

functions in the insect. Interference with biosynthesis or its control would result in hormone deficiencies or excesses, either of which might prove detrimental to the animal. The same applies to potential techniques for disrupting transport, degradation, or entry into target cells. Through rational screening several compounds have been identified with such properties. A group of natural compounds (precocene I and II) and chemically related analogues was discovered by Bowers et al.<sup>41</sup> Precocenes appear to destroy juvenile hormone producing cells in *corpora allata* and thereby cause precocious (hence the name) development of miniature adults in a limited number of insect species. Another compound, ethyl 4-[2-*tert*-butylcarbonyloxy]butoxy-

(41) W. S. Bowers, T. Ohta, J. S. Cleere, and P. A. Marsella, *Science*, **193**, 542 (1976).

benzoate (ETB), described by Staal,<sup>5</sup> is selective as an antagonist of juvenile hormone for a few lepidopteran species (G. B. Staal, personal communication).

Compounds that antagonize juvenile hormones are potentially more useful for insect control than those that mimic them because of less need for critical timing in application, a shorter response time, and the additional inhibitory effects on insect reproduction. The possibility for interference with JH production, transport, and target binding appears to be far from exhausted and may benefit from increased investigation.

*We wish to thank our collaborators, whose names appear in the references, and Mr. Clark Riley, for drawing Figure 1. A part of the work in our laboratory was supported by grants from the National Institutes of General Medical Sciences, U.S. Public Health Service, and the National Science Foundation.*

## "Ordered" Distribution of Electrically Charged Solutes in Dilute Solutions

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About 40 years ago, Bernal and Fankuchen<sup>1</sup> carried out detailed X-ray analyses of plant viruses (mainly tobacco mosaic virus) in wet and dry gel states and found distinct intermolecular reflections. They also observed similar X-ray patterns for concentrated solutions. They concluded that the virus particles were distributed equidistantly not only in the gel states but also in the concentrated solution. They observed that solutions down to a concentration of 20% showed "as perfect reflection as crystal".

Subsequently, Riley and Oster<sup>2</sup> observed one or more reasonably well-defined small-angle X-ray diffractions at high concentrations of proteins such as bovine serum albumin and suggested that the molecules took up mean positions equidistant from each other.

As a cause of such equidistance in solutions, Bernal and Fankuchen suggested *attractive* forces between the particles balancing *repulsive* forces (probably of electrostatic nature) and pointed out a similarity to the interaction of metal atoms with their positive nuclei and clouds of negative electrons.

Generally speaking, the solute distribution in solution is the direct outcome of solute-solute, solute-solvent, and solvent-solvent interactions. The complete description of the distribution is sine qua non for thorough understanding of solution properties. Obviously, potential calculations leading eventually to prediction of physicochemical properties can be possible only when

proper assumptions of solute distribution are made. One example is the theory of strong electrolyte solutions by Debye and Hückel,<sup>3</sup> who assumed the Boltzmann distribution for ions and obtained satisfactory agreement with experiments at high dilutions. Polyelectrolyte dilute solutions have often been approached in terms of the so-called cell model for macroion distribution,<sup>4</sup> although agreement with experiments has been much less satisfactory for various reasons. Liquid crystals constitute another well-known case which demonstrates the importance of correlation between solute distribution and solution properties.

It would readily be accepted that solute species, electrically charged or not, are distributed regularly in highly concentrated solutions. This regular spacing might be expected to be destroyed by thermal motion progressively as the solute concentration is lowered. Recent studies show, rather unexpectedly, that some degree of ordering still persists even at relatively low concentrations of electrically charged species such as simple ions, macroions, proteins, ionic micelles, and polymer latex particles. Although many unsolved problems await future investigation, especially for macroion systems, we wish to examine here relevant experimental work on various solution systems in order to provide a basis for a (not fragmentary but) unified interpretation on the structure of dilute solutions of charged solutes.

