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Phase Transition in Concentrated Latices and the Electrical Double Layer on Their Surfaces

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The phase diagrams of monodisperse latices were constructed under the various conditions. The variable of the phase diagrams, the particle size, the surface charge densities of the latices, the counter-ion valences, and the medium temperature were taken up. The results, especially, the coexistent/ordered boundary curves were analysed in terms of the closed packing of the effective particle volumes which consisted of the latex particles which were surrounded by the electrical double layer. The value of 1.5 kT ergs[†] of electrical repulsion, when used as a criterion in the DLVO potential to back-calculate the weight fraction of solid contents as a function of KCl concentration, yields a curve that is very similar to the experimental boundary curve. The same agreement was found in the curves mapped out for the other latices with a different particle size and a different surface charge density using KCl as an electrolyte. In the boundary curve constructed using $MgCl_2$, however, the agreement with the analyses was not enough where the divalent cation would be adsorbed preferentially on their surfaces as a Stern layer charge. The temperature effect could be reasonably explained by the same procedure.

Monodisperse polymer latices which usually appear milky white, exhibit beautiful irridescent colours under a certain condition. This irridescence is due to the Bragg reflection of visible light by the orderly arrays of the uniform spherical particles of latices.[1)]

To date, several attempts have been made to give a reasonable explanation as to their order-disorder phase transitions. One explanation is based on the double layer interactions between the particles:[2,3)] The latex particle in an aqueous system may be regarded as an effective particle volume whose size is determined by the thickness of an electrical double layer on its surface and the boundary curve between the ordered and coexistent states corresponds to the closed packing of the effective particle volumes with a critical thickness of an electrical double layer.

Another approach is based on the concept of the Kirkwood-Alder transition[4)] which is expected only from the pure computer calculations. Their approach accounts for the presence of reasonable coexistent states of ordered and disordered structures.[5)]

The problem is that these analytical works have been performed using very limited experimental data and only a few authors have mapped out the phase diagrams by themselves. In this work, the conditions for the occurrence of ordered and disordered structures were studied systematically under the various conditions. As the parameters of the phase diagram, the particle size and the surface charge densities of latices, the valency of added counter ions, and the medium temperature were taken up. Thereafter, the resulted phase diagrams, especially, the coexistent/ordered boundary curves were analysed according to the concept of closed packing of the effective particle volumes using the DLVO theory.[6)]

Experimental

Latex Samples. In this work, three kinds of polystyrene latices were employed. Sample-A was prepared by an emulsion polymerization using sodium dodecyl sulfate as an emulsifier and $K_2S_2O_8$ as a polymerization initiator. Sample-B and -C were polymerized in the absolute absence of conventional emulsifiers.[7)] Table 1 shows their preparation conditions and the characteristic results. The particle diameters were determined by measuring the diameters on an electron micrograph which was equipped with a projection scope. The diameters for Sample-A and -C are almost the same, and the diameter for Sample-B is about threefold more than either of the other two. Size distribution of these samples is kept very narrow, with $D_w/D_n < 1.01$.

The surface charge densities of these latices were determined by potentiometric and conductometric titrations according to the method described by Van den Hul and Vanderhoff.[8)] The charge densities for Sample-A and -B are not so different, but the density is extremely high for Sample-C which is prepared by incorporating a small amount of ionic comonomer (sodium *p*-vinylphenylsulfonate) into the polystyrene chains.[9)]

All samples were dialysed fully against pure water, and deionized by the ion-exchange resins to remove the ionic impurities, and then they were condensed by ultrafiltration using a Visking tube up to 30% of solid contents by the volume

Table 1. Preparation and characterization of polystyrene latices

Sample	Polymerization conditions			Characterization		
	Styrene (g dm^{-3})	Svps[a)] (g dm^{-3})	$K_2S_2O_8$ (g dm^{-3})	Diameter $2a$ Å	Surface charge σ_0 μC cm^{-2}	ζ-Potential mV (25 °C, 10^{-3} mol KCl)
A	1.5×10^2	—	0.5	1960	0.9	−42
B	1.3×10^2	—	0.8	5720	0.7	−33
C	1.0×10^2	0.5	0.5	1650	7.0	−60

a) Sodium *p*-vinylphenylsulfonate.

