ORDERED STRUCTURE OF LATICES DEPOSITED ON SEMIPERMEABLE MEMBRANE

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Monodispersed latex particles in aqueous solutions were deposited on a semipermeable membrane through which electrolytes permeated, and it was found that a two-dimensional ordered structure of these particles was formed under a certain condition. The mechanism of ordering was studied qualitatively using the DLVO theory, and the formation of an ordered structure was found to be closely related to the existence of the secondary minimum of the potential between the substrate surface and the particles.

1. Introduction

Stable colloidal particles in aqueous solutions are in random Brownian motion, but under certain conditions they form an ordered structure like solids. It is known that a three-dimensional ordered structure of charged latices is formed when the ionic strength is sufficiently low and the particle concentration is relatively high.⁶⁾ The mechanism of this ordering has been explained by the theory of Kirkwood-Alder transition,²⁾ in which the ordering is considered to be due to the repulsive force resulting from the electrostatic double layer around the particle surface.⁵⁾

Two-dimensional (2D) ordering of colloidal particles is also possible. The ordering of $0.2\text{ }\mu\text{m}$ latices at an air-water interface was observed by Pieranski.^{1,1)} This ordering was explained also by the Kirkwood-Alder transition, because the large separation distance between ordered particles suggested the existence of the interparticle repulsion force. Onoda⁹⁾ succeeded in finding an experimental condition for the formation of 2D ordering of $2\text{--}7\text{ }\mu\text{m}$ latices with surfactants at the air-water interface. This ordering was attributed to the secondary potential minimum resulting from

superposition of the electrostatic repulsive and van der Waals attractive energies.

Yasui and Higashitani¹³⁾ have recently reported that when small salt particles are dosed into a concentrated suspension of monodispersed latex particles, latices around the salt particle deposit on the salt surface and the deposit is partly ordered in structure. This result indicates that a 2D ordered structure of latices is possibly formed by a 2D surface with an equal salt concentration. Such a surface can be realized such that a concentrated suspension of latices is separated from an electrolyte solution by a semipermeable membrane as shown schematically in **Fig. 1**. As the electrolyte permeates through the membrane, the electrostatic double layer near the membrane surface is compressed and particles deposit on the membrane. The conformation of deposited particles depends on experimental conditions. Typical SEM photographs of ordered and disordered deposits are shown in **Fig. 2**. In the present study, a method of forming 2D ordered structure of uniform latices is proposed and the mechanism of ordering is discussed.

2. Experimental

Aqueous dispersions of polystyrene latex (PSL) particles of $0.8\text{ }\mu\text{m}$ diameter were prepared by the

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Fig. 1. Schematic drawing of the principle for deposition of colloidal particles on a semipermeable membrane

Fig. 2. Typical SEM photographs of deposited particles. (Particle concentration = $3 \times 10^{11} \text{ cm}^{-3}$) (a) Ordered structure (NaCl concentration = $1 \times 10^{-2} \text{ mol/l}$) (b) Disordered structure (NaCl concentration = $1 \times 10^{-1} \text{ mol/l}$)

method reported elsewhere.⁷⁾ It was confirmed by electron microscope that PSL particles are mono-dispersed in size and spherical in shape. Electrolytes used were chlorides of different cation valencies of reagent grade: NaCl, CaCl_2 and LaCl_3 .

Experiments in particle deposition were carried out by a simple device. A plexiglass tube of 10 cm^3 volume was filled with an electrolyte solution of a given concentration and the mouth was covered with a semipermeable membrane, stretched and cramped on the tube by a ring. A cellulose membrane of 0.1 mm thickness (VISKASE cellulose tube for dialysis) was employed as the membrane. It was soaked in methanol for 1 hour and then kept in water for 24 hours before use. The tube was dipped upside down into the colloidal solution in a beaker of 50 cm^3 volume such that the upper electrolyte solution was separated from the lower colloidal solution by the horizontal membrane at 1 cm depth from the colloid-air interface. After the tube was kept in the solution long enough for particles to form a cake of deposits, the membrane with the cake was taken out and dried at room temperature. The dried cake was easily peeled off from the membrane and a very thin layer of the cake was

Fig. 3. Power spectrum of the image of deposits and the autocorrelation coefficient. (Particle concentration = $3 \times 10^{11} \text{ cm}^{-3}$, NaCl concentration = $1 \times 10^{-2} \text{ mol/l}$) (a) Intensity of power spectrum at the spatial frequency corresponding to particle diameter vs. the angle on 2D spectrum. (b) Auto-correlation coefficient vs. the angle difference.

