Activity and Activity Coefficients of Ionic Latex Particles in Solutions

M. Sugimura,[†] T. Okubo,[†] N. Ise,*[†] and S. Yokoyama[‡]

Contribution from the Department of Polymer Chemistry, Kyoto University, Kyoto, Japan, and Ashigara Laboratories, Fuji Photo Film Company, Minamiashigara, Kanagawa, Japan. Received January 4, 1984

Abstract: The mean activity coefficients (γ) of highly charged polymer latex particles, which are known to form ordered structures in solution, were measured by the isopiestic method. The value of $\ln \gamma$ decreased linearly with the cube-root of the concentration in the range covered, in accordance with the results obtained earlier for soluble polyelectrolytes. Thus, the argument on the relationship between the cube-root dependence of the mean activity coefficient and the presence of ordering, or lattice-like ionic distribution, was substantiated. By using the basic thermodynamic relation, the single-ion activities and activity coefficients of the latex ions and of the counterions (protons) were estimated. The single-ion activity of the latex ions (a_{2p}) decreased sharply with increasing latex concentration, as was earlier observed for soluble macroions, whereas that of the protons (a_{2g}) increased. The remarkable decrease of a_{2p} indicates the presence of an attractive interaction between the latex ions through the intermediary of the counterions. This is consistent with the independently observed fact that the interparticle distance ($2D_{exptl}$) is smaller than the theoretical average distance ($2D_0$).

In earlier publications,[1] it was pointed out that the *mean* activity coefficient of hydrophilic polyelectrolytes[2] decreased linearly with the increases in the cube root of the concentration in dilute regions. It was immediately noticed that the concentration range, where the cube-root dependence was found to hold, was much wider for polyelectrolytes than for simple electrolytes.[4] The mean activity coefficient is a measure of the non-ideality, which is caused mainly by Coulombic interaction in the case of ionic solutions. The Coulombic potential is inversely proportional to the interionic distance, which is again inversely proportional to the cube root of the electrolyte concentration, provided that ionic species are distributed in a lattice-like structure. This argument[5] was obviously highly qualitative, but we thought the ordering of macroions plausible. At that time, the experimental fact, which appeared to support this kind of ordering, had been only the very low intensity of light scattered from salt-free polyelectrolyte solutions,[6-8] which was claimed to be due to destructive interference by ordering of macroions. Recently, the situation on the ordering of macroions has been made clear, thanks to the small-angle X-ray scattering.[9-14] However, the analysis is still indirect in the sense that we need to assume the validity of the Bragg equation. In this respect, polymer latex particles provide a most direct method for investigations of the distribution of electrically charged entities in solutions; they are large enough to be seen under a microscope. Hachisu et al.[18] used a metallurgical microscope as an ultramicroscope and for the first time photographed the ordering of the latex particles in low-salt solutions. Thus, the existence of the ordered structure has already been confirmed by the naked eye.

It would be interesting to study whether the cube-root rule is obeyed for the activity coefficient of these polymer latex particles. In the present article, we measured the mean activity or activity coefficient of electrically charged polymer latex particles by isopiestic measurement and discussed the single-ion activities of the counterions and latex ions. It is reminded that the activity is one of the most basic thermodynamic quantities, by which the pros and cons of any interpretation and theoretical inference can and must be finally judged, but unfortunately it is very often overlooked in the work on polyelectrolytes and colloidal particles. Actually, this is the first report on the activity or activity coefficient of polymer latex particles.

