

“Ordered” Structure in Dilute Suspensions of Highly Charged Polymer Latices as Studied by Microscopy. 2. The Influence of Ionic Strength, Dielectric Constant, Temperature, and Viscosity[†]

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Abstract: Dilute suspensions of highly charged polymer latex particles were studied by ultramicroscopy. The center-to-center interparticle distance ($2D_{\text{exp}}$) was directly measured for the particles in ordered regions. $2D_{\text{exp}}$ decreased with increasing concentration of coexisting salt, and further increase in the ionic strength naturally destroyed the ordered structure. The $2D_{\text{exp}}$ value decreased with decreasing dielectric constant of binary mixtures of water and various organic solvents, suggesting that the interparticle attraction proposed earlier by us became stronger. The spacing decreased though slightly with increasing temperature, which may be due to the variation in the dielectric constant of water with the temperature. The dynamic motion of free particles was studied by a video device. When the particle concentration was low and the salt concentration was high, the particles showed Brownian motion. The root-mean-square displacement was found to decrease with increasing solvent viscosity, and agreement with the Einstein-Stokes theory was satisfactory.

In previous review articles, ionic solute particles have been suggested to commonly form ordered arrangement in dilute solutions, irrespective of the molecular mass and geometry.¹⁻³ For the study of solution structure, polymer latex particles are the most reliable and convenient systems, because they are large enough to be seen by the naked eyes with an ordinary (not electron) microscope. In Part 1 of this series,⁴ we took advantage of this point and studied the interparticle distance in the ordered structure as a function of concentration and found that the observed distance $2D_{\text{exp}}$ was much smaller beyond the experimental uncertainty than the theoretical distance calculated from the concentration of particles by assuming a uniform distribution throughout the suspension ($2D_0$). Most recently, Yoshiyama et al. performed the Kossel line analysis on polymer latex suspensions and found that the interparticle distance was also smaller than what can be expected from a uniform distribution.⁵ This experiment substantiates positively the conclusion obtained from the microscopic study.

The difference between $2D_{\text{exp}}$ and $2D_0$, which was determined by the microscopy and the Kossel line analysis, was particularly clear at concentrations below 1% and for highly charged latices.⁶ This fact strongly indicates that there exists an interparticle attraction. In other words, there coexist ordered regions, in which the particles are distributed more or less regularly, and disordered regions, in which the particles show random motions. We have called this situation the two-state structure. Recently successful photography⁷ of the two-state structure has provided visible evidence of the presence of the attraction.⁸

A similar conclusion was reached from the small-angle X-ray scattering on macroion solutions.¹⁰ On the basis of the influence of the addition of salt, we strongly believe that the attraction is of an electrostatic nature, as was first suggested by us some time ago.^{11,12} This was recently theoretically proven to be the case by Sogami.^{13,14} In the present paper, we wish to make the situation clearer by studying the latex suspension microscopically with various ionic strengths, dielectric constants, densities, and viscosities of the solvent. As before, our attention has been focused on highly charged latex particles and dilute suspensions.

Experimental Section

Materials. The latex particle (SS-37) used was a copolymer of styrene and styrene sulfonate and was prepared by an emulsion polymerization

Table I. Properties of Polymer Latices Used

	diameter, (Å)	no. of SO ₃ H groups in a particle	charge density (μC/cm ²)
G5301 ^a	3690 ± 100	1.9 × 10 ⁵	7.2
SS-37	4540 ± 100	1.7 × 10 ⁵	4.4

^a In the previous paper from us,⁴ the number of SO₃H for this latex was reported as 2.7 × 10⁵. Subsequent detailed conductometric and potentiometric titrations indicated the presence of weak dissociable ionic groups (presumably COOH), in addition to the SO₃H groups. The newly given figure refers to the value obtained after the COOH correction. In the work at high pH the difference between these two values is not important but the new value should be used at the low pH employed in the present work.

technique with potassium persulfate as an initiator. G5301 was a product of Japan Synthetic Rubber Co. (Tokyo). Copolymerization was carried