### Thermodynamic Measurements

The thermodynamic properties of simple electrolyte solutions such as the mean activity coefficient, osmotic

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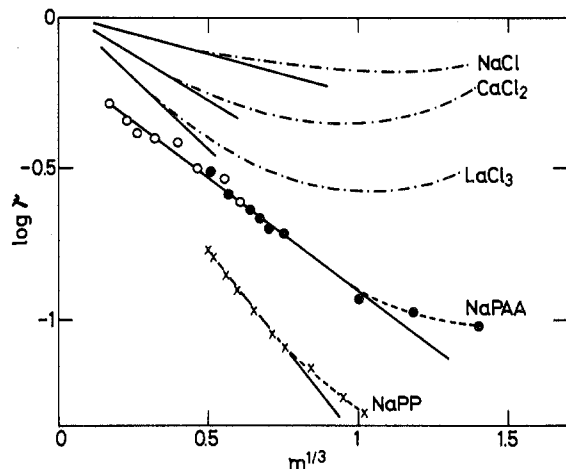
Tsuneo Okubo is a native of Niigata, Japan, and received his B.S., M.S., and Ph.D. degrees from Kyoto University, the Ph.D. in 1969. He is now Associate Professor in the Department of Polymer Chemistry at Kyoto.

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**Figure 1.** Cube-root plots of the mean activity coefficients of sodium polyacrylate (NaPAA), sodium polyphosphate (NaPP), NaCl, CaCl<sub>2</sub>, and LaCl<sub>3</sub> in aqueous solution at 25 °C. For the polyelectrolytes, log  $\gamma$  was shifted by an arbitrary value. What could be measured was the concentration dependence of log  $\gamma$  (but not the magnitude). The activity coefficient data for simple electrolytes were taken from ref 24 and those for the polyelectrolytes from ref 16 and 19.

coefficient, heat of dilution, partial molal volume, and so on are known to obey the square-root law, when the solute concentration ( $m$ ) is sufficiently low, in accordance with Debye–Hückel theory.<sup>3</sup> For the mean activity coefficient,  $\gamma$ , eq 1, where  $b$  is a constant, holds. As the

$$\log \gamma = 1 - bm^{1/2} \quad (1)$$

concentration is raised, however, the square-root law no longer holds; it is reported that a cube-root dependence is valid instead.<sup>5–12</sup> Thus we have eq 2, where

$$\log \gamma = a' - b'm^{1/3} \quad (2)$$

$a'$  and  $b'$  are constants.

Log  $\gamma$  is a measure of the deviation from ideality. In electrolyte solutions this deviation is mostly due to electrostatic potential, which is inversely proportional to the interionic distance ( $r$ ). The quantity  $r$  is inversely proportional to  $m^{1/3}$  if the solute ions are distributed according to a latticelike structure. Although this argument is entirely qualitative, the cube-root relation has been claimed to suggest the existence of a “superlattice”<sup>7</sup> or “diffuse lattice”,<sup>8</sup> which is characterized by more or less regular spacing of the ions in dilute solutions. As will be described later, the small-angle X-ray scattering (SAXS) studies of simple electrolyte solutions at comparatively high concentrations support a quasi-lattice model.

In 1965, we measured the mean activity coefficients of polyelectrolytes directly for the first time.<sup>13</sup> A

cube-root relation (eq 3) was found to hold for a variety

$$\log \gamma = a'' - b''m^{1/3} \quad (3)$$

of synthetic polyelectrolytes;<sup>14–21</sup>  $a''$  and  $b''$  are constants. The cube-root plots of log  $\gamma$  of sodium polyacrylate (NaPAA)<sup>16</sup> and sodium polyphosphate (NaPP)<sup>19</sup> in water are given in Figure 1. It is seen that the cube-root rule holds for the polyelectrolytes in a much wider concentration region than for low molecular weight electrolytes. This fact was taken as suggesting that a more or less regular distribution of macroions is formed with greater ease than for simple electrolytes.<sup>22</sup> It was suggested that the main cause for this regularity was an intermacroion attraction through the intermediary of gegenion–macroion attractions balanced by intermacroion repulsions, which we called the intermacroion linkage. The essential idea is that for two macroions repulsion is operative at small distances as expected and attraction is unexpectedly exhibited at larger distances, providing an equilibrium separation with a minimum of potential energy. We come back to this problem later.

In this connection, it is noteworthy that Vaslow found a  $\lambda$ -point type of transition in the heats of dilution and the partial molal volumes of simple electrolyte solutions.<sup>25</sup> He suggested two possible sources of the transition, namely, a change of solution structure and a change of ion distribution.