Experimental Section

Highly charged latices were synthesized by the method described in the patent literature.[19] Styrene was emulsion copolymerized in the presence of divinylbenzene as a cross-linking agent and of potassium persulfate as the initiator. The polystyrene latex particles obtained were

Table I. Characteristics of Latices Used

latex	diameter, Å	charge no. per particle	charge density, μC/cm^3
no. 3	620	3.5×10^5	4.5×10^8
no. 4	600	2.8×10^5	4.0×10^8
no. 5	550	1.5×10^5	2.8×10^8
no. 6	620	1.4×10^5	1.8×10^8

sulfonated by sulfur trioxide. Elemental analysis showed that 29–73% of the total styrene units were sulfonated. The purification of the latices

(1) (a) Ise, N.; Okubo, T. *J. Phys. Chem.* **1966**, *70*, 1930–1935. (b) Ise, N. *Adv. Polym. Sci.* **1971**, *7*, 536–593.

(2) Hydrophobic polyelectrolytes (DNA and polyglutamate)[3a] were found not to display the cube-root dependence in a wide range of concentration. This tendency was also reported later by Dolar.[3b]

(3) (a) Ise, N.; Okubo, T. *Macromolecules* **1969**, *2*, 401–407, 407–411. (b) Dolar, D. "Polyelectrolytes"; Selegny, E., Ed.; Reidel: Dordrecht, 1974; pp 97–113.

(4) (a) Frank, H. S.; Thompson, P. T. *J. Chem. Phys.* **1959**, *31*, 1086–1095. (b) Desnoyers, J. E.; Conway, B. E. *J. Phys. Chem.* **1964**, *68*, 2305–2311.

(5) See, for example: Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions"; Butterworths: London, 1959; Chapter 9.

(6) Guinand, S.; Boyer-Kawenoki, P.; Dobry, A.; Tonnelat, J. *C. R. Hebd. Seances Acad. Sci.* **1949**, *229*, 143–145.

(7) Doty, P.; Steiner, R. F. *J. Chem. Phys.* **1949**, *17*, 743–744.

(8) Fuoss, R. M.; Edelson, D. *J. Poly. Sci.* **1951**, *6*, 767–774.

(9) Plestil, J.; Mikes, J.; Dusek, K. *Acta Polym.* **1979**, *30*, 29–32.

(10) Ise, N.; Okubo, T.; Hiragi, H.; Kawai, H.; Hashimoto, T.; Fujimura, M.; Nakajima, A.; Hayashi, H. *J. Am. Chem. Soc.* **1979**, *101*, 5836–5837.

(11) Ise, N.; Okubo, T.; Yamamoto, K.; Kawai, H.; Hashimoto, T.; Fujimura, M.; Hiragi, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7901–7906.

(12) Ise, N.; Okubo, T.; Yamamoto, K.; Matsuoka, H.; Kawai, H.; Hashimoto, T.; Fujimura, M. *J. Chem. Phys.* **1983**, *78*, 541–545.

(13) Ise, N.; Okubo, T.; Kunugi, S.; Matsuoka, H.; Yamamoto, K.; Ishii, Y. *J. Chem. Phys.*, in press.

(14) The small-angle X-ray scattering (SAXS) gives a single, broad peak for macroions at low-salt conditions. We believe that the ordering of macroions is real, though detailed discussion is found elsewhere.[15,16] A similar peak was observed by the small-angle neutron scattering (SANS),[17] and the agreement in the Bragg spacing obtained by the two scattering methods is gratifying, as pointed out by us.[13] Although we think that the SANS data also reflect the existence of the ordered structure, they have been interpreted in terms of the so-called isotropic model. If this model is generally valid, the scattering behavior should be independent of molecular weight. However, our SAXS measurements clearly show that this is not the case.

(15) For a review, see: Ise, N.; Okubo, T. *Acc. Chem. Res.* **1980**, *13*, 303–309.

(16) Ise, N. *Colloid Surf. Sci. Symp.* **1983**, No. 57.

(17) For example: Nierlich, M.; Williams, C. E.; Boné, F.; Cotton, J. P.; Daoud, M.; Farnoux, B.; Jannink, G.; Picot, C.; Moan, M.; Wolf, C.; Rinaudo, M.; deGennes, P. G. *J. Phys. (Paris)* **1979**, *40*, 701–704.