- (1) Ise, N.; Okubo, T. *Acc. Chem. Res.* **1980**, *13*, 303.
- (2) Ise, N., presented at the first FRG-Japan Joint Seminar on Polymers, Kyoto, Japan, Aug 1984. Ise, N. *Macromol. Chem. Suppl.*, **1985**, *12*, 215.
- (3) Ise, N. *Angew. Chem.*, in press.
- (4) Ise, N.; Okubo, T.; Sugimura, M.; Ito, K.; Nolte, H. J. *J. Chem. Phys.* **1983**, *78*, 536.
- (5) Yoshiyama, T.; Sogami, I.; Ise, N. *Phys. Rev. Lett.* **1984**, *53*, 2153.
- (6) This difference becomes negligible at high concentrations such as above 10%. The particle spacing is then determined simply by the exclusion volume effect (repulsive interaction) of the particle. Thus it would be difficult to obtain useful information on the true nature of the interparticle interaction (in other words, the contribution of attractive interaction) from investigations of such concentrated suspensions. The information from these concentrated systems inevitably shows the exclusive role of repulsive interaction, and led so many authors to the conclusion that the properties of the systems can be successfully described only by repulsive interactions. This conclusion, however, is basically wrong. As we have emphasized repeatedly, condensed systems cannot exist without net attractive interactions.
- (7) Ise, N.; Okubo, T.; Ito, K.; Dosho, S.; Sogami, I. *Langmuir* **1985**, *1*, 176.
- (8) The often expressed view that the inequality relation $2D_{\text{exp}} < 2D_0$ is due to the sedimentation effect of the particles in suspensions is also rejected by this observation, because the ordered region and the disordered region were found in a *horizontal* (not perpendicular) plane. Since the particle density of the polystyrene sphere is about 1.05, the influence on the value of $2D_{\text{exp}}$ is unavoidable but not so large as to invalidate our conclusion. The fact that the sedimentation effect is *qualitatively* unimportant in our argument, particularly in the inequality relation, is also supported by the Kossel line analysis, which was carried out for the middle part of the suspension and still proved the inequality relation as observed by the microscopy for the bottom part of the suspension. It should also be noted that the inequality relation was concluded by the laser light scattering from suspensions of highly charged polymer latex by Kato et al. (ref 9). Since the light scattering was performed from the middle portion of the suspension, it can be claimed that the inequality relation is not due to the sedimentation effect as far as the qualitative aspect is concerned.

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out without an emulsifier. The electron micrography provided information on the diameter and the monodispersity. These latices were carefully and thoroughly, though probably not completely, purified with cation- and anion-exchange resins (Amberlite IR-120B and IRA-400) and washed with pure water obtained through a Milli-Q Reagent-Grade Water system by repeated ultrafiltration with the use of an Amicon Model 202 and Diaflo XM300. Completeness of the wash was checked by the disappearance of the UV absorptions at 220–420 nm from the filtrate. The particle charge density was determined by conductometric titrations with a Wayne–Kerr autobalance precision bridge, Model B331, in combination with the potentiometric titration. Table I gives the properties of the latices used.

The ion-exchange resins were purified as described before.⁴ Organic solvents used were methanol, ethylene glycol, dimethylformamide, and dimethyl sulfoxide to change the dielectric constant. They were all of reagent grade. Sucrose was also reagent-grade material and used without further purification.

Microscopic Observations. Two reversed-type metallurgical microscopes were used: model MG of Olympus Co., Tokyo, and Carl-Zeiss Axiomat IAC. The solution cell used was the same as that described previously.⁴ The particles in suspension were illuminated from the bottom of the cell through the object glass, as was fully described by Hachisu et al.¹⁵ The suspension temperature was controlled by circulating thermostated water through a specially designed jacket around the cell. Ion-exchange resin was put into the latex suspension in order to remove ionic impurities from the glass wall, as described before,⁴ except in the experiments in the presence of foreign salt.

