

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(6) A close look at Figure 1A indicates that $N(z)$ decreases with increasing z and, after passing through a minimum around z = 50−80 μm, increases slightly to the bulk value N_{interior}. Further study is in progress to examine whether this z-dependence is real or not.

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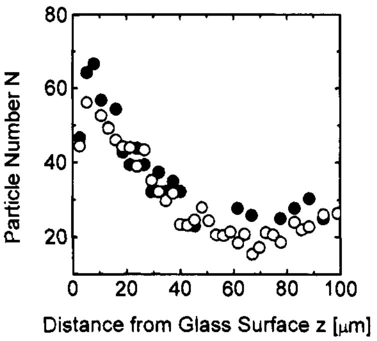

Figure 2. Particle distributions in H_2O and in a density-matched dispersion. [Latex]: 0.065 vol %. Diameter: 0.56 μm. Charge density: -5.5 μC/cm^2. Covered area: 37 × 31 μm^2. Dispersion media: H_2O and an H_2O-D_2O mixture. ○: solvent density = 0.997. ●: solvent density = 1.046.

charged particles and the plate. The presence of a large amount of salt (10^{-4} M) shields the electrostatic interaction considerably so that the adsorption is hindered.

The effect of particle sedimentation on $N(z)$ is worth considering, because the density of the particles[7] (1.047) was slightly larger than that of pure H_2O. The particle distributions were measured in both pure H_2O and density-matched dispersions prepared by mixing H_2O and D_2O. As shown in Figure 2, $N(z)_{d=0.997}$ and $N(z)_{d=1.046}$ agreed quite well with each other. This result shows that the sedimentation due to the density difference between the particles and the dispersion medium is not the driving force for the positive adsorption.

Electrostatic interaction is the most probable factor for the positive adsorption, though there are some unresolved problems. It should be noted that the z-range of the higher particle concentrations ($z = 5-40$ μm) is unexpectedly large. This implies that there must be contributions from particle−particle interactions in addition to the particle−plate interaction. Intuitively, we might expect that the charged plate would attract latex particles sitting in the neighborhood of the plate (say, at $z = 5$ μm). These particles would then attract other particles at larger distances by the same mechanism. In other words, particles at larger distances are attracted by the plate through the mediation of the other particles and the counterions. Since the influence of the plate diminishes with increasing z, particles at very large distances are no longer affected by the plate so that only the particle−particle interaction remains and may be overwhelmed by the kinetic energy, causing the particles to move nearly independently of one another. This situation can also be described in the way reported by Tata et al.,[8] who showed how vapor−liquid condensation was induced by a charged plate at the low latex concentrations employed in the present experiments.

To substantiate the above explanation, the long-range electrostatic attraction between like charged entities has to be justified theoretically. There are several theoretical attempts to formulate the attraction as was reviewed by Schmitz.[9] Furthermore, it is necessary to pay due attention to a theoretical approach by Ninham.[10] It is worth scrutinizing these theories in light of experimental data that have been and are being accumulated.

Because both the particles and the plate were in focus at closer than about 2 μm, the particle distribution could not be determined in this z-range. However, it is recognizable that the number of particles at $z < 5$ μm increases (not decreases) with z. This shows that standard double-layer interaction theory could only be qualitatively correct in the very close vicinity of the interface, as was experimentally demonstrated by Kepler and Fraden.[11]

It is worth mentioning that a similar positive adsorption has been observed at the air−solution interface in surfactant solutions.[12] In a neutron reflection study of a surfactant solution above the cmc, layers of concentrated micelles were found beneath the surfactant monolayer even though the micelles and the monolayer had like charges on their surfaces. The surfactant concentration in the first micelle layer was double the bulk concentration. It was thus concluded that there is an effective attractive interaction between the like charged micelles and the "wall".

Though so far completely overlooked, such an electrostatic positive adsorption seems to be an important factor to be considered in various fields involving ionic interfaces and entities, for example, cell−cell recognition and wetting.

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