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Review

Thermodynamic and Kinetic Properties of Polyelectrolyte Solutions. A Unified Interpretation in Terms of Manning's Theory[1]

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ABSTRACT: Recent studies on the thermodynamic properties and catalyses of polyelectrolytes are reviewed. The mean and single-ion activity coefficients, the solubility of polyelectrolytes sparingly soluble in water, the partial molal volume, the heat of dilution, the diffusion coefficient, and the second virial coefficient are discussed in terms of Manning's theory. Remarkable rate-enhancing effects of polyelectrolytes for similarly charged ionic species and rate-retarding influence for oppositely charged species are shown to be described by Manning's theory in combination with the Brønsted–Bjerrum theory. A similar approach to the helix formation of polynucleotide is described.

I. Introduction

Synthetic polyelectrolytes, or polymeric electrolytes, are highly simplified model compounds of biologically important macromolecules. Thus, the study of synthetic polyelectrolytes, especially the thermodynamic properties of dilute solutions, can provide valuable information toward the understanding of the physicochemical behavior of biological macromolecules in solution. To this end, intensive thermodynamic studies, experimental and theoretical, have been therefore carried out on synthetic polyelectrolyte solutions. In addition, enormous effort has recently been directed toward the catalytic influence of polyelectrolytes with the purposes, explicit or implicit, of "imitating" biological catalysts, that is, enzymes, or of obtaining a basic understanding of the mechanism of enzymatic reactions. In spite of tremendous research activity, it seems to us that there lacked a penetrating interpretation by which various solution properties of the polyelectrolytes could be accounted for, not in a fragmented fashion, but in a unified way. This situation is obviously in sharp contrast with low molecular weight (simple) electrolytes, whose solution properties including classical thermodynamics, transport phenomena, and kinetic aspects as well as can be in principle understood in terms of the Debye–Hückel pictures.

Quite recently, Manning developed a limiting law for polyelectrolyte solutions. In this theory, only one nonadjustable parameter, ξ, was introduced, unlike previously developed theories which contained generally plural parameters. The characteristics of Manning's theory certainly encourage us to dissect whether the theory can furnish a sound basis for unified interpretation of varieties of polyelectrolyte properties.

In this report, recent studies on some thermodynamic quantities (such as mean- and single-ion activity coefficients, partial molal volume, diffusion coefficient, etc.,) and also on the catalytic influences of polyelectrolytes are reviewed. It will be our purpose to show that these seemingly diversified aspects in question can be understood, at least qualitatively, by Manning's theory and Brønsted–Bjerrum's theory. The former theory allows us to evaluate the electrostatic free energy of the solutions, from which other thermodynamic quantities can be calculated easily. As is well-known, the Brønsted–Bjerrum theory relates the rate constant with the activity coefficients of reactants and activated complex and has been found to be satisfactory in quantitative interpretation of the primary and secondary salt effects.

II. Thermodynamic Aspects of Polyelectrolyte Dilute Solutions

A. Single-Ion and Mean Activities of the Solutes. The activity is the most fundamental thermodynamic quantity, and various other properties are derived from the dependences of the activity on volume, pressure, temperature, concentration, and so on. The single-ion and mean activity coefficients have been measured in several laboratories.[2–4] Theoretical discussion on these quantities was developed often by using Lifson–Katchalsky theory (rodlike models)[5,6] and coiled models.[7,8]

According to Manning's theory,[9,10] a real polyelectrolyte chain is replaced by an infinite linear charge and a single nonadjustable parameter, ξ, given by eq 1, is introduced,

$$\xi = e_0^2/DkTb \tag{1}$$

where b is the distance between neighboring charges on the macroion and D and e_0 are the dielectric constant and the electronic charge. The intense interaction between gegenions (counterions) and macroions (which generate extremely high