[†] 1 erg = 10^{-7} J.

fraction.

Electrophoresis. The electrophoretic measurements of the latex samples were performed in a Rank Brothers micro-electrophoresis apparatus, using a rectangular cell. A complete parabolic curve for the velocity as a function of cell depths was measured on each sample and electrophoretic mobility(particle velocity at the level of zero liquid flow) was given at the reproducibility in samll percentages. The mobility of the particle was measured in various concentrations of KCl and $MgCl_2$. Also, the measurements were conducted under the different medium temperatures. Zeta-potential for the particle in each condition was calculated from the electrophoretic mobility with an allowance of Henry correction (if possible, Wiersema correction[10] was applied). The typical results obtained at 40 °C are shown in Fig. 1, in the form of a curve of zeta-potential against the molar concentration of each electrolyte.

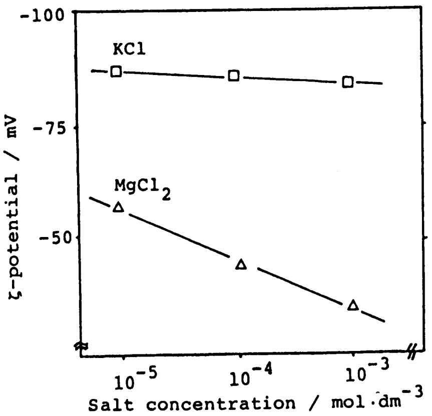

Fig. 1. Curves of zeta-potential of polystyrene latex (Sample-C) against molar concentration of salts at 40 °C.

Phase Diagrams. The conditions for the occurrence of ordered and disordered structures were measured using a slight modification of the method described by Hachisu *et al.*[5] The modification is related to the equilibration time of sample and the short equilibration took in this work brought about a reasonable removal from gravitational effect of the latex samples. The concentrated latices were diluted in Pyrex-stoppered vials of 10 cm^3 to desired solid content levels with some salt solutions of several concentrations, and left in the thermostat which was kept at various temperatures. After 3 d (Hachisu's work took the equilibration of 2 weeks), the conditions for the occurrence of ordered and disordered structures were studied making use of the irridescence exhibited by the ordered structures as an indicator.

In relation to the electrical double layer effects, phase diagrams were constructed with the volume fractions of solid content as the ordinate and log molar concentrations of electrolyte in the medium as the abscissa.

Results and Discussion

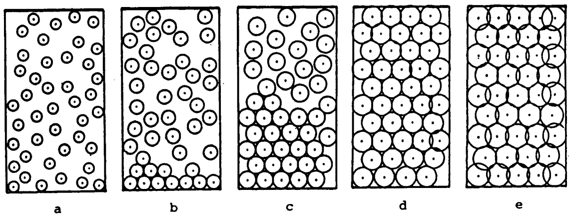

Fig. 2. Schematic representation of the phase changes in a monodisperse latex.
b: Disordered/coexistent boundary, d: coexistent/ordered boundary.

The phase changes in the monodisperse latices are depicted schematically in Fig. 2. Under a constant volume of solid, at high electrolyte concentrations, the electrical double layer around each particle is thin, the particles do not interact with each other and are distributed randomly (Fig. 2a). Decrease in electrolyte concentration leads to an increasing effective radius of the particle, and at a definite point, the interaction between the paticles becomes more favourable energetically to accommodate some of these particles in an ordered state which corresponds to the disordered/coexistent boundary state as shown in Fig. 2b. The existence of this state would be based on thermodynamic reasons where the entropy of the system is minimized by creating coexistent regions rather than going directly to an ordered state.[3] As the electrolyte concentration is further reduced, the system steadily increases the fraction of the ordered state (Fig. 2c), and finally the effective particle volumes are all in the closed-packed ordered arrangement as shown in Fig. 2d which is called a coexistent/ordered boundary state. In the present experiment, this coexistent/ordered boundary is thought as an important criterion and analysed in the terms of closed packing of effective particle volumes of the latex particles using the DLVO theory. Also, a further decrease in the electrolyte concentration leads to an overlap of the effective particle volumes (Fig. 2e), and then strong repulsive potentials will build up.