Next, we must mention the concentration dependence of single-ion activities of macroions,  $a_{2p}$ ,<sup>26</sup> which is often overlooked. The observed  $a_{2p}$  decreases drastically with increasing polymer concentration.<sup>28,29</sup> Although a similar concentration dependence is expected also for neutral polymers in solution when the solvent–solute interaction is intense according to the Flory–Huggins theory, this dependence is in contrast with that usually found for simple electrolytes and low molecular weight neutral solutes. It would not be readily acceptable, because the activity is by definition the ratio of the fugacities (or vapor pressures) of a species at a concentration of interest and in the reference state. For

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(26) It is well-known that the concept of single-ion activity has no sound thermodynamic significance, because of the liquid-junction problem. For polyelectrolyte solutions, the situation is more serious because the equation usually used for the estimation of the potential cannot be claimed to be correct, as was pointed out by us earlier.<sup>27</sup> The argument in the text, therefore, would be valid only qualitatively.

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an ideal solution, the vapor pressure and hence the activity increase linearly with increasing concentration (Raoult's law). Thus the sharp decrease of  $a_{2p}$  suggests the presence of strong "attractive" interaction between macroions. This interpretation is consistent with the intermacroion linkage mentioned above; in other words, macroions newly added (by increasing concentration) are snapped up by the macroion clusters already present so that the clusters become larger, with resulting apparently heavier "weight" of the macroions, which corresponds to lower vapor pressure and hence lower activity.<sup>28</sup>

Although not many data are available, the single-ion activities of surfactant ions were found also to decrease with increasing concentration above the critical micelle concentration (cmc).<sup>30-34</sup> In this concentration range, the surfactant ions form micelles by ("attractive") hydrophobic interaction so that their vapor pressures (and hence activities) are lowered.

### Light Scattering Studies

Light scattering is essentially due to the fluctuation of concentration. If this fluctuation is diminished by any force acting between solute species, the intensity of scattered light must be lowered. Guinand et al.<sup>35</sup> found that the scattering intensity at 90 °C of polyacrylate solutions was drastically decreased to one-fiftieth of that of the un-ionized acid. Doty and Steiner<sup>36,37</sup> suggested that this diminution in the intensity is due to a nonrandomness produced by repulsion between macroions. The addition of an indifferent salt greatly diminished this effect, causing larger intensity. Kirkwood and Mazur<sup>38</sup> predicted theoretically by using a screened Verwey-Overbeek potential that spherical macroions formed an ordered structure at sufficiently low salt concentrations.

By measuring dynamic light scattering, Schurr et al.<sup>39,40</sup> observed that the diffusion coefficient of poly-L-lysine-HBr decreased "catastrophically" with decreasing salt concentration. They attributed the small diffusion coefficient in the "extraordinary" phase at low salt concentrations to an ordered distribution of macroions. This interpretation is easily acceptable if the ordered distribution is a consequence of "attractive" interaction between macroions as mentioned above. Quite recently, Schurr et al. observed discontinuous changes in conductance<sup>41</sup> and viscosity<sup>42</sup> of poly-L-lysine-HBr-NaBr solutions; they were suggested to be due to an extraordinary-ordinary phase transition. Stigter<sup>43</sup> considered the extraordinary phase to be similar to a cylinder model containing parallel rods, basing

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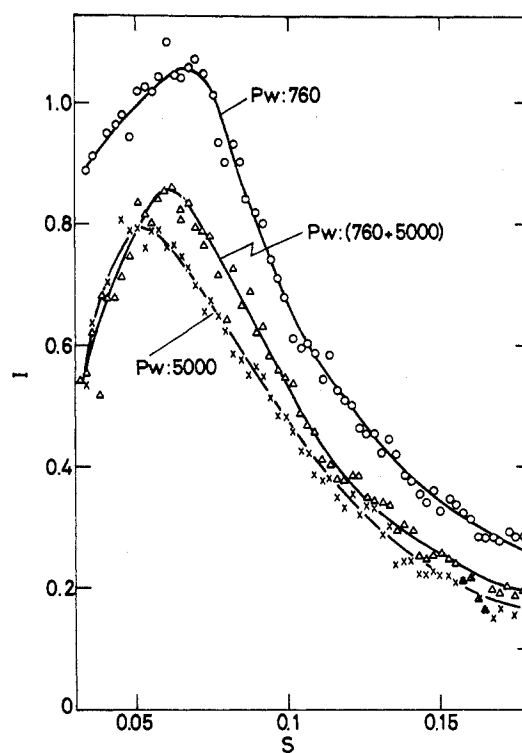


Figure 2. SAXS intensity of NaPAA solution: influence of degree of polymerization. [NaPAA] was approximately 0.02 g/mL,  $\alpha = 0.5$  (taken from ref 51).