The interparticle distance $2D_{\text{exp}}$ was determined from pictures taken on 35-mm film. In the cases of the binary solvent systems, the distance was measured every 24 h after the latex suspension was brought into the cell. It was checked that the spacing did not change after 24 h. Thus the $2D_{\text{exp}}$ values for the binary solvent systems given in the present paper are those obtained after the 24-h setting. In the case of simple salt-containing systems the distance was measured intermittently after the suspension was set in the cell, until the value became constant. The $2D_{\text{exp}}$ values given here for the salt-containing suspensions are those observed after 1 week. Hexagonal arrangements of the particles were observed, except at high temperature at which square, in addition to hexagonal, arrangements existed. The $2D_{\text{exp}}$ value was determined from the hexagonal arrangement.¹⁶ It should be mentioned that the microscopic observation was, or had to be, done in the suspension layer within 10 μm from the cell bottom, partly because of the turbidity of the latex suspension. Since one might assume that the surface effect of the object glass at the bottom of the cell has an influence on the measurements under these circumstances, let us describe the details of the experimental procedure we used. By adjusting the focus position, we could determine how far from the surface of the object glass we were. Second, it was not at all difficult to distinguish the particles in direct contact with the surface of the object glass from those moving or sitting inside suspension, because the former did not show any movement at all whereas the latter showed random motion or substantial oscillatory motion. Even the free particles in the first or second layer from the surface of the object glass (about 10^4 Å apart from the glass surface) showed random motion as described by the Einstein theory on the Brownian motion.¹⁷ This suggests that the surface effect did not reach the first or second layer. Furthermore, the $2D_{\text{exp}}$ value observed did not change with the distance of the particle under consideration from the object glass. Exactly speaking, the variation of $2D_{\text{exp}}$ with the distance from the glass could not be observed. Nonetheless, $2D_{\text{exp}}$ was determined for the particles as far apart as possible from the bottom of the cell.

The root-mean-square displacement of free particles was measured by following the particle center as a function of time by using the following video-digitizer system: the micrograph was recorded on a video-tape-

(9) Kato, T.; Masuda, H.; Takahashi, A. *Polymer Prepr. Jpn.* **1982**, *31*, 2249.

(10) For example: Ise, N.; Okubo, T.; Kunugi, S.; Mastuoka, H.; Yamamoto, K.; Ishii, Y. *J. Chem. Phys.* **1984**, *81*, 3294.

(11) Ise, N.; Okubo, T. *J. Phys. Chem.* **1966**, *70*, 1930.

(12) Ise, N.; Okubo, T. *J. Phys. Chem.* **1966**, *70*, 2407.

(13) Sogami, I. *Phys. Lett. A* **1983**, *496*, 199.

(14) Sogami, I.; Ise, N. *J. Chem. Phys.* **1984**, *81*, 6320.

(15) Kose, A.; Ozaki, M.; Takano, K.; Kobayashi, Y.; Hachisu, S. *J. Colloid Interface Sci.* **1973**, *44*, 330.

(16) At high particle concentrations, Hachisu et al. (ref 15) published a picture showing the coexistence of hexagonal and square arrangements. They claimed that these two correspond to the 111 and 100 planes of a face-centered cubic lattice, respectively. The analysis of $2D_{\text{exp}}$ in the text naturally relies on the invariance of the lattice structure (with changes of experimental variables such as ionic strength) in the region, where the microscopic observation is done.

(17) Einstein, A. *Ann. Phys. (Leipzig)* **1905**, *17*, 549.

Table II. Interparticle Distance at Various Concentrations of Coexisting Salt^b

[NaCl], M	$2D_{\text{exp}}$, ^a Å
0	12700
1.71×10^{-6}	12600
1.71×10^{-5}	11300
6.84×10^{-5}	8000
1.37×10^{-4}	no ordering

^aThe error limit of $2D_{\text{exp}}$ is generally ± 1000 Å, but the standard deviation of the data given in this table was obtained to be $\pm 100 \sim \pm 300$ Å. In this respect, it is to be reminded that we are using essentially an ultramicroscope, whose resolving power is much higher than that of the ordinary optical microscope. ^bLatex: SS-37. Latex concentration: 2.01%, room temperature.

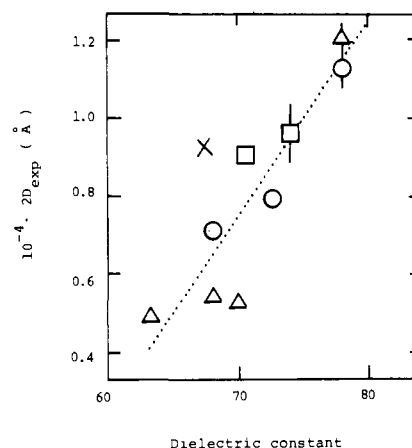


Figure 1. Interparticle distance observed in the ordered structure of a latex suspension in the binary mixtures of ethylene glycol (O), methanol (X), dimethylformamide (Δ), and dimethyl sulfoxide (□), latex: G5301, [latex]: 1.3 vol %, room temperature. The dotted line represents the optimal relation between $2D_{\text{exp}}$ and dielectric constant, which will be used in Figure 2.

recorder (Sony, VO-5850, VO-5800) with the aid of a video camera (HAMAMATSU C1965). Each frame was regenerated, and the position of the particle was input into a computer by a light-pen (FORA FVW-300). The position of a specific particle was read out as a function of time by repeating the same procedure. From each frame the coordinates of 20 particles were read out. The root-mean-square displacement was obtained with the aid of a microcomputer (NEC PC9801E).