The size of the effective volumes at the coexistent/ordered phase boundary will be related to the particle separation at which some critical electrostatic repulsions are operating; the separation distances, (H), are calculated using the following relation in assuming that the particles in ordered phase are arranged in a hexagonal array.[3]

$$H = 2a[V_f(1 + \rho_p/\rho_s(1/\phi - 1))^{1/3} - 1], \tag{1}$$

where a is the radius of the particles, ρ_p and ρ_s the densities of the particles (1.05 g/ml for polystyrene) and the suspending fluid (1.00 g/ml for water), and ϕ the critical volume fraction at the coexistent/ordered phase boundary, and V_f is the packing density for a closed-packed arrangement, thus the value of 0.74 was chosen for regularly closed-packed spheres.

Furthermore, the interparticle distances at the critical boundary state can be estimated using the DLVO theory by assuming that at such a condition some definite repulsive energies which may be comparable to the thermal energies, are operating to maintain the ordered structures. As the formula to estimate the double layer potential, a following relation derived by Overbeek was employed.[6]

$$\begin{aligned} V_R &= 3.469 \times 10^{19}\varepsilon(kT)^2(a\gamma^2/z^2)\exp(-\kappa aH) \\ \kappa &= (8\pi nz^2e^2/\varepsilon kT)^{1/2} \\ \gamma &= [\exp(ze\psi_o/2kT) - 1]/[\exp(ze\psi_o/2kT) + 1] \end{aligned} \tag{2}$$

in the above equation, ε is the dielectric constant of the medium, k the Boltzmann constant, T the absolute temperature, z the valency of the counter ion, n the counter ion density, e the elementary charge and ψ_0 the surface potential of the particles. If we assume the values of critical potential to maintain the ordered structure, the interparticle distances(H) can be calculated from Eq. 2, and, by introducing the H-values into Eq. 1, we can back-calculated the weight fraction of the solid(ϕ) as a function of electrolyte concentration-(n) through Eq. 2. Hereafter, the boundary curve calculated following the above process would be called an analytical boundary curve. In Fig. 3 the analytical boundary curves with the experimental phase diagram of Sample-A, using KCl as the electrolyte, are compared. Each analytical line shows the calculated phase boundary for respective critical V_R which is illustrated on the figure. In this calculation, ζ-potential measured at the respective salt concentration was employed in place of ψ_0 in Eq. 2. As can be seen from Fig. 3, 1.5 kT ergs as a criterion of V_R yields a curve that closely fits the experimental coexistent/ordered boundary curve and the accordance attains the whole electrolyte levels examined. According to the computer analyses for the nature of the potential well in ordered state, revealed that with only 0.5 kT of interaction between the individual particles, it would require more than 8 kT to escape from the twelve nearest neighbours.[3] Under such an analysis, the value of 1.5 kT ergs estimated by the present calculation is a significant barrier as a criterion for the phase transition.