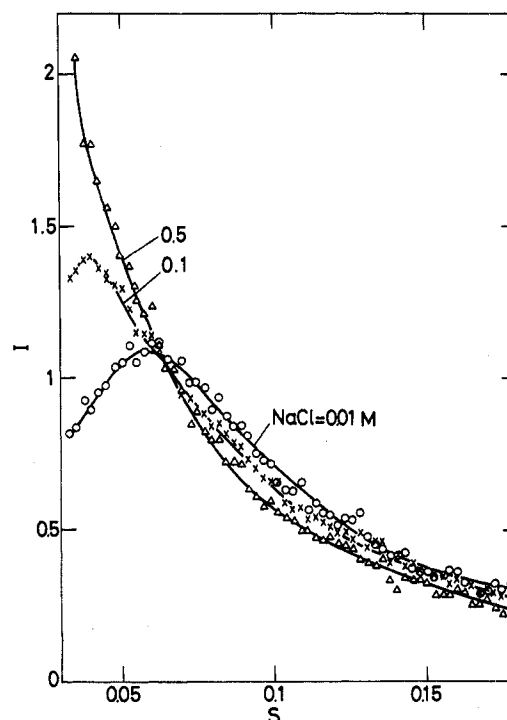


Figure 3. SAXS intensity of NaPAA solution: influence of NaCl. [NaPAA] = 0.02 g/mL, degree of polymerization (Pw) = 1470,  $\alpha = 0.5$  (taken from ref 51).

his views on Onsager's theory<sup>44</sup> of the transition from random to parallel orientation of polymer chains.

### Small-Angle X-ray Scattering (SAXS) Studies

SAXS measurements of simple electrolytes such as  $MgCl_2$ ,  $BaCl_2$ ,  $CaCl_2$ , and  $SrCl_2$  in concentrated solutions (1.5–7.1 M) have clearly demonstrated the pres-

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Table I  
SAXS Data of Sodium Salts of Polyacrylate and Polymethacrylate in Dilute Aqueous Solutions

poly-electrolyte	degree of neutralization, $\alpha$	concn, g/mL	$2D_{\text{exptl}}$ , Å	$2D_0$ , Å	$2D_{\text{th}}$ , Å
NaPAA	0.8 <sup>a</sup>	0.0445	62		41
	0.65 <sup>b</sup>	0.03	71	169	49
	0.65 <sup>b</sup>	0.02	83	194	60
	0.65 <sup>b</sup>	0.01	113	244	85
	0.4 <sup>a</sup>	0.0445	64		39
	0.4 <sup>b</sup>	0.02	93	190	58
	0.2 <sup>a</sup>	0.0445	77		38
	0.2 <sup>b</sup>	0.02	111	186	57
NaPMA <sup>c</sup>	0.8	0.0331	72	146	51
	0.4	0.0331	73	141	49
	0.2	0.0331	106	139	48
	0.2	0.0296	114	144	51
	0.2	0.0166	140	175	68
	0.2	0.0099	181	208	88

<sup>a</sup> From ref 49, degree of polymerization > 1400.

<sup>b</sup> From ref 50 and 51, degree of polymerization = 1020.

<sup>c</sup> From ref 49, degree of polymerization = 590.

ence of distinct peaks.<sup>45,46</sup> Bahe<sup>47</sup> reported that the X-ray scattering curves were compatible with a "loose" face-centered cubic lattice.<sup>48</sup>

The SAXS studies of polyelectrolytes in dilute solutions are being carried out by two groups using recently developed counter devices independently.<sup>49,50</sup> *These studies show the presence of well-defined peaks in the scattering intensity curves except at very low degrees of neutralization ( $\alpha$ ) and also except in the presence of a large amount of foreign salt.* Figures 2 and 3 give typical scattering intensity curves for aqueous solutions of sodium polyacrylate (NaPAA).<sup>51</sup> Most noteworthy in Figure 2 is the fact that the mixture of two different fractions of NaPAA gives (not two but) a single peak. This seems to exclude a possibility that the observed peak is due to *intra*-macroion ordering. It strongly suggests the existence of an ordered distribution of macroions in polyelectrolyte solutions. The dependences of the peak position on salt concentration (see Figure 3) and on the degree of neutralization (to be mentioned below) also suggest that the ordering is of *inter*-molecular nature.