(18) Kose, A.; Ozaki, M.; Takano, K.; Kobayashi, Y.; Hachisu, S. *J. Colloid Interface Sci.* **1973**, *44*, 330–338.

[†] Kyoto University.
[‡] Fuji Photo Film Company.

was done by ultrafiltration against distilled water (Amicon Co. Lexington MA, Model 202 membrane-Diaflo XM300) and by ion-exchange resins (Amberlite MB-3). According to electron micrographs, the latex particles were monodisperse (within ±5%) and almost perfect spheres. From these micrographs we estimated the diameter. The ionic group contents of the latices were determined by titration with NaOH solution. The characteristics of the latices obtained are listed in Table I. The single-ion activities of protons, the counterions of the sulfonated latex, were measured with a glass electrode and a pH meter, F-7(SS) (Horiba Manufacturing Co., Kyoto, Japan). Potassium chloride was of the Suprapur grade of Merck, which was used without further purifications. Water was deionized by using cation- and anion-exchange resins (Amberlite IR-120B and IRA-400) and further purified by the Milli-Q reagent grade Water System. Its specific conductance was 8×10^{-8} mho/cm.

The apparatus for the isopiestic vapor-pressure measurements was of Sinclair's type which was used before for soluble polyelectrolytes.[20] The sample solutions and KCl (reference) solutions were set in silver cups on a copper block in a desiccator which was placed on a table in a thermostated bath. The desiccator was moved back and forth horizontally at 100 times per min in order to attain rapid equilibrium. Usually at least 3 days were needed for attaining the isopiestic equilibrium.

Results and Discussion

The practical osmotic coefficient of polyelectrolyte (ϕ_z) was calculated by the equation

$$\phi_z = \frac{2m_{KCl}\phi_{KCl}}{(Z+1)(m/Z)} \tag{1}$$

where m_{KCl} is the concentration of the reference potassium chloride solutions, m is the concentration of sulfonate groups of the latices, Z is the stoichiometric valency of latex ion, and ϕ_z and ϕ_{KCl} are the practical osmotic coefficients of the latex solutions and potassium chloride solutions, respectively. It should be noted that the osmotic coefficients dealt with in the present paper are the ones defined on the basis of the stoichiometric number of ions, not of the free ions. The ϕ_{KCl} values were obtained from literature.[21] The mean activity coefficient of latices (γ_z) was calculated by using the Gibbs–Duhem equation

$$\ln (\gamma_z/\gamma_{z0}) = \phi_z - \phi_{z0} + 2\int_m^{m_0}[(1-\phi_z)/\sqrt{m}]\,d\sqrt{m} \tag{2}$$

where the subscript 0 corresponds to m_0, a reference concentration (0.1 equiv/1000 g of solvent in this paper). Furthermore, the single-ion activity coefficients were estimated as follows. The mean activity coefficient γ_z can be written by the single-ion activity coefficients of latices γ_{2p} and of counterions γ_{2g}:

$$\gamma_z^{1+z} = \gamma_{2g}^z\gamma_{2p} \tag{3}$$

where γ_{2g} was obtained by the measurement of pH and m.