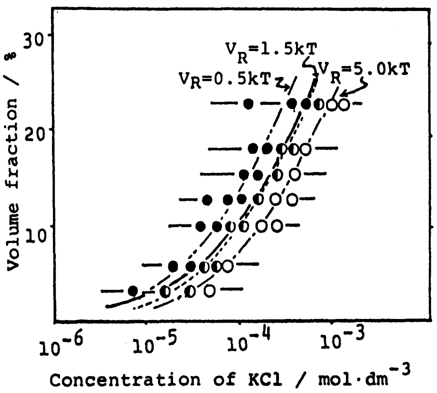

Fig. 3. Phase diagram of Sample-A ($2a$=1960 Å, σ_0=0.9 μC cm^{-2}) constructed using KCl at 25 °C.
●: Ordered state, ○: disordered state, ◐: coexistent state. Each curve shows the experimental (——) and the analytical coexistent/ordered boundary curve assuming the various critical potentials; (-·-·-): V_R=0.5 kT, (------): V_R=1.5 kT, (-··-··-): V_R=5.0 kT.

This critical value of 1.5 kT ergs is also confirmed by the direct observation study on the interparticle distances in the ordered state near the phase boundary.[11]

This analytical procedure may be used to predict the effect of the particle size, the surface potential, the valency of counter ion and the temperature of the medium on the phase boundary curves, since the interparticle potential between the particles varies also by these variables. To see the effects of the particle size, Fig. 4 shows a comparison of the experimental and an analytical boundary curve for the Sample-B ($2a$=5720 Å) using KCl. In these analyses, 1.5 kT ergs was used as a criterion of phase transition potential. Increasing the particle size, favours the disordered state as expected from the double layer theory. But the agreement between the experimental and the analytical boundary curves is very limited at the high electrolyte region and there are definite discrepancies in the low electrolyte level. These would be based on the gravitational settling of the large particles, where the particles form a sediment rather quickly to their own gravity of the large mass and the soft repulsive potential at the low electrolyte level.

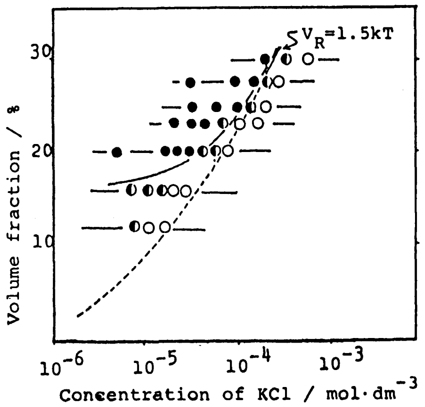

Fig. 4. Phase diagram of Sample-B($2a$=5720 Å, σ_0=0.7 μC cm^{-2}) constructed using KCl at 25 °C.
●: Ordered state, ○: disordered state, ◐: coexistent state. Each curve shows the experimental (——) and the analytical coexistent/ordered boundary curve assuming the critical potential of V_R=1.5 kT (------).

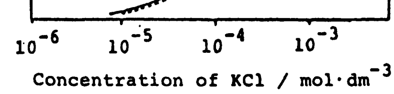

Fig. 5. Phase diagram of Sample-C ($2a$=1650 Å, σ_0=7.0 μC cm^{-2}) constructed using KCl at 25 °C.
●: Ordered state, ○: disordered state, ◐: coexistent state. Each curve shows the experimental (——) and the analytical coexistent/ordered boundary curve assuming the critical potential of V_R=1.5 kT (------).

Figure 5 represents the effect of the surface potential on the phase transition curve. The Sample-C used here has the surface charge density of 7 μC cm^{-2}. As can be seen in Fig. 5, the ordered state becomes much more favourable and the analytical boundary curve which can calculated using the value of ζ-potential for the ψ_0 in Eq. 2 and the critical V_R of 1.5 kT ergs, agreed exactly with the whole range of electrolyte concentration in the experimental. From such an accordance with the analytical curve, it is apparent that ζ-potential is a good measure for the electrostatic repulsion of colloid particle and is allowed analytically to use ζ-potential instead of the Stern layer potential.