In Table I, some results of SAXS measurements of NaPAA<sup>49-51</sup> and sodium polymethacrylate (NaPMA)<sup>49</sup> are summarized.  $2D_{\text{exptl}}$  denotes the calculated interparticle distance obtained by the Bragg equation and  $2D_0$  is a theoretical interparticle distance obtained with an assumption of simple cubic distribution of macroions. It is to be noted that  $2D_{\text{exptl}}$  is smaller than  $2D_0$  in dilute solutions. This indicates that the ordered structure does not spread over the whole solution but is localized. It might be plausible that the ordered region coexists with a disordered region in dilute solu-

tion. We further note that a theoretical distance,  $2D_{\text{th}}$ , calculated assuming an asymmetric lattice of fully stretched rodlike macroions of infinite length is always smaller than  $2D_{\text{exptl}}$ , although the two values are approximately of the same order. (This assumption was made in a theory by Lifson and Katchalsky.<sup>52</sup>) This disagreement indicates probably that the macroions are not fully stretched under the experimental conditions used.

It must be noted that  $2D_{\text{exptl}}$  changes with the degree of polymerization (see Figure 2).  $2D_{\text{exptl}}$  values for NaPAA were 94 and 126 Å for the degrees of polymerization 760 and 5000, respectively. On the other hand,  $2D_{\text{th}}$  does not change. We also note that *the  $2D_{\text{exptl}}$  value decreased with polymer concentration as expected (see Table I) whereas it increased with salt concentration.* For example,  $2D_{\text{exptl}}$  was 88, 106, and 157 Å at [NaCl] = 0, 0.01 and 0.1 M for NaPAA<sup>51</sup> (degree of neutralization = 0.5, polymer concentration = 0.02 g/mL, and weight-average degree of polymerization ( $P_w$ )  $\approx$  1400). The salt concentration dependence shows that what was affected by the shielding effect due to simple ions must be attractive interaction between the macroions. (If repulsive force were the factor responsible for the ordering,  $2D_{\text{exptl}}$  should decrease with the addition of salt, which is not the case.) This is consistent with the idea mentioned above that the intermacroion linkage (attraction) is formed through the intermediary of gegenions. Furthermore, as is seen from Table I,  $2D_{\text{exptl}}$  decreased with increasing degree of neutralization, suggesting again the important role of electrostatic attraction between the macroions.

Well-defined X-ray scattering peaks and similar results were obtained for aqueous solutions of the hydrobromide of poly-L-lysine.<sup>53</sup> Preliminary measurements show that this is also the case for aqueous lysozyme solutions.<sup>54</sup>

Even for spherical micelles of typical ionic surfactants (potassium caprate and potassium laurate, for example) in aqueous media, X-ray diffraction gave the so-called I band, which was interpreted as related to the interparticle distance in a three-dimensional lattice structure.<sup>55,56</sup>

The organization of biopolymers in concentrated solution was much earlier investigated. Schmidt et al.<sup>57</sup> carried out SAXS measurements of various solutions of spherical viruses. The scattered intensity curves of turnip yellow mosaic virus showed bumps or even maxima. Furthermore, Guinier et al.<sup>58</sup> deduced that orderliness in hemoglobin solution was less for sickle cells than for normal corpuscles. As mentioned before, Riley et al.<sup>2,59</sup> suggested that there exist latticelike structures in solution for hemoglobin, egg albumin, serum albumin, and thymonucleic acid. Bernal and Fankuchen<sup>1</sup> also reported a regularity in two dimensions

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for tobacco mosaic virus solutions.

### Small-Angle Neutron Scattering (SANS) Studies

Neilson et al.<sup>60</sup> and Enderby et al.<sup>61</sup> found peaks in the neutron diffraction patterns for aqueous solutions (2.8–6.6 M) of NiCl<sub>2</sub> and noticed that the peak position was proportional to the cube root of concentration. This strongly favors a quasilattice model of ionic distribution.