Because of technical difficulties, a large number of particles could not be treated. In the present work, 20 particles were studied. Accordingly, we must admit that the accuracy of the experimental data to be reported here is not very high, although improvement since our previous work⁷ has raised accuracy. We have carried out the data analysis in the present paper with this point kept in mind.

Results

A. Interparticle Distance in the Ordered Region. (i) Salt Concentration Dependence. Table II gives the values of $2D_{\text{exp}}$ for SS-37 in the presence and absence of sodium chloride. Before going into detail, it must be remembered that the presence of large amounts of simple salts destroys the ordering. Thus the interparticle distance in the ordered structure could be observed only in the limited range of simple salt concentrations. In other words, we could determine the $2D_{\text{exp}}$ for SS-37 (at a latex concentration of 2.01 vol %) only up to 6.84×10^{-5} M, as shown in Table II. The precise control of the concentrations of simple salt at such low levels is not so easy, although not at all impossible. Nevertheless, $2D_{\text{exp}}$ appears to decrease with increasing salt concentration. A similar trend was also confirmed for other latices such as G5301.

(ii) Dielectric Constant Dependence. By using binary mixtures of organic solvent and water, the dielectric constant of the solvent was varied. Figure 1 shows the $2D_{\text{exp}}$ values determined at various dielectric constants. The interparticle distance seems to decrease with decreasing dielectric constant, although the experimental points scatter fairly widely. We thought that the difference in

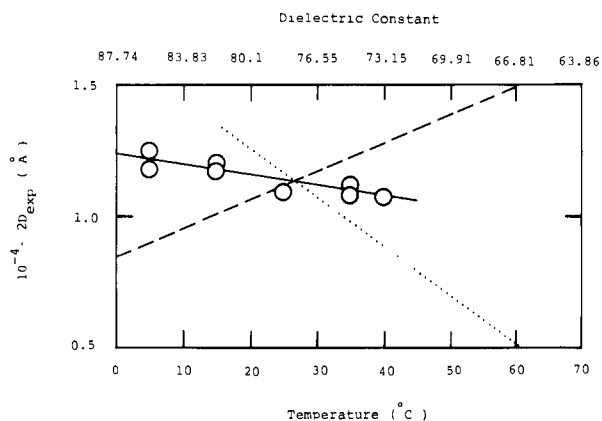


Figure 2. Temperature dependence of the interparticle distance observed for G5301. [latex]: 2.0 vol %, solvent:water. The dotted line corresponds to that in Figure 1, and the dashed line gives the $2D_{\text{exp}}$ values obtained after the temperature correction of the dielectric constant.

Table III. Root-Mean-Square Displacement of Free Latex Particle at Various Concentrations of Latex and Salt at 25 °C^a

[latex], %	[NaCl], M	$10^{-4}(\bar{x}^2)^{1/2}$, ^b Å
1.0	10^{-2}	1.2 ± 0.7
	10^{-3}	0.6 ± 0.5
	10^{-4}	0.6 ± 0.5
	10^{-5}	0.6 ± 0.5
0.1	10^{-2}	1.1 ± 0.7
	10^{-3}	1.0 ± 0.6
	10^{-4}	1.0 ± 0.7
	10^{-5}	1.4 ± 0.6
0.01	10^{-2}	1.4 ± 0.9
	10^{-3}	1.1 ± 0.8
	10^{-4}	1.3 ± 0.6

^a Latex: SS-37. ^b The theoretical value for $(\bar{x}^2)^{1/2}$ by the Einstein-Stokes theory: 1.47×10^4 Å.

the density of the mixed solvent was a possible cause for this scattering, but no correlation between the $2D_{\text{exp}}$ value and the density could be found.