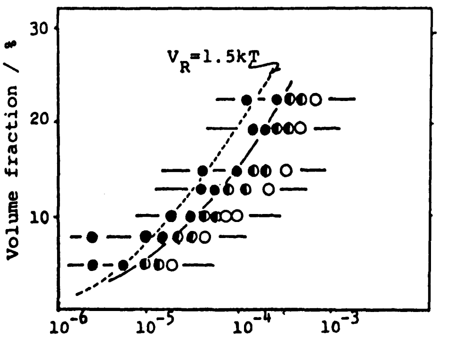

Fig. 6. Phase diagram of Sample-A ($2a$=1960 Å, σ_0= 0.9 μC cm^{-2}) constructed using $MgCl_2$ at 25 °C.
●: Ordered state, ○: disordered state, ◐: coexistent state. Each curve shows the experimental (——) and the analytical coexistent/ordered boundary curve assuming the critical potential of V_R=1.5 kT (------).

Figure 6 shows the phase diagram that was constructed using the electrolyte containing the divalent cation. In this coexistent/ordered boundary curve, there is some discrepancy on the whole electrolyte levels. It is probable that the divalent cation will be adsorbed preferentially on the latex surface as a Stern layer charge and the effective diffuse layer charge for the double layer repulsion would become much lower than the added electrolyte concentrations. According to Vanderhoff *et al.*,[12] Ba^{2+} ions adsorb extensively on the surface sulfonate groups of the latex particles and show an inflection point on the conductometric titration curve based on the strong fixation of Ba^{2+} ions. So, we can assume that the degree of deviation from the analytical curve reflects the extent of adsorbability of each counter ion in the Stern layer.

As a final parameter, the influence of temperature was studied. As can be seen in Fig. 7, over the whole electrolyte levels the ordered state becomes unfavorable at the high temperatures. It is because of this reason that the high temperature makes the double layer more diffusive. The precise analyses of temperature effects were carried out by taking into account the effects of medium dielectricity, ζ-potential and temperature itself. The results are compared to the experimental values on the two special salt concentrations. As can be seen in Fig. 8, the trends are the expected ones and qualitatively agree with the experimentals except for the results at the high temperatures of more than 40 °C, where the structural effects on desorption of the Stern layer ions exist, the desorbed ions would make unfavourable the ordered state and increase the volume fraction of the boundary.

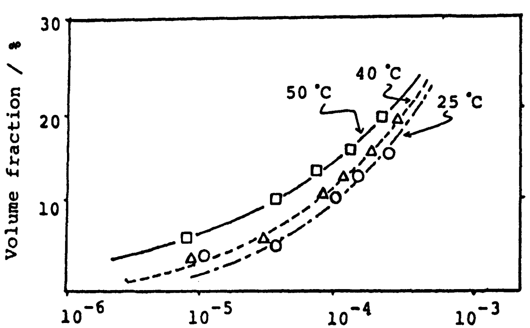

Fig. 7. Temperature dependence of the ordered/coexistent boundary curves of Sample-A constructed using KCl.
—○—: 25 °C, —△—: 40 °C, —□—: 50 °C.

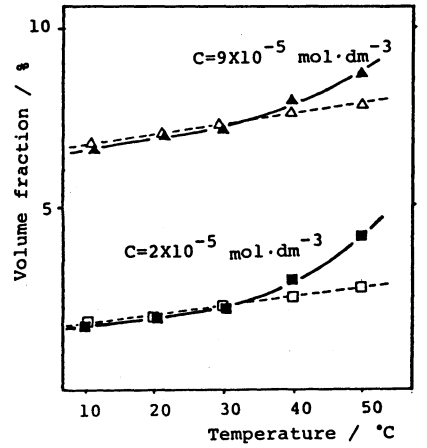

Fig. 8. Comparison of the temperature effect of phase boundary with the analytical one on the two KCl concentrations.
——: Experimental, ------: analytical.

At any rate, it can be concluded from the present work that the disordered/ordered phase transition in the concentrated latices is controlled largely by the electrostatic repulsion between the particles and the critical boundary condition of the coexistent/ordered state is reasonably explained by the DLVO electrostatic potential. Also, it is realized that the phase boundary analyses provides useful information on the nature of the electrical double layer and contributes as a new technique in the study of the electrical double layer.

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