For polyelectrolyte systems, French groups have carried out SANS measurements for aqueous dilute solutions of sodium polymethacrylate,<sup>62–65</sup> sodium poly(styrenesulfonate),<sup>66–68</sup> sodium carboxymethylcellulose,<sup>65,69</sup> and poly- $\alpha$ -L-glutamate.<sup>70</sup> In most cases, a distinct peak was observed in the scattering intensity curve, and it was taken as evidence for organization among macroions. As was mentioned in the SAXS section above, the Bragg distance from the SANS measurements also increased with decreasing concentration of sodium polymethacrylate (degree of polymerization = 150) and the peak became less clear with the addition of a simple electrolyte.<sup>64</sup> Furthermore, it seems to be possible to conclude from Figure 3 in ref 64 that the Bragg distance increases with increasing concentration of added simple salt. This is in accord with our SAXS result mentioned above.<sup>51</sup> In a very recent paper,<sup>68</sup> the Bragg distance was also reported to decrease with polymer concentration for sodium poly(styrenesulfonate) (the degree of polymerization was 343). The addition of salt was reported not to change the Bragg distance for this material, a result not in agreement with our SAXS measurement on polyacrylate ( $P_w \approx 1500$ ). The SANS measurements of polyglutamate (degree of polymerization in the range of 23–560) showed no variation of the Bragg distance with the degree of polymerization,<sup>70</sup> which is in disagreement with the SAXS results on polyacrylates of  $P_w = 760$  and 5000. These disagreements are believed to be due to difference in the degrees of polymerization of the materials used. We note that the Bragg distances obtained from the SANS measurements were always smaller than  $2D_0$  values, in accord with the SAXS results mentioned above.

### Visual Observation of Ordered Spacing of Polymer Latex Particles in Solutions

It has long been known that solutions of monodisperse latex particles show iridescence, namely, the Bragg diffraction of visible light due to ordered distribution of the particles.<sup>71–75</sup> Williams and Crandall<sup>76</sup>

found, by investigating Bragg diffraction of laser light, that at low concentrations of aqueous suspensions of polystyrene spheres only a body-centered cubic structure exists whereas it coexisted with face-centered cubic at high concentrations.

Polymer latex particles are large enough to allow direct observation by visible light. Taking advantage of this, Hachisu et al. could demonstrate unequivocally the presence of a regular latticelike distribution of the particles in dilute solution by using a metallurgical microscope.<sup>77</sup> It is now unquestionable that these particles form ordered structures even at low concentrations (0.1 vol. %). As was the case for the macroion systems, the formation of the ordered structure for the latex case was also favored by low ionic strength.<sup>77</sup> The interparticle distance directly measured from photographs increased with dilution, as was observed for macroion systems.

### Concluding Remarks<sup>78</sup>

The experimental data that we have presented support strongly the idea that electrically charged solutes form "ordered" structures not only in highly concentrated solutions but also at relatively low concentrations, regardless of their shapes and sizes. The common characteristic of these solutes is that they exert powerful electrostatic interaction with each other in solution.

For highly concentrated solutions, it may be accepted, the "ordered" structure may exist throughout the entire volume of a solution. Even when the concentration is lowered, there still exist ordered arrangements in solutions. Of particular importance is that the interparticle distance ( $2D_{\text{exptl}}$ ) in this ordered region, which is responsible for the Bragg diffraction, is always smaller than the average interparticle distance ( $2D_0$ ), as was found from the SAXS (Table I) and SANS measurements.

In order for this situation to be physically realizable, we *must* conclude that the ordered region is localized. In this case there may be two possibilities: first, all of the solute particles may be in the ordered region, or second, a portion of the particles may be in the ordered region and the rest in the disordered state. Although overlooked by many workers, the photograph taken by Hachisu et al.<sup>77</sup> shows clearly *the ordered region coexisting with the disordered region* for polymer latex particles even at a concentration of 1 vol. %. Furthermore, they described "At one moment an ordered portion . . . disintegrated into disorder and in the next

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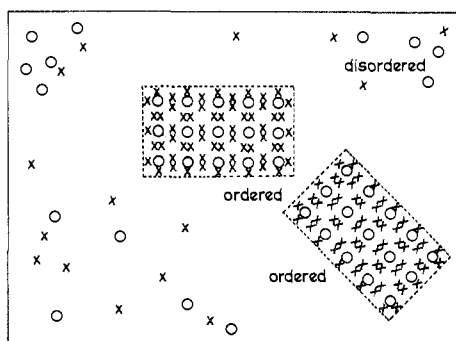
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(78) We note that the magnetic birefringence measurements by Maret et al.<sup>79</sup> also indicate the presence of ordering for a polypeptide in solution. The conclusion derived was that a local parallel ordering of rodlike molecules appeared above a certain concentration with regular lateral next-neighbor distance up to several hundred angstroms. This is quite reasonable for polymers of rather short chain (degree of polymerization was 34) as employed by Maret et al.