It would be pertinent to make a brief comment here on single-ion activity or activity coefficients. These are quantities inaccessible to exact thermodynamics and only the mean activities or activity coefficients are physically significant.[22] Even if this most strict attitude is temporarily and intentionally ignored, as is the case, for example, when potentiometric titrations are carried out, we have a special problem pertaining to the single-ion activity coefficient for polymeric electrolytes; that is, the basic equation usually employed for the estimation of the liquid-junction potential is not warranted in solutions containing polymeric electrolytes (without salts).[23] The problem we are faced with is that the measurement of the single-ion activity in polyelectrolyte solutions cannot be claimed to be justified or unjustified. Thus, it would be worth "measuring" the single-ion activity or activity coefficient for highly charged solutes and discussing the results in light of information obtained from other experimental quantities, even though quantitative discussion would not be possible.
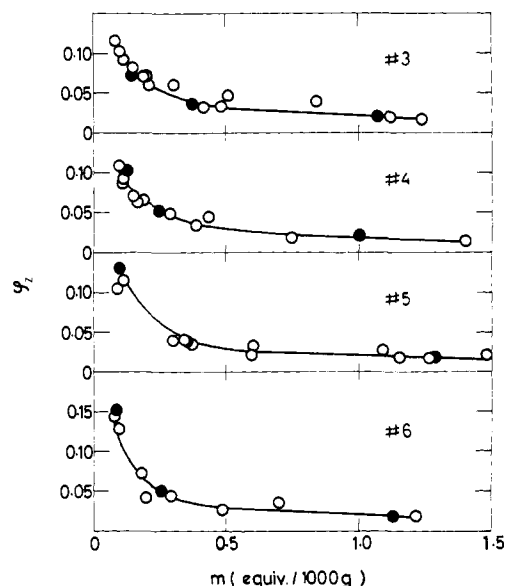
(19) U.S. Patent 31 816 127, 1977.
(20) Okubo, T.; Ise, N.; Matsui, F. *J. Am. Chem. Soc.* **1967**, *89*, 3697–3703.
(21) Reference 5, p 481.
(22) Guggenheim, E. A. *J. Phys. Chem.* **1929**, *33*, 842–849.
(23) Ise, N.; Okubo, T. *J. Phys. Chem.* **1966**, *70*, 3025–3026.

Figure 1. Osmotic coefficients of aqueous solutions of highly charged polymer latices at 25 °C. Measurements were made twice for each material (O and ●).
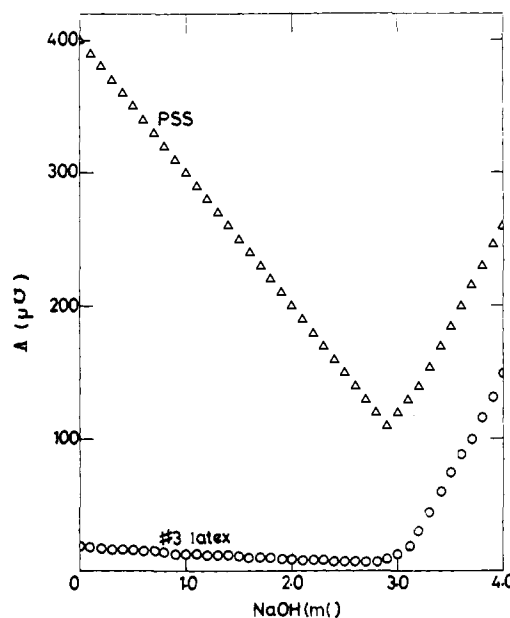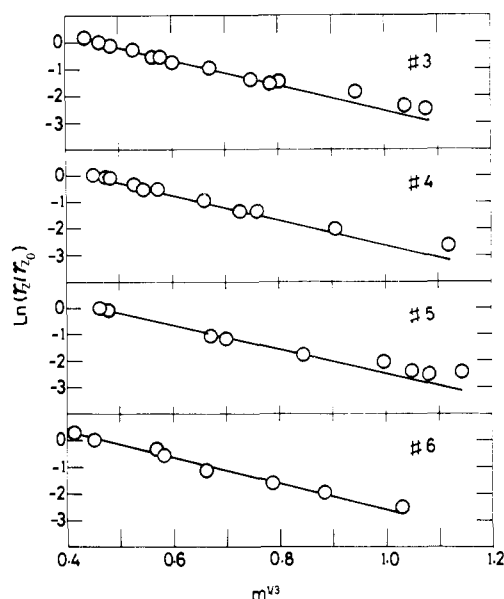

Figure 2. Conductometric titration of the latex (no. 3) and soluble polystyrenesulfonic acid (PSS) by 0.01 N NaOH solution at 25 °C.