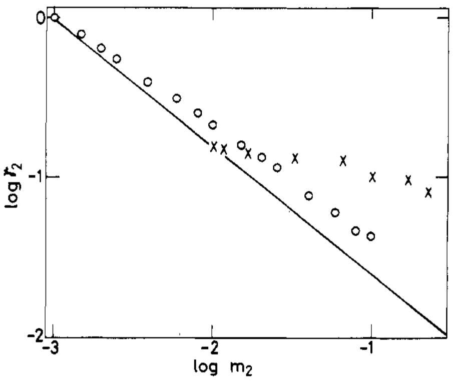

Figure 1. Comparison of the observed γ_2 of HPSS and NaPAA with those predicted by Manning's theory: (○) observed, HPSS (from ref 4); (×) observed, NaPAA (from ref 45); (—) Manning's theory.

electrostatic field) is known to deprive some of the gegenions of the freedom of motion. When the valency of gegenion is denoted by Z_{2g}, it is assumed gegenions condense on a macroion to lower ξ to Z_{2g}^{-1}, and for $\xi \le Z_{2g}^{-1}$ no condensation of gegenions occurs.

The usefulness of the Manning theory for the single-ion activity coefficient of gegenion and the mean activity coefficients of polyelectrolyte was discussed by Manning himself.[9-12] Here, we would like to refer only to the fact that the observed concentration dependences of the mean activity coefficients, γ_2, for $(1 - Z_{2p})$ or $(2 - Z_{2p})$ type polyelectrolytes (Z_{2p} = valency of the macroion) are also fairly well interpreted by Manning's theory. Comparison of the γ_2 data of sodium polyacrylate (NaPAA) and poly(styrenesulfonic acid) (HPSS) with the theory is shown in Figure 1. (Note that the activity and the activity coefficient in this paper are the values relative to those at a reference concentration. In Figure 1, the reference is 10^{-3} M.) Experimentally, the log γ_2 vs. log m_2 plots give a straight line with a negative slope as predicted by Manning's theory (solid line), where m_2 denotes the polyelectrolyte concentration (equivalent per L of solution). The agreement of the theory and experiment was satisfactory for HPSS whereas this was not the case for NaPAA. In Table I, the observation for the calcium salt of poly(vinyl)sulfuric acid (CaPVAS)[13] was compared with the theory, where good agreement was obtained. It should be mentioned that the concentration dependence of the γ_2 of NaPAA and several other polyelectrolytes fit experimentally the cube-root rule.[3] This might be due to the fact that the measurements were carried out in a limited range of concentration.

Table I
Comparison of the Observed Mean Activity Coefficient of CaPVAS in Aqueous Media at 25 °C with Manning Theory

Concn of CaPVAS, M	log γ_2 Osbd[a]	log γ_2 Calcd
0.228	−0.46	(−0.46)
0.275	−0.49	−0.51
0.350	−0.53	−0.57
0.469	−0.59	−0.65
0.563	−0.62	−0.70
0.708	−0.65	−0.76
0.856	−0.67	−0.81

[a] From isopiestic measurements.[13]

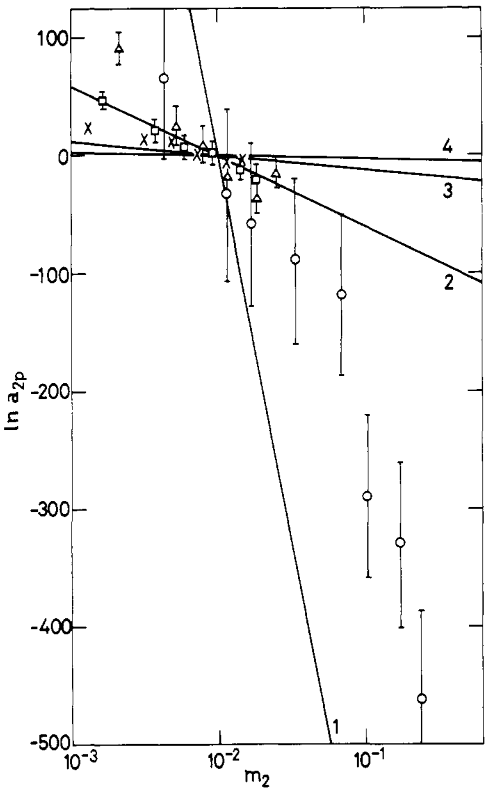

Figure 2. Comparison of the observed a_{2p} of NaPAA and NaPVAG with those predicted by Manning's theory: (○) observed, NaPAA, curve 1, theory, NaPAA; (△) observed, NaPVAG-N3, curve 2, theory, NaPVAG-N3; (□) observed, NaPVAG-N2, curve 3, theory, NaPVAG-N2; (×) observed, NaPVAG-N1, curve 4, theory, NaPVAG-N1.