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**Figure 4.** Schematic presentation of the two-state structure of polyelectrolyte solutions (taken from ref 51). In this illustration, the macroion is represented by a circle for convenience. This does not mean that all the macroions assume a spherical shape. It might be possible that the macroion is stretched in solution even at relatively high concentrations. Under such a circumstance, also, a two-dimensional ordered region would be possible, in equilibrium with free rodlike macroions in the disordered region. (X) Gegenion; (O) macroion.

moment an ordered aggregate appeared at another place...". By analogy with this latex system, it might be suggested that, also in other systems under consideration, the ordered and disordered regions coexist and fluctuate with time. The whole situation is thus similar to the structure of water: in some volume elements the water molecules form an ordered ice structure which is in dynamic equilibrium with free water molecules in a disordered state, and the ice structure fluctuates with time. On the basis of the foregoing argument, we proposed a two-state structure for dilute solutions of electrically charged species, as is schematically drawn in Figure 4 for "spherical" macroions.<sup>51</sup>

A second conclusion concerns identification of the main cause for the formation of ordered clusters. Evidently, we must assume that an attractive force between macroions is responsible for the cluster formation, because  $2D_{\text{exptl}}$  is smaller than  $2D_0$ . As was mentioned above, many authors (with a few exceptions) claimed that "repulsive" force between macroions is responsible for the ordering. If this interpretation were correct, the local clustering would be impossible and the macroions must distribute in a regular manner with a distance  $2D_0$  in the entire solution. Experimentally, this is not the case. Obviously the most important factor is the attractive interaction between the macroions and the gegenions (causing intermacroion attraction) which balances the repulsive interaction between the macroions or between the gegenions, as was earlier concluded correctly by Bernal and Fankuchen.<sup>1</sup> In this connection, it would be useful for readers to consider the basic factors responsible for the stability of ionic crystal, namely "(1) attractions between one ion and the oppositely charged ions coordinated around it, and (2) the repulsion between the ions of like sign at somewhat larger separations".<sup>80</sup> It seems that we are prone erroneously to ignore (or underestimate) the first factor for macroion systems.

A brief comment appears to be necessary on the (polymer) concentration dependence of the Bragg distance. When solute particles distribute in a three-dimensional, regular way, the interparticle distance must be proportional to the cube root of concentration.

Similarly, two-dimensional regularity (parallel ordering of rodlike macroions, for example) corresponds to a square-root dependence. As a matter of fact, Bernal and Fankuchen found the square-root dependence for tobacco mosaic virus in wet gel state,<sup>1</sup> and Riley and Oster<sup>2</sup> observed the cube-root dependence for spherical proteins such as human hemoglobin and the square-root relationship for nonspherical macroions (bovine serum albumin and thymonucleic acid) in concentrated solution.

This kind of reasoning has again been taken up recently: first Moan<sup>64</sup> and Rinaudo and Domard<sup>70</sup> noted that the scattering vector at the peak (and hence the reciprocal of the Bragg distance) in neutron scattering is proportional to the square root of concentration for polymethacrylate (at a degree of neutralization of 0.6) and for sodium polyglutamate of a degree of polymerization of 50. Moan pointed out<sup>64</sup> that this dependence is in agreement with predictions by a lattice model (Lifson-Katchalsky theory) and by an isotropic model, whereas Rinaudo et al.<sup>70</sup> ascribed the dependence to the lattice model. Similarly, Dušek et al.<sup>49</sup> claimed, on the basis of SAXS experiments, that the square-root dependence is valid for polymethacrylate not only at full neutralization, but also at a low degree of neutralization (0.2), and is consistent with the Lifson-Katchalsky model. It must be pointed out, however, that these concentration dependences can be justified only when the ordered structure covers the entire volume of the system as is practically the case in the wet gel state or in concentrated solutions. As far as dilute solutions are concerned, in which the ordered region does not spread all over the solution volume, it is questionable to use the analytical concentration of electrolytes for discussion of bulk solution properties.