The error limit in a_z and a_{2g} was estimated to be 10% at worst. In order to estimate the error limit in a_{2p}, a 20% error in a_z and a_{2g} was assumed; the uncertainty in $\ln a_{2p}$ was then 25%. This is of course an overestimation but reflects our judgement that only very remarkable changes in this quantity should be discussed. We note that the changes in $\ln a_{2p}$ with concentration which will be discussed below (Figure 5) are still larger than this overestimated limit.

Figure 1 shows the osmotic coefficients (ϕ_z) of the latex solutions. The values of ϕ_z were much lower than those found for soluble polyelectrolytes. Figure 2 shows the titration curves of the no. 3 latex and soluble polystyrenesulfonic acid with a 0.01 N sodium hydroxide solution. The conductance of the latex solution was low and very little affected by the addition of sodium hydroxide below the equivalent point whereas the conductance of the polystyrenesulfonic acid was high and drastically decreased. These phenomena imply that protons, counterions of the latex, are much more tightly bound to the latex than those of linear polystyrenesulfonic acid are to the linear macroions and account for the difference in ϕ_z values at least partly. The strong binding

Figure 3. Cube-root plots of the mean activity coefficients of the latices in aqueous solutions at 25 °C. γ_{z0}: the mean activity coefficient at the reference concentration.

Figure 4. Mean and single-ion activity coefficients of the latex (no. 3) in aqueous solutions at 25 °C.

of the counterions would have been caused by the fact that the latices are extensively (29–73% of the total styrene groups) sulfonated not only on the particle surface but also at the inner part of the particle.

Figure 3 shows the natural logarithm of the mean activity coefficients (γ_z) of the latices as a function of the cube root of the latex concentration. The cube-root dependence is obvious. Although direct observation by the microscopic method of the ordering of the latex particles used in the present paper was not possible because of their relatively small dimensions (diameter 500–600 Å), it is almost certain that the particles form ordered structures in the concentration range covered by the isopiestic measurements. Our positive statement is based on the facts that (1) the ordering is confirmed for larger latex particles (diameter about 2000 Å up) by the microscope and (2) much more dilute solutions of the latex particles (no. 4 and no. 5) in the present paper were found to demonstrate the Bragg diffraction of laser light.[24] Thus, the interpretation of the $m^{1/3}$ dependence of the mean activity coefficient in terms of the lattice-like ionic distribution is no longer so speculative as it appeared before[1] and is proven to be at least useful because it has stimulated further attempts to study macroionic distribution experimentally.

Figure 4 shows the mean activity coefficients (γ_z), single-ion activity coefficients of the latex ion (γ_{2p}), and single-ion activity coefficients of the counterions (γ_{2g}). The values of γ_{2g} were lower than 1, and γ_z and γ_{2p} decreased with increasing concentration whereas γ_{2g} was almost constant against the variation of concentration. The constancy of γ_{2g} was often noted for various soluble polyelectrolyte systems. The drastic decrease of γ_{2p} with increasing concentration is noteworthy and is in accord with our previous observation on soluble polyelectrolyte systems,[25] which was later confirmed by Vesnaver et al.[26]

