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Conference Note (Invited)

»Ordering« Phenomena of Ionic Solutes in Dilute Solutions*

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In 1965 we carried out the determination of the mean activity coefficient of polyelectrolytes (γ), curiously enough for the first time.[1] Shortly thereafter we realized that ln γ showed the cube-root dependence on polymer concentration for hydrophylic macroions, instead of the square-root dependence.[2] This dependence was interpreted as implying the presence of more or less ordered distribution of the macroions in solutions, following the reasoning presented by Frank.[3] Although the argument was highly qualitative, our inference was in accord with those advanced by Doty, Fuoss et al.[4] based on the very low intensity of scattered light from low salt polyelectrolyte solutions. As the driving forces of such an ordered arrangement, we suggested that the counterions present in between the macroions played an important role, namely an attractive interaction between the macroions was generated through the intermediary of the counterions. This conclusion was supported by the drastic decrease of the activity of the macroionic species with increasing concentration of polymer.[5] This trend disagreed clearly with the concentration dependence of simple ions and with the prediction of the Raoul law, which show an increasing tendency of the activity in the presence of relatively weak interaction or in its complete absence.

The situation with polyelectrolytes had not been clarified until various new scattering techniques were introduced. We are studying the problem by using the small-angle X-ray scattering (SAXS) for »invisible« macroions. Simultaneously we are performing the microscope observation for charged polymer latex particles in suspension, which are large enough to be visible. In the following, we describe recent results obtained in our group, which

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show the presence of highly distorted lattice-like ordered arrangements of macroions and latex particles. For earlier results, see our review article.[6]

Small-Angle X-ray Scattering

The SAXS experiments continuosly show the presence of the single, broad peak for various synthetic and biologically important ionic polymers at low salt conditions. In the case of bovine serum albumin (BSA)[7] a single broad scattering peak can be observed when the protein is electrically charged, namely at high and low pH's. Near the isoelectric point, the peak disappears. This observation is consistent with the data for (anionic) polystyrene sulfonate (PSS),[8] (cationic) polyallylamine hydrochloride PAA-HCl)[9] and (nonionic) polyvinylpyrrolidone (PVP).[8] For synthetic polyelectrolytes, it is possible to study the molecular weight (MW) dependence of the scattering behavior. The recent data on PSS confirm the previous ones on polycrylate and poly-L-lysine[10,11] in that the peak position and intensity depend on MW; the peak position shifts towards smaller scattering vector with MW except at very high MW's. The mixing of two fractions of different MW's gives a new peak in between the original two peaks, indicating that the peak is due to intermolecular, not intramolecular, order. Then the approximate intermacroion distance ($2\,D_{exp}$) can be calculated by the Bragg equation. The $2\,D_{exp}$ values are found to be smaller than the average intermacroion distance ($2\,D_0$) when the solutes are highly charged as is the case for synthetic macroions, confirming the presence of an attractive interaction. Further, the $2\,D_{exp}$ unexpectedly decreases with increasing number of charges of macroions for weak macroions.[7,9–12] The $2\,D_{exp}$ increases with increasing salt concentration and the peak disappears at high salt conditions for all macroions studied.

Ionic micelle solution shows also a SAXS peak.[13] Taking advantage of the spherical shape, the observed scattering intensity is separated into the particle term and interference term. From the latter the correlation function is calculated. Furthermore, the intermicellar distance estimated from the peak of correlation function is in rough agreement with the $2\,D_0$, indicating the weakness of the attraction for such low-charge density species as micelles.

Microscope Observation

The ordering of polymer latex particles in suspension can be proven by Hachisu's method using microscope because of the large diameter.[14] The micrograph shows almost always hexagonal arrays, usually partially distorted, of latex particles. The interparticle spacing ($2\,D_{exp}$) which can be estimated without the Bragg equation is smaller than the average spacing ($2\,D_0$) for high charge particles.[15] The $2\,D_{exp}$ value decreases with decreasing dielectric constant of binary mixtures of water and organic solvent suggesting that the interparticle attraction becomes stronger. The spacing decreases though slightly with increasing temperature, which may be due to the variation of the dielectric constant of water with temperature. The spacing also decreases with increasing salt concentration at low salt conditions and the ordering is destroyed at high salt conditions.

The observed inequality relation, $2D_{\mathrm{exp}} < 2D_0$, suggests the existence of the attraction and hence the two-state structure, in which non-space-filling ordered regions coexist with disordered region of an low particle density. Such a situation can be observed for the latex suspension with the microscope. An example is demonstrated in Figure 1.[16] In the left-hand side are seen the hexagonally packed particles. The particles in the right-hand side show free motion which can be approximately described by the Einstein theory on the Brownian motion.[17] In between we notice the particles with much smaller displacements. We clearly see the solid-liquid-gas-like partition of the particles. It is important to note that there is no mechanical constraints between the solid and gas states, in other words, there is free boundary between the staes. Quite generally, condensed systems cannot exist without attraction.