Next, we discuss the single-ion activity of macroion, a_{2p} $(= \gamma_{2p}M_{2p} = \gamma_{2p}m_{2p}/Z_{2p})$, where γ_{2p} is the stoichiometric single-ion activity coefficient of macroion and M_{2p} and m_{2p} are the molar and ionic concentration of macroion, respectively. a_{2p} is given for $(Z_{2g} - Z_{2p})$-type polyelectrolytes in the presence of 1-1 salt as follows, according to Manning's theory,

$$\ln a_{2p} = -\frac{Z_{2p}\xi^{-1}}{2Z_{2g}^{2}} \ln [\xi^{-1}m_2 + 2m_3] + \ln m_2 + \text{constant} \qquad (2)$$

$$\text{for } \xi \ge 1/Z_{2g}$$

where m_3 indicates the equivalent concentration of the foreign salt. It should be mentioned that the validity of the single-ion activity concept (and the liquid junction problem) has been questioned, particularly in polyelectrolyte-containing solutions.[14] Thus the following argument would be valid only qualitatively. With this reservation, the comparison of the observed values of a_{2p} of NaPAA and sodium salts of poly(vinyl alcohol) partially acetalized to various degrees with glyoxylic acid (NaPVAG)[15] with the theory is shown in Figure 2. The solid straight lines denote the theoretical. The values of ξ and Z_{2p} used are listed in Table II. As is clear from the figure, Manning's theory predicts qualitatively (1) the linear relation between ln a_{2p} and ln m_2, (2) the negative slope, and (3) the increase of the (negative) slope with Z_{2p}. The sharp decrease of the single-ion activity of the macroions with increasing concentration reflects the situation that an increase in concentration does not imply an increase of "thermodynamically free" macroion species. We believe that newly added macroions lose their fugacity because they are "caught" by macroions already present by intermacroion linkage through the intermediary of gegenions (see section IIG).[15,16] This concentration dependence is characteristic compared with simple electrolytes or neutral polymers. The activity of the latter increases with concentration, except for the case where solvent–solute interaction is intense or the χ_1 parameter is large.[17] It is theoretically predicted as is shown in Figure 3 that, by the addition of foreign salt, a_{2p} becomes larger and

Table II
Characteristics of Polyelectrolytes at 25 °C and in Water

Polyelectrolyte	ξ	Z_{2p}	Degree of polymerization
CaPVAS	0.65	386	1700
NaPAA	2.85	1640	1640
CaPAA	2.85	640	640
NaPVAG-N3	0.30	179	1700
NaPVAG-N2	0.14	86	1700
NaPVAG-N1	0.09	51	1700
NaPSS	2.85	1090	1090
PEI·HCl	1.88	100	100
NaCMC (D.E. = 1.4)	1.37	46	100
NaCMC (D.E. = 0.75)	0.90	30	100
NaPES	2.85	770	770
DACS	1.37		

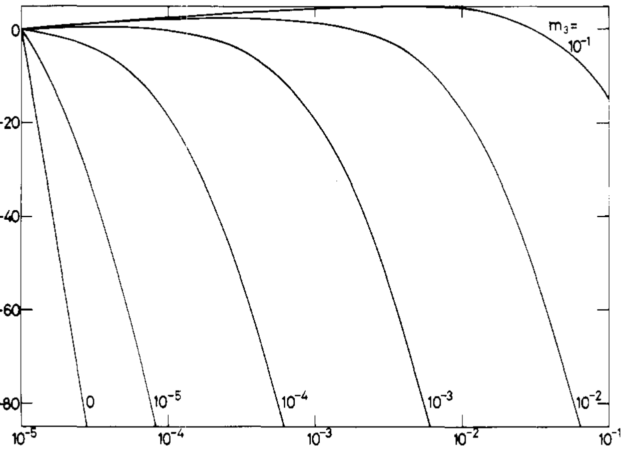

Figure 3. $\ln a_{2p}$ vs. m_2 plots in the presence of a foreign salt estimated from Manning's theory: $Z_{2g} = 2$, $\xi = 1.5$, $Z_{2p} = 1000$, $m_3 = 0\text{–}0.1$ *M (1:1 salt)*.