Figure 5 gives the mean activity (a_z), single-ion activity of the latex ions (a_{2p}), and single-ion activity of the counterions (a_{2g}) (in the natural logarithm scale). The a_{2g} was obtained from the (analytical) concentration of the counterions by assuming the constance of γ_{2g}. It is remarkable that (1) a_z stayed constant, (2) a_{2g} increased, and (3) a_{2p} *decreased* with an enormous rate with the increase in the latex concentration, in common with the experimental results we observed earlier on soluble polyelectrolyte
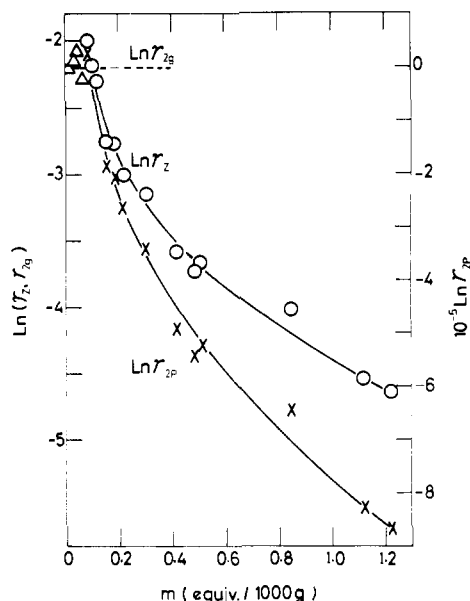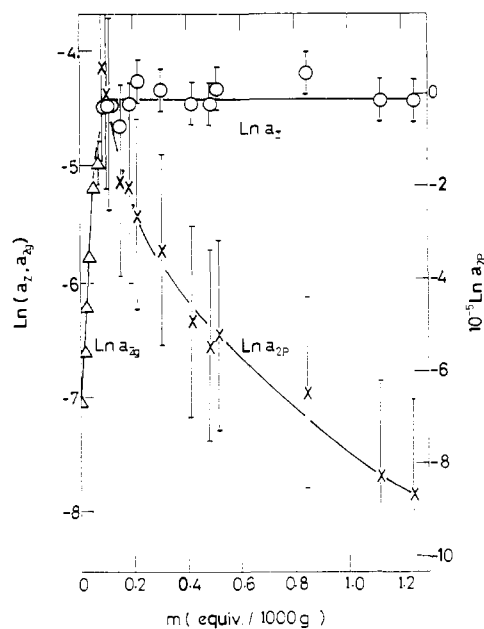

Figure 5. Mean activity of the latex (a_z) and the single-ion activities of the latex ions (a_{2p}) and of the counterion (a_{2g}) at 25 °C. Latex: no. 3, counterion: H$^+$. The vertical bar denotes the estimated error limit. See the text.

systems.[25] These concentration dependences are worth somewhat detailed discussion. Although it appears to have been almost completely ignored or neglected in recent papers on activity or activity coefficients in polyelectrolyte solutions, the activity is defined as the relative fugacity and the relative vapor pressure for a perfect gas; in other words it is a measure of the volatility of the species in question. Furthermore, we know that the Raoult law ($a = N$, where N is the mole fraction) holds for the ideal solution. In such a solution, it is easy to accept that a, vapor pressure, and hence the number of the species in the gas phase increase linearly with concentration. If we carefully examine the experimental results on latex particles as shown in Figure 5 with these axiomatic situations in mind, we realize that the polymer latex solutions are far from ideal, as would be easily accepted, and the latex ions become more and more involatile with increasing concentration: a newly added latex ion does not have the same fugacity to escape the solution phase to the gas phase as the previously added (or already present) latex ions. This situation

(24) Kato, T.; Masuda, H.; Takahashi, A. *Polym. Prep. Jpn.* **1982**, *31*, 2249–2253; **1983**, *32*, 720.

(25) Ise, N.; Okubo, T. *J. Phys. Chem.* **1966**, *70*, 2407–2409.

(26) Vesnaver, G.; Span, J.; Dolar, D. *Makromol. Chem.* **1977**, *178*, 2429–2435.

is a sharp contrast to that of simple electrolyte ions, whose single-ion activity (not activity coefficient) increases with increasing concentration in spite of net Coulombic attraction.[27] Thus, it would be inferred on the basis of the remarkable rate of the decrease of a_{2p} that strong attractive interactions must exist between the latex ions to prevent the "evaporation" of the latex ions from the solution phase to the gas phase. The thinkable mechanism of this attraction is that the latex ion attracts its counterions, which in turn attract other latex ions. As was earlier proposed for soluble macroions,[1] the latex ions thus attract each other through the intermediary of their counterions. If this attraction exists, a "cluster" of latex ions (and counterions) would be produced in solution; that is, a two-state structure is maintained.[15] The cluster size would become larger with the latex concentration. The larger the size, the more difficult the evaporation would be. This explains the observed decrease of a_{2p} with increasing concentration.