(iii) Temperature Dependence. Figure 2 shows the temperature dependence of $2D_{\text{exp}}$ for G5301. The spacing apparently decreases with increasing temperature, though slightly. This tendency was reversible; both rising and lowering temperature gave the same results. It should be emphasized that the dielectric constant of water changes with the temperature from 83.8 at 10 °C to 73.15 at 40 °C.¹⁸ The observed $2D_{\text{exp}}$ value was corrected by using the optimal linear relation on the dielectric constant dependence of the interparticle spacing shown by the dotted line in Figure 1, and the results are shown by the dashed line in Figure 2.

B. Root-Mean-Square Displacement of the Particles in Disordered Region. (i) **Salt Concentration Dependence.** Table III shows the root-mean-square displacement $((\bar{x}^2)^{1/2})$ of the particles under experimental conditions, where no ordering could be found under the microscope, i.e., where the particle concentration was low enough or the salt concentration was high enough. Although the experimental uncertainty was large, the general trend was that the $((\bar{x}^2)^{1/2})$ value was close to that predicted by the Einstein-Stokes theory of Brownian motion¹⁷ except at high latex concentrations and low salt concentrations. A definite conclusion cannot be drawn until a much larger number of particles are treated, but the observed tendency appears to be reasonable. For example, the presence of a large amount of salt causes a shielding effect so that each particle behaves independently of each other, as the theory assumes. Similarly at a low latex concentration the particles would be able to move more freely than at higher concentrations.

(ii) Influence of Temperature. Figure 3 shows the influence of temperature on the root-mean-square displacement of free

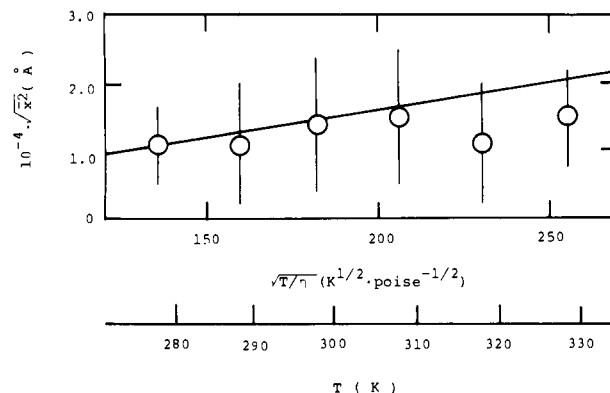


Figure 3. Influence of temperature on the root-mean-square displacement of free latex particles. Latex: SS-37, [latex]: 0.01%, [NaCl]: 1.0×10^{-5} M.

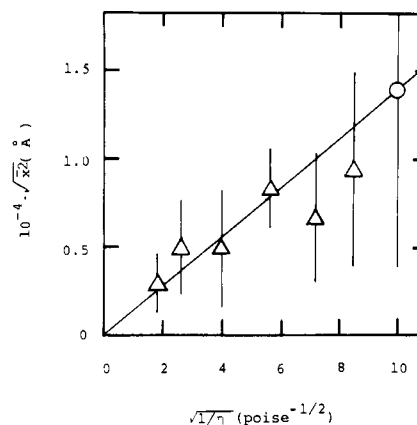


Figure 4. Viscosity dependence of the root-mean-square displacement of free latex particles in aqueous sucrose solutions: latex: SS-37, [latex]: 0.01 vol %, [NaCl]: 1.0×10^{-5} M, room temperature. The circle denotes the root-mean-square displacement in water without sucrose.

particles. Since the viscosity of water is sensitive to temperature, the ratio of the two quantities was given on the abscissa. Here again the experimental uncertainty (given by the vertical bar) is large, but the experimental data are seen to be in good agreement with the Einstein-Stokes theory (denoted by the straight line).

(iii) Viscosity Dependence. The root-mean-square displacement of free particles was measured in an aqueous sucrose solution, and the results are shown in Figure 4. The sucrose concentrations were between 10 and 60 wt %.

Discussion

(i) Interparticle Distance. The observed dependence of $2D_{\text{exp}}$ on the salt concentration is apparently consistent with the DLVO theory on colloid stability.¹⁹ Obviously the theory tells us that the position of the secondary minimum shifts toward smaller distances with increasing ionic strength when the Hamaker constant is assumed to be constant. Thus as far as the observed variation of the $2D_{\text{exp}}$ itself is concerned, the theory seems to be satisfactory. However, the theory shows that the secondary minimum deepens with increasing ionic strength, again when the Hamaker constant is kept constant. The observed fact is that the ordering can be destroyed when an excess amount of salt is added. This means that the potential minimum must eventually become shallower with increasing ionic strength. This feature cannot be accounted for in terms of the DLVO theory.²⁰

(19) Verwey, E. J. W.; Overbeek, J. Th. G. "Theory of the Stability of Lyophobic Colloids", Elsevier, Amsterdam, 1948.