even starts increasing with m_2 at high salt concentrations. These results clearly show that the electrostatic shielding effects by the foreign salt ions are significant. Recently the dependences of a_{2p} on the parameters ξ and Z_{2p} were discussed in detail using Manning's theory.[18]

B. Solubility of Polyelectrolytes Sparingly Soluble in Water. The activities of sparingly soluble polyelectrolytes, in the presence and absence of foreign salt, must be equal to each other. Thus the following equation holds,

$$S/S^* = \gamma_2^*/\gamma_2 \tag{3}$$

where S denotes the solubility of polyelectrolyte and the asterisk indicates the reference state (the absence of foreign salt, i.e., $m_3 = 0$, in most cases). Since the γ_2 term can be estimated by Manning's theory, the solubility can be calculated from eq 4 and by the Newton–Raphson method by using a computer.[19]

$$f(S) = \ln (S/S^*) + \frac{Z_{2p}}{2\xi Z_{2g}(Z_{2g} + Z_{2p})} \ln \left\{\frac{\xi^{-1}S^* + 2m_3^*}{\xi^{-1}S + 2m_3}\right\} - \frac{Z_{2p}(1 - Z_{2g}\xi)}{\xi Z_{2g}(Z_{2g} + Z_{2p})} \ln (S^*/S) + \frac{Z_{2p}}{2\xi^2 Z_{2g}(Z_{2g} + Z_{2p})} \times \left\{\frac{S^*}{\xi^{-1}S^* + 2m_3^*} - \frac{S}{\xi^{-1}S + 2m_3}\right\} = 0 \tag{4}$$

We measured the solubility of CaPAA in the presence of foreign salts.[20] The results are shown in Figure 4. The solid curve is the theoretical one. Good agreement between the experimental and theoretical values is obtained. The solubilities of a polyelectrolyte complex between poly(4-vinyl-N-pentylpyridinium) cations and poly(styrenesulfonate) anions were also measured and discussed recently by us.[20]

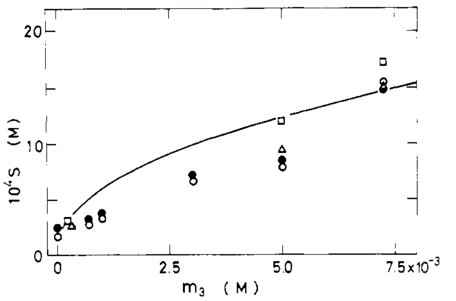

Figure 4. Solubility of CaPAA as a function of the concentration of a foreign salt at 25 °C: (○) NaCl (from titration of PAA); (●) NaCl (from atomic absorption of Ca); (△) KCl (titration); (□) LiCl (titration); (—) theory ($Z_{2g} = 2$, 1:1 salt, $Z_{2p} = 640$, $\xi = 2.85$, $S^* = 2 \times 10^{-4}$ M).

C. Partial Molal Volume. The investigations on the partial molal volume ($\overline{V}_2{}^0$) of polyelectrolyte, which is a pressure derivative of the mean activity coefficient, have been extensively carried out.[21–31] Skerjanc first discussed theoretically the concentration dependence of the apparent molal volume ($\overline{V}_2$) of polyelectrolyte by using theories of Lifson–Katchalsky and Manning.[29] Using Manning's theory, $\overline{V}_2$ is given as,

$$\overline{V}_2 - \overline{V}_2{}^0 = \frac{Z_{2p}RT}{2\xi Z_{2g}\xi P}\left(\frac{\partial \ln D}{\partial \ln P}\right) \ln m_2 + \text{constant} \tag{5}$$

where P denotes the pressure. $\overline{V}_2$ should increase with concentration when the electrostatic contribution is predominant compared with other interactions such as hydrophobic forces. In Figure 5, the observed $\overline{V}_2$ values of NaPAA (relative to that at $m_2 = 0.05$) were compared with eq 5. The theory is seen to reproduce positive slopes observed, inspite of the large experimental error involved. Skerjanc reported that $\overline{V}_2$ of poly(styrenesulfonate)s agreed with the theory.[29]