The following three points have to be made. First, the existence of the attraction between the highly charged latex ions was recently demonstrated by our direct measurement of the interparticle distance $(2D_{expt})$,[29] which showed that $2D_{expt}$ was smaller than $2D_0$, a theoretical interparticle distance calculated from the latex concentration by assuming uniform distribution of the latex particles throughout the solution. Kato et al., who found that the latex particles used in the present study showed the Bragg diffraction upon laser light scattering, also concluded that $2D_{expt}$ was smaller than $2D_0$.[24] Furthermore, the SAXS and SANS studies[11-13,17] indicate that the relation $2D_{expt} < 2D_0$ holds also for soluble synthetic macroions.[30] Thus, the attractive interaction can be claimed to exist not only in the latex solutions but also in the synthetic polyelectrolyte solutions. Second, the attractive interactions were recently proven by a theory of Sogami.[31,32] His

theory shows that the pair potential between two colloidal particles or macroions has a minimum as a consequence of balancing of the electrostatic repulsions and attractions. The inspection of the mathematical derivation reveals that this interparticle attraction comes into existence as a result of strong electrostatic attraction between the particles and their counterions, as was inferred above. Third, the sharp decrease of a_{2p} is in contradiction with the widely accepted view that macroions or colloidal particles simply repel each other because of the charges of the like sign. Being strongly influenced by the DLVO theory on colloidal stability,[33] this view is widespread. For example, the ordering phenomena of latex particles and macroions were ascribed to the interparticle repulsion by so many authors. If this interpretation were correct, a_{2p} might increase with increasing concentration at a much larger rate than that predicted by the Raoult law. As is demonstrated in Figure 5, this is not definitely the case. The observed fact, namely $2D_{expt} < 2D_0$, clearly implies the presence of an attractive interaction as well as the repulsive one and is consistent with the sharp decrease of a_{2p}.

Finally, a comment is necessary on the completely opposite trend of a_{2g} shown in Figure 5. In this respect, we have to realize that one latex particle produces one latex ion and Z counterions. In the present case, Z amounts to about 10^6. Since counterion condensation takes place, the real number of the counterions would be much lower; the preliminary transference experiment[34] on latex particles shows that about 5% of the total counterions are free. If this result is applied to the present system, the effective valency would be about 5×10^4. Since the vapor pressure is proportional to the number of the species in question, the unsymmetrical changes of a_{2p} and a_{2g} are reasonable. It is to be reminded that the mean activity a_z is kept constant with increasing concentration in spite of the remarkable decrease in a_{2p} and the relatively small increase in a_{2g}.

(27) The attractive nature of the overall Coulombic interionic interaction in dilute solutions of simple electrolyte is reflected in the negative free energy of interaction in the Debye–Hückel theory.[28]

(28) Debye, P. J. W.; Hückel, E. *Phys. Z.* **1923**, *24*, 185–206.

(29) Ise, N.; Okubo, T.; Sugimura, M.; Ito, K.; Nolte, H. J. *J. Chem. Phys.* **1983**, *78*, 536–540.

(30) It is to be noted that the observed SANS peak was interpreted in terms of an isotropic model in ref 17, as mentioned already. However, $2D_{expt} < 2D_0$ is seen to hold if we apply the Bragg equation to the SANS data.

(31) Sogami, I. *Phys. Lett.* **1983**, *96A*, 199–203.

(32) Sogami, I.; Ise, N. *J. Chem. Phys.*, submitted.

(33) See, for example: Verwey, E. J. W.; Overbeek, J. Th. G. "Theory of the Stability of Lyophobic Colloids"; Elsevier: Amsterdam, 1948.

(34) Okubo, T.; Ito, K.; Ise, N., in preparation.