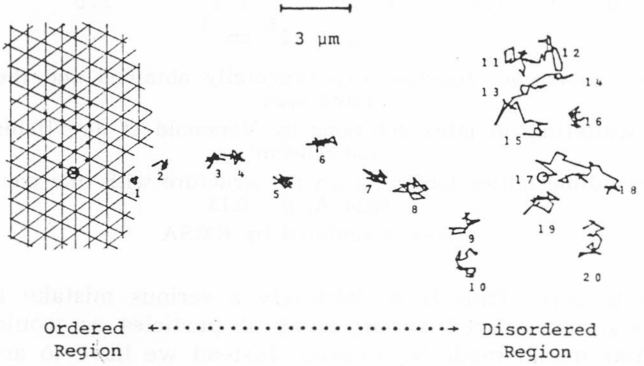

Figure 1. Non-space-filling ordered structure in coexistence with disordered regions in polymer latex suspension and the trajectory of the particles in the disordered region in 1 sec. Latex: copolymer of styrenesulfonate and styrene prepared by emulsion copolymerization, Diameter: 4500 A, Number of charges per particle: 1.76×10^6 SO_3H, Concentration: 2.0%, Film speed: 24 frames/sec, Exposure: 1/67 sec. The $2D_{\mathrm{exp}}$ in the ordered region is measured to be 10^4A, whereas $2D_0$ is 1.5×10^4. It must be reminded that the figure shows the organization of the particles in a horizontal, not perpendicular, plane, so that the non-space-filling ordering is not due to the gravitational influence. The trajectories are determined by following the centers of the particles as a function of time using 24 consecutive still pictures of the 16-mm movie film. Taken from Ref. 16 by the courtesy of the American Chemical Society.

Paracrystalline Distortion

Figure 1. is misleading in that it gives an impression that the ordered regions are so static and perfect. The analysis of the movie or video film indicates that the particles in the ordered regions oscillate around the equilibrium (lattice) point in a quite violent manner. Although this motion is still too small to see in the scale of Figure 1., the amplitude of the vibrational motion amounts to about 10% of the interparticle specing.[18] Furthermore, the lattice points are not distributed at all in an ideal manner. It is quite easy to observe crystal imperfections and non-linear arrangement of the particles under the microscope. This is particularly true at low concentrations. Nonetheless, the root-mean-square displacement of these parti-

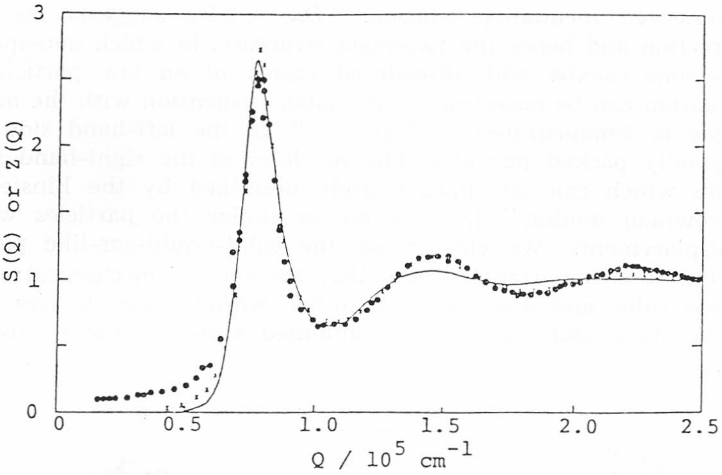

Figure 2. The interference function experimentally obtained and theoretically calated ones.

circles: light scattering on latex solutions by Versmold et al.[22] [latex] = 1.34×10^{18} particles/m^3

curve: paracrystalline lattice factor for an fcc structure with interparticle spacing = = 9824 A, $g = 0.15$

cross: calculated by RMSA

cles is close to zero. Thus it is definitely a serious mistake to imagine so rigid and ideal an ordered arrangement of particles as would be inferred from molecular model made by plastics. Instead we have to accept distorted paracrystalline structure suggested by Hosemann[19] and thermal motion of the particles. We extend the original treatment to cubic lattice systems and compare the theoretical statistical lattice factor ($Z(Q)$) with the structure factor experimentally observed ($S(Q)$).[20] It is demonstrated that $Z(Q)$ has many peaks when the degree of the distortion (g) is low, but it has only a single broad peak when the g value is large. In the case of ionic micelles, the $S(Q)$ curve is best fitted with $Z(Q)$ with g values of about 0.2 for fcc structures.[13] The g value becomes larger with decreasing concentration, which is reasonable. The $S(Q)$ curves obtained by laser light scattering[21,22] and neutron scattering[23] of latex suspensions can be reproduced fairly satisfactorily by the calculation with g values of 0.15 ~ 0.19 for fcc structures, as is shown in Figure 2.[20] Another interesting aspect with this calculation is that the observed $S(Q)$ curves can be reproduced by the calculation based on the RMSA method,[22] a liquid theory, and at the same time by the paracrystalline theory. This agreement might be taken as implying that the ordered structure in latex suspensions is intermediate between the liquid structure and the solid crystal, but this would be too an optimistic view because a repulsive interaction was assumed in the RMSA calculation, which is in contradiction with the microscopic observation, namely the existence of the two-state structure. Fruther quantitative discussion seems necessary.

Using the pictures showing the particle distributions taken by the microscope, the diffraction pattern is calculated by the two-dimensional discrete Fourier transform by computer. From the pattern of random distribution, no scattering peak is obtained, whereas that of ordered arrangement gives the reciprocal lattice. The picture showing localized ordered lattice and disordered regions (the two-state structure) gives the intermediate scattering pattern.

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SAŽETAK

Fenomeni »uređenja« ionskih otopljenih tvari u razrijeđenim otopinama

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Pokazano je, da mjereni logaritam koeficijenta aktiviteta polielektrolita pokazuje ovisnost o trećem korijenu iz koncentracije polimera. Raznim fizikalnim metodama, kao što su ogib rentgenskih zraka pod malim kutem i elektronska mikroskopija, pokazani su dokazi o uređenim domenama koje ne popunjavaju prostor. Rezultati pokazuju, da se takvi kondenzirani sistemi ne mogu održavati bez sila privlačenja pa da se parakristalna distorzija može tumačiti postojanjem struktura s dva stanja.