left on the membrane. The microstructure of the residual cake around the membrane center was observed by a darkfield microscope and the image was analysed by an image processor.*) A 2D power spectrum of the image was calculated using the Fast Fourier Transform, and the intensity of the power spectrum at the spatial frequency corresponding to the particle diameter, I , was plotted against the angle around the center of the 2D spectrum, θ , as shown in Fig. 3(a). It is possible to evaluate the degree of ordering with this spectrum, but here the autocorrelation of the relation of I vs. θ was introduced to avoid the influence of the intensity of the background image. The degree of ordering was then evaluated by the value of DO , defined by the following equation.

$$DO = 1 - (S_{min}/S_{max}) \quad (1)$$

where S_{min} and S_{max} are the minimum and maximum

* The ordering of particles observed by this method was confirmed by an SEM photograph taken using the frozen-replica method. The replica was prepared as follows. The membrane with the cake was frozen in liquid nitrogen immediately after it was taken out of the electrolyte solution. The frozen cake was cut by a knife in a vacuum chamber and a vapor of platinum and carbon was deposited on the cross section. The cake was dissolved in a solvent and the image printed on the residual replica was observed by electron microscope.

values of the autocorrelation coefficient respectively. DO is unity when the image is perfectly ordered. DO decreases with the destruction of ordering, but it is not necessarily zero for a completely disordered image.

A separate experiment was carried out to determine the critical coagulation concentration (CCC). Dispersions were settled for 5 hours after stirring in solutions of given electrolyte concentrations for 5 minutes, and the value of CCC was determined from the relation of the absorbance of supernatant vs. the electrolyte concentration.

The zeta potential of particles was measured by microelectrophoresis.

3. Results and Discussion

Dependence of the degree of ordering on the particle concentration N_p is examined and the results are shown in Fig. 4. It is clear that the value of DO increases with N_p and becomes almost constant at $N_p > 10^{11} \text{ cm}^{-3}$. This indicates that the ordering depends on the flux of particles depositing on the membrane surface, and it is likely to be a necessary condition for ordering that a sufficient number of particles be supplied before captured particles are fixed firmly on the substrate surface. Dispersions of $N_p = 3 \times 10^{11} \text{ cm}^{-3}$ were employed in the succeeding experiments.

Figure 5 shows changes of the weight, W , of particles deposited on the unit surface area around the membrane center. Since the deposition rate around time $t=0$ is hardly known by the present experimental method, these results cannot be directly correlated with the ordering of particles near the membrane surface to which our attention was paid, but the following points are indicated. The deposition proceeds rapidly at the early stage, but the rate is reduced with time, probably because the flux of electrolyte through the membrane decreases with increasing thickness of deposits. The deposition rate varies also with the electrolyte concentration C_e and no deposition is observed at $C_e \leq 1 \times 10^{-3} \text{ mol/l}$, where the potential well between the particle and substrate surfaces is shallow or disappears, as discussed later.

Figure 6 shows the dependence of DO on NaCl concentration. It is found that the value of DO is constant at about 0.9 at $C_e \leq 7 \times 10^{-3} \text{ mol/l}$, but as C_e increases the value of DO falls to about 0.3 and remains constant at $C_e \geq 0.1 \text{ mol/l}$. Here the critical ordered concentration COC and the critical disordered concentration CDC of electrolytes are defined as onset concentrations to the constant values of DO , as shown in Fig. 6. Similar features of DO vs. C_e are found in the cases of CaCl_2 and LaCl_3 solutions, as shown in Fig. 7, though the magnitudes of COC and CDC decrease and the ordering becomes less reproducible

Fig. 4. Dependence of DO on N_p for $1 \times 10^{-2} \text{ mol/l}$ NaCl solution

Fig. 5. Change of weight of deposits for NaCl solutions

Fig. 6. Dependence of DO on NaCl concentration

Fig. 7. Dependence of DO on concentration of CaCl_2 and LaCl_3

with increasing cation valency.

The dependence of *CDC* and *COC* on the valency of cations, *Z*, is shown in Fig. 8 and is compared with the dependence of *CCC* on *Z*. As expected by the Shultz Hardy rule, the value of *CCC* is proportional to *Z^m*, where the power *m* is approximately equal to 2.5 in this case. It is worth noting that the dependence of *COC* and *CDC* on *Z* is very similar to that of *CCC*, except that the magnitudes are smaller than those of *CCC*. This implies that the ordering is closely related to the potential between the particle and substrate surfaces, especially with the secondary minimum.