It should be noted here that the $\overline{V}_2$ of hydrophobic polyelectrolytes such as tetraalkylammonium salts of polyacid,[22] sodium polymethacrylate, and poly(4-vinyl-N-n-butylpyridinium) bromide,[23] were practically concentration independent, or even decreased with concentration. This is not explainable by the Manning theory, which takes into account only the electrostatic interactions. It may be accepted that the iceberg water structural effect by the hydrophobic interactions between the hydrophobic polymer and water tends to lower $\overline{V}_2$ with concentration, as was earlier discussed by Wen and Saito for tetraalkylammonium halides.[32]

D. Heat of Dilution. The heat of dilution (ΔH_{dil}) of polyelectrolyte solutions, which is a temperature derivative of the mean activity coefficient, has been measured mainly by two groups. The theoretical equation for ΔH_{dil} for ($Z_{2g} - Z_{2p}$)-type polyelectrolytes can be derived from Manning's theory as follows:[33]

$$(\Delta H_{\text{dil}})_{m_2 \to m_2{}^*} = \frac{NkT}{2Z_{2g}{}^2\xi}\left(1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}\right) \ln \left(\frac{m_2}{m_2{}^*}\right) \quad \text{for } \xi > 1/Z_{2g} \tag{6}$$

where N is Avogadro's number and $m_2{}^*$ is a reference concentration of polyelectrolyte solutions, where dilution was carried out from m_2. Comparison of the theory and experiment has been tried for several polyelectrolytes. First, theory predicts that the ΔH_{dil} changes linearly with $\ln m_2$. This theoretical outcome is in agreement with observations for sodium poly(styrenesulfonate) (at low concentrations),[34] for sodium carboxymethylcelluloses (NaCMC) of two different charge densities,[33] and for sodium polyphosphate (NaPP)[35] (see Figure 6). Similar agreement is also reported for hydro-

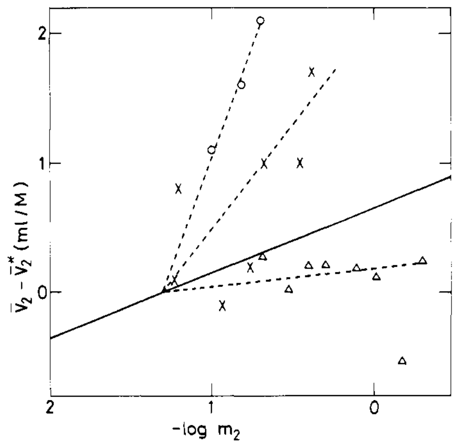

Figure 5. Comparison of the observed $\bar{V}_2 - \bar{V}_2^*$ values of NaPAA in water with those predicted by Manning's theory: (○) Tondre-Zana (from ref 27); (×) Ise-Okubo (from ref 22); (△) Roy-Chowdhury-Kale (from ref 23); (—) theory. ($\bar{V}_2^* = \bar{V}_2$ at $m_2 = 0.05$.)

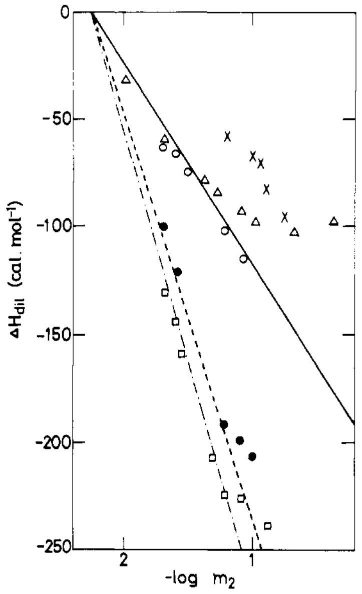

Figure 6. The heat of dilution of sodium carboxymethylcellulose (CMC), sodium poly(styrenesulfonate), sodium polyphosphate, and sodium polyacrylate at 25 °C: CMC, (□) degree of etherification (D.E.) = 0.75, (●) (D.E.) = 1.4; NaPP (○), NaPSS (△), and NaPAA (×). Manning theory for NaPP, NaPSt, NaPAA (—), for NaCMC (D.E. = 0.75) (- - -), and for NaCMC (D.E. = 1 4) (- • -).