We also note that de Gennes et al.<sup>81</sup> suggested an isotropic model for solutions of macroions. The SAXS and SANS measurements on macroion solutions do not exclude this model at present, although it is not consistent with the dependence of the SAXS data on the degree of polymerization and it certainly does not apply to other charged systems considered here. Furthermore, features of solution structure originating from the nature of water might be responsible for the observed neutron and X-ray diffraction. For example, we have to pay due attention to the  $\lambda$ -point transitions and their significance, pointed out by Vaslow<sup>25</sup> (vide supra), and to the cooperative bond lattice of water which was proposed to exist at low temperatures by Angell et al.<sup>82,83</sup> Obviously it is necessary to carry out further experiments for nonaqueous solutions in order to examine the role of water in the observed long-range ordering.

It is clear that, although many kinds of experimental evidence indicate ordered distributions of electrically charged particles in dilute solutions, the proposed interpretations of the ordered states vary from author to author. Even in the framework of the two-state structure, we have no information at present on how fast the macroion clusters fluctuate. In this respect, it might be possible that the observed ordering is due to

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spinodal decomposition. In order to reach a more conclusive interpretation, measurement of the lifetimes of the ordered regions in macroion solutions would be necessary. Furthermore, we have no information at the moment as to how large the ordered clusters are.<sup>84</sup>

(84) An approximate estimate of the dimensions of the ordered region is made as follows: since  $2D_{\text{expt}}$  is roughly one-half of  $2D_0$  under our experimental conditions (see Table I), the total volume of the ordered region must be at most one-eighth of the volume of the solution, provided that all the macroions are in the ordered region. If this condition is not fulfilled, the ordered region must occupy a smaller space.

Further intensive study is certainly necessary in order to clarify the essential characteristics of the structure of ionic solutions.

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## Structure of a Green Bacteriochlorophyll Protein

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The conversion of sunlight into chemical energy is essential for life as we know it, and the ability to effect this interconversion, albeit very inefficiently, must have occurred very early in evolution.

The light-gathering and energy-transducing systems in green plants and other photosynthetic organisms that we see today have evolved to become very efficient, but they are also complex. The remarkable efficiency of photosynthesis is now known to result from the participation of a variety of chemical components. While all the steps involved in the conversion of a quantum of light energy into chemical energy are not understood, the following outline of the process is well established.<sup>1-3</sup>

First, light energy is absorbed by an "antenna" system, consisting primarily of chlorophyll molecules (Figure 1) but also including pigments such as carotenoids and xanthophylls, which help ensure that the full spectrum of light is used. As we shall discuss in more detail below, there is now good evidence that the chlorophyll molecules, and probably the other pigments as well, are closely associated with protein.

The light energy collected by the antenna is rapidly transferred from one antenna chlorophyll to another until it reaches special chlorophyll molecules in a "reaction center" or "energy trap" where the first step in energy transduction, a charge separation, occurs. Typically, 300 antenna chlorophyll molecules might absorb light and feed it to one reaction center. In the purple photosynthetic bacteria it has been established that in the reaction center the initial charge separation consists of the transfer of an electron from a special pair

of chlorophylls to an electron acceptor. The primary acceptor has recently been identified as a bacteriopheophytin molecule. Subsequently, the electrons are funneled through the biochemical electron-transport chain in which the potential energy generated by the charge separation is converted into energy-rich chemical bonds. In green plants and algae there are actually two distinct reaction centers and two electron-transport chains which combine to reduce carbon dioxide to carbohydrate and oxidize water to molecular oxygen, producing NADPH and ATP in the process.

By absorbing incident light with an antenna system, rather than with the reaction center chlorophyll itself, it is possible to ensure that the complex electron-transport systems are utilized efficiently. At normal light intensities, a single electron-transport chain can convert the excitation energy collected by several hundred chlorophyll molecules, and for this reason only 1% or less of the total chlorophyll in green plants and photosynthetic bacteria is found in the reaction centers, the remainder being in the antenna system.

Because of the role of chlorophyll in both the collection and trapping of light energy, there has been considerable interest in determining the arrangement of this ubiquitous pigment in photochemical systems. Although the chemical structures of the commonly occurring forms of chlorophyll have long been known, it has proven very difficult to obtain reliable information on the environment and organization of the pigment *in vivo*.

A major experimental difficulty arises from the fact that most of the light-harvesting and transducing components of all known photosynthetic organisms are incorporated within membranes within the cells and are very difficult to extract and isolate in an active form.

In the higher plants and algae, both the light-absorbing chlorophyll and the reaction centers are in-

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