Figure 9 shows the zeta potential ζ of particles vs. κ for electrolytes of various cations. Here κ is the reciprocal double-layer thickness which is given by $(e^2 n Z^2 / \epsilon k T)^{1/2}$,^{*} where *n* is the cation concentration, *e* the elementary electric charge, ϵ the dielectric constant of the solvent, *k* the Boltzmann constant and *T* the temperature. According to the Gouy-Chapman theory with the Debye-Huckel approximation,¹⁰⁾ the zeta potential, as well as the potential at the diffusion layer, is a function of κ alone, so that the correlation between ζ and κ should be expressed by a single curve irrespective of *Z*. The disagreement shown in the figure implies that ions are partly fixed on the particle surface as the Stern layer, and so the exact value of the surface potential is hardly evaluated. In addition to this difficulty, the deposition process is not completely in a steady state; concentrations of electrolyte and particles near the membrane surface will vary with time. Hence it is hard to estimate the exact conditions around the membrane surface. Nevertheless, it is worth estimating the mechanism of ordering at least qualitatively by use of the DLVO theory.

Gregory⁴⁾ found that the following expression for the van der Waals attractive potential *V_A* between a sphere and a plate is a good approximation of the exact equation derived by Clayfield,³⁾

$$V_A = -\frac{Aa}{6h} \left(\frac{1}{1 + 14h/\lambda} \right) \quad (2)$$

where *A* is the Hamaker constant, *a* the particle radius, *h* the distance between the particle and substrate surfaces, and λ the characteristic wavelength of interaction, assumed to be 100 nm. When the sphere and plate are composed of similar materials, the interaction potential *V_R* due to the electric double layer is given by

$$V_R = 4\pi a \epsilon \psi_0^2 \ln[1 + \exp(-\kappa h)] \quad (3)$$

where ψ_0 is the potential of the sphere and plate surfaces. This is a good approximation at $\psi_0 < 60$ mV and $\kappa a > 1$.¹⁾ The following points are assumed in

* The electrolytes used here were treated as symmetric, because it is known that this assumption does not incur too much error.⁸⁾

Fig. 8. Dependences of *CCC*, *CDC* and *COC* on *Z*. () represents the value of *COC* extrapolated from the data in Fig. 7

Fig. 9. Zeta potential of particles vs. reciprocal double-layer thickness

evaluating the potentials by Eqs. (2) and (3). (1) Since our attention is paid to the very early stage of deposition, the electrolyte concentration at the substrate surface is equal to the concentration in the reservoir and the effect of the existence of neighbouring particles is negligible. (2) Surface potentials of the particle and substrate are nearly equal to the zeta potential of particles in the deionized solution, that is, 50 mV. (3) The value of *A* can be estimated in such a way that the peak of the potential curve disappears at *Ce* = *CCC*. Values of *A* for NaCl and CaCl₂ solutions are estimated to be 4×10^{-20} and 5×10^{-20} J respectively. These magnitudes are in fair agreement with those reported elsewhere.¹²⁾

Potentials between the substrate surface and particles at the *CCC*, *CDC* and *COC* of NaCl and CaCl₂ solutions are calculated with the above assumptions as shown in Figs. 10 and 11 respectively.

Fig. 10. Potential curves between substrate surface and particles for electrolyte solutions of monovalent cation. ($A = 4 \times 10^{-20}$ J is assumed.)

Fig. 11. Potential curves between substrate surface and particles for electrolyte solutions of divalent cation. ($A = 5 \times 10^{-20}$ J is assumed.)

It is indicated that particles must be captured in the secondary minimum for the formation of ordered structure. Particles in the secondary minimum can move two-dimensionally along the substrate surface to form their stable conformation. As C_e increases, the gap between the potential minimum and the substrate surface is reduced. This reduction will make the hydrodynamic resistance to the 2D movement of particles stronger and the Brownian motion of captured particles more restricted. On the other hand, the particles are free to move at the lower value of C_e , which results in the increase in value of DO . But if the value of C_e is too low and the depth of the secondary minimum becomes shallow, particles are

hardly captured on the surface. This is the reason why the deposition rate decreases with decreasing electrolyte concentration.

4. Conclusions

The following conclusions are drawn from these experiments.

- 1) A two-dimensional ordered structure of mono-dispersed particles can be formed on a semipermeable membrane through which electrolytes permeate.
- 2) The formation of 2D ordered structure is closely related to the existence of the secondary minimum of the potential between the particle and substrate surfaces.
- 3) The following mechanism is suggested for the 2D ordering of this experiment. The electrolyte permeates through the membrane to reduce the repulsive force between the particle and substrate surfaces, and the secondary potential minimum is formed. When the minimum is sufficiently deep and separated from the substrate surface, captured particles move around to adjust themselves and form an ordered structure. As C_e increases, the movement of captured particles is restricted because of the small gap between the particle and the substrate surface, and so the structure of deposits becomes less ordered. At $C_e > CCC$, particles are captured in the primary minimum directly and the structure becomes disordered. On the other hand, the value of DO increases with decreasing C_e , but when the depth of the secondary minimum is too shallow the detachment of particles occurs and the net deposition rate is reduced.

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