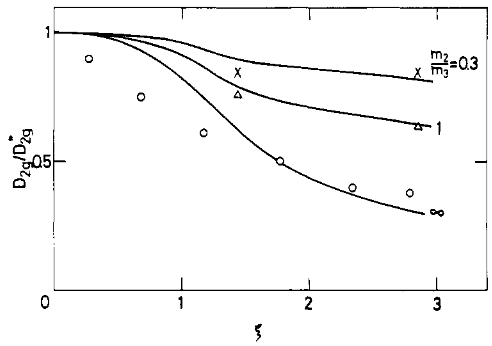

Figure 7. Comparison of the observed D_{2g} of NaPAA with those predicted by Manning's theory: (○) observed (ref 40), $m_2/m_3 = \infty$; (△) observed (ref 39), $m_2/m_3 = 1$; (×) observed (ref 39), $m_2/m_3 = 0.3$; (—) theory (eq 7 and 8).

chloride of polyethylenimine[35] at low concentrations; discrepancy at higher concentrations would be due to the branched structure of the polymer.

Experimentally, the ΔH_{dil} value became smaller with increasing temperature for NaCMC and NaPAA.[33] This tendency can be accounted for by eq 6. For NaPAA, excellent agreement was noticed at 40 °C, whereas the agreement at 25 °C was less satisfactory. We note that the mean activity and partial molal volume data for NaPAA at 25 °C were not well reproduced by the theory either.

Manning's theory is found to be invalid for polyelectrolytes containing hydrophobic components. The ΔH_{dil} observed for tetraalkylammonium salts of polyacrylic acid showed a sign opposite to that predicted by the theory.[36a] The observed ΔH_{dil} decreased with decreasing degree of sulfonation for partially sulfonated polystyrene, which is not explainable by eq 6.[36b] This situation is entirely reasonable, because only electrostatic interactions (but not hydrophobic interactions) were taken into account in Manning's theory. Recently, Boyd et al. measured the heat of dilution and the enthalpy of mixing for NaPSS and other anionic polyelectrolytes. These thermal quantities were predicted satisfactorily by Manning's theory in a diluted region of polyelectrolyte.[37]

E. Diffusion Coefficient. The application of Manning's theory to the self-diffusion of gegenions and coions was carried out first by Manning himself.[38] The condensed gegenions were assumed to have zero mobility. The uncondensed gegenions and coions were considered to perform Brownian motion subject to the locally inhomogeneous electric field created by the macroions. The resulting equation for the self-diffusion coefficient, D_{2g}, for uncondensed gegenions is

$$D_{2g}/D_{2g}^* = (\xi^{-1}X + 1)(X + 1)^{-1} \times [1 - \tfrac{1}{3}A(1;\xi^{-1}X)] \qquad \xi \geq 1 \qquad (7)$$

$$D_{2g}/D_{2g}^* = 1 - \tfrac{1}{3}A(\xi;X) \qquad \xi \leq 1 \qquad (8)$$

where D_{2g}^* is the coefficient in the absence of macroions and $A(1;\xi^{-1}X)$ and $A(\xi;X)$ are rapidly converging series given by eq 32 of ref 38. X denotes m_2/m_3. As is clearly seen in Figure 7, the experimental data for NaPAA in the presence[39] and in the absence[40] of salt are in good agreement with the theory at larger ξ values. Ander et al. also measured the diffusion coefficients of gegenions and coions of H_2O + sodium poly(styrenesulfonate) (or sodium alginate, or sodium ι-carrageenan) + foreign salt systems and discussed the results using Manning's theory.[41]