(20) In the framework of the DLVO theory, it would be possible to account for this change of the potential depth by adjusting the Hamaker constant, which we find unsatisfactory from the point of view of the self-consistency of the theory.

(18) Malmberg, G. G.; Maryott, A. A. *J. Res. Natl. Bur. Stand. (u.s.)* 1956, 56, 1.

It should be noted that the observed ionic strength dependence is explainable by Sogami's theory.^{13,14} Although the readers are referred to ref 14 for further details, Figure 3 of this reference clearly shows, first, that the position of the minimum shifts toward smaller distances with increasing ionic strength, and, second, that the potential valley becomes deeper and then shallower after the minimum.²¹ This situation can be easily accepted if we admit that the electrostatic attraction is created by the counterions present in between the particles. With increasing number of counterions, the attraction must become stronger. When the ionic strength is increased by addition of foreign salt, the number of counterions can be increased but the number of coions also increases. Obviously the counterions intensify the attraction whereas the coions display a counterinfluence. Because of the repulsive interaction between the particle and the coions, the increase of the coions in the vicinity of the particles with increasing ionic strength must take place at a higher ionic strength than that of the counterions. Thus the intensification of the attraction comes first, and the shielding effect of the coions becomes substantial at a higher ionic strength. The decrease of the $2D_{\text{exp}}$ with decreasing dielectric constant might indicate that the attraction mentioned above was made stronger. Although this seems to be plausible, we have to take into account the variation of the effective valency with the dielectric constant. In other words, the dissociation states of the ionizable groups must change with dielectric constant. Since no further information is available, we cannot draw the final conclusion now.

The observed temperature dependence of the interparticle distance is surprising, because the thermal expansion of the ordered structure at a higher temperature is expected to cause larger interparticle spacing. This expectation may be correct, if the changing dielectric constant is actually corrected for temperature as shown by the dashed curve in Figure 2. In other words, the ordered structure expands with rising temperature if the dielectric constant is kept constant and the key factor of the apparent decreasing tendency of the spacing is the temperature variation of the dielectric constant.²²

It seems interesting to compare the information obtained here for polymer latex systems with that obtained for linear macroions. The latter was also found to form an ordering in dilute solutions by the small-angle X-ray scattering. The Bragg spacing for macroions such as polyacrylate,²³ poly-L-lysine,²⁴ and polystyrene sulfonate¹⁰ was found to increase with increasing concentration of added salt, whereas $2D_{\text{exp}}$ for latex decreased. The reverse tendency observed for the latex systems and for the macroions would be due to the fact that the macroions have molecular conformation more sensitive to the salt concentration than the latex sphere.²⁵ Actually the hydrodynamic radius determined by the dynamic light scattering of the latex particles shows a very small variation with the salt concentration.²⁶ Although no ex-

perimental evidence on the conformation of macroions at the concentrations employed in the X-ray scattering is available, only a minor objection to the sensitivity of the conformation of macroions toward salt concentration appears to exist.²⁷ We also note that the observed temperature dependence of $2D_{\text{exp}}$ for polystyrene sulfonate¹⁰ and bovine serum albumin²⁸ is the same as that observed for lattices in the present paper, indicating the overwhelming influence of the temperature variation of the dielectric constant of the solvent, namely water.

(ii) **Displacement of Free Particles.** The experimental data obtained indicate that the random motion of the latex particles can roughly be described by Einstein-Stokes theory of the Brownian motion, in agreement with the conclusion earlier reached by Ottewill et al.²⁹ However, the deviation from the theory is obvious for lattices of high charge densities when the latex concentration was raised or when the salt concentration was lowered, which is due to enhanced interparticle interaction. The agreement with the theory might be rationalized by recent transference experiments by us,³⁰ which showed that an unexpectedly large portion of counterions were associated with the particle. For example, in the case of the particles similar to SS-37, the fraction of free counterions (protons) was only about 0.1 at concentrations of $1.5 \sim 7.5\%$ ($1.6 \times 10^{-4} \sim 9.3 \times 10^{-4}$ equiv L⁻¹). In other words, 90% of the sulfonate groups are neutralized. Thus, the particles are much less charged than expected from the analytical valency shown in Table I. It would not be unreasonable under such a circumstance that the free latex particles demonstrate approximately random motion as predicted by the Einstein-Stokes theory, which was constructed for noninteracting particles.

Conclusion

The interparticle distance ($2D_{\text{exp}}$) of the latex particles in ordered structure and the motion of free particles were studied by ultramicroscopy. The $2D_{\text{exp}}$ value decreased with increasing salt concentration, up to 6.84×10^{-5} M for a latex, SS-37, at a concentration of 2%. When the salt concentration was further increased, the ordered structure was destroyed. The value of $2D_{\text{exp}}$ decreased with decreasing dielectric constant in binary mixtures of organic solvent and water, which implies intensification of electrostatic attraction between the latex particles. With increasing temperature, $2D_{\text{exp}}$ decreased though slightly, which was suggested to be due to the temperature dependence of the dielectric constant of water. It was pointed out that the overall salt concentration dependence of $2D_{\text{exp}}$ was in agreement with Sogami's theory.^{13,14} The root-mean-square displacement of the free particles could be described by the Einstein-Stokes theory on Brownian motion, when the particle concentration was low and the salt concentration was high. Furthermore, the root-mean-square displacement was found to be practically independent of temperature. When the viscosity of the solvent was adjusted by adding sucrose to water, the root-mean-square displacement was also in agreement with the Einstein-Stokes theory.

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(26) In ref 9, it was shown for a highly charged latex particle that the radius of gyration from the laser light scattering decreased from 913 Å in water to 680 Å in a NaCl solution at 3 M. The hydrodynamic radius determined by dynamic light scattering decreased from 836 Å in water to 550 Å in the NaCl solution. However, below 0.01 M of NaCl, both these radii were practically ionic strength independent.

(27) In some theoretical treatments, linear macroions were often assumed to be stretched out like a rod. This model might be correct at the limit of infinite dilution or at very low concentrations. However, this model does not seem to hold at much higher concentrations in which we are interested at the present. (For detailed discussion, see ref 3 and 10.) Instead we believe that the coiled model is valid. Then it would be feasible that macroions are strongly subject to salt addition.

(28) Matsuoka, H.; Ise, N.; Okubo, T.; Kunugi, S.; Tomiyama, H.; Yoshikawa, Y. *J. Chem. Phys.* **1985**, *83*, 378.

(29) Cornell, R. M.; Goodwin, J. W.; Ottewill, R. H. *J. Colloid Interface Sci.* **1979**, *71*, 254.

(30) Ito, K.; Ise, N.; Okubo, T. *J. Chem. Phys.* **1985**, *82*, 5732.

(21) In Sogami's theory, the potential minimum was produced by a balance of electrostatic repulsion and likewise electrostatic (not van der Waals type) attraction between charged species. The distinct difference between the DLVO theory and Sogami's theory should not be overlooked.

(22) In order to check Sogami's theory with experimental data in a quantitative way it is necessary to have information of the net valency of the latex particle at various salt concentration, dielectric constant, and temperature, which is not available at the present. Thus we describe only qualitative comparison with the theory in the present article. Although a systematic comparison between the theory and experiments is in progress, we are obtaining gratifying results. For example, the observed values of the spacing with changing temperature given in Figure 2 ($1.1 \times 10^4 \sim 1.3 \times 10^4$ Å) can satisfactorily be reproduced by the theory with reduced values for the valency.

(23) Ise, N.; Okubo, T.; Yamamoto, K.; Matsuoka, H.; Kawai, H.; Hashimoto, T.; Fujimura, M.; Hiragi, H. *J. Am. Chem. Soc.* **1980**, *102*, 7901.

(24) Ise, N.; Okubo, T.; Yamamoto, K.; Matsuoka, H.; Kawai, H.; Hashimoto, T.; Fujimura, M. *J. Chem. Phys.* **1983**, *78*, 541.

(25) In this respect, an amendment must be made to our previous statement. In the earlier papers on linear macroions (ref 10, 23, and 24), we stated that the observed increasing tendency of the Bragg spacing ($2D_{\text{exp}}$) with increasing concentration of added salt indicated the presence of an attractive interaction between the macroions. Although the conclusion, that the attraction exists, is correct, since $2D_{\text{exp}}$ was found to be smaller than $2D_0$, the previous reasoning was not complete.