F. Interaction Parameters and Second Virial Coefficient in Ternary Solution. In the previous review[3] by one of us, various interaction parameters were discussed using experimental data. The parameters are those between polyelectrolyte and polyelectrolyte (β_{22}), between polylectrolyte and simple electrolyte (β_{23}), and between simple electrolyte and simple electrolyte (β_{33}) given by the following equation.[42]

$$\beta_{ij} = \nu_i \, \partial \ln \gamma_i / \partial m_j' \qquad (9)$$

where m' is the molal concentration and ν_i denotes the number of moles of ions formed from 1 mol of electrolyte i. The calculated values of β_{22} from Manning's theory increased sharply with increasing m_2 for small m_3, whereas it was almost independent of m_2 when m_3 is high. These tendencies of β_{22} are very similar to the observed ones.[43] However, quantitative comparison between the calculation and the observation is difficult, because the experiments were carried out at high polyelectrolyte concentration.

According to Scatchard,[44] the second virial coefficient, B_2, at $m_2 = 0$, can be given in terms of the interaction parameters as follows,

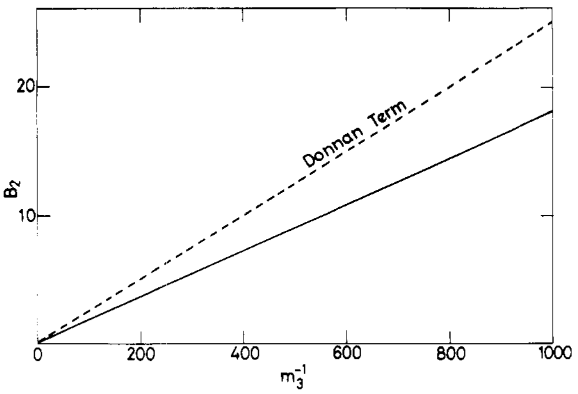

Figure 8. Estimation of the second virial coefficient, B_2, from Manning's theory: $\xi = 2.85$, $Z_{2g} = 1$, $Z_{2p} = 3000$, molecular weight = 3 000 000, (1-1) foreign salt 25 °C.

$$B_2 = \frac{10^3}{2W_2^2}\left[\frac{Z_{2p}^2}{m_3} + \beta_{22} - m_3\left(\frac{Z_{2p}}{m_3} + \beta_{23}\right)^2/(2 + \beta_{33}m_3)\right] \tag{10}$$

where W_2 is the molecular weight of the polyelectrolyte. In Figure 8, B_2 values calculated are plotted against m_3^{-1} (solid line); a linear relationship is seen to exist between B_2 and m_3^{-1}. This linearity is due to the fact that β_{22} and β_{23} are practically linear functions of m_3^{-1} and that the inequality $|\beta_{22}| \gg |\beta_{23}| \gg |\beta_{33}|$ holds. It should be mentioned here that B_2 lies near the so-called Donnan contribution as is seen from Figure 8 and as was often claimed.[2] It was experimentally found, however, that the order of the magnitude of $Z_{2p}^2/2m_3$, which corresponds to the Donnan term, is comparable to that of β_{22}, and the β_{22} term is partly canceled out by the contributions from β_{23} and β_{33}. Experimentally we found that the B_2 of the system H_2O + sodium polyacrylate (NaPAA) + sodium chloride is apparently close to the Donnan term.[43] From the above argument, we claim again that the observed agreement between B_2 and the Donnan term is deceptive in hiding β_{ij} (particularly β_{22}) being extremely large. The ratios of B_2 estimated by the Manning theory to the contribution from the Donnan term are listed in Table III as a function of ξ. The ratio first decreases with increasing ξ and then increases.

G. Miscellaneous Thermodynamic Quantities. Since we discussed both the mean activity coefficient and heat of dilution (ΔH_{dil}) of polyelectrolyte in the previous section, we can consider now the electrostatic free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) of polyelectrolytes. From the fundamental thermodynamic relations and the Manning theory, ΔG, ΔH, and ΔS (per base mol of macroions) are given as follows for ($Z_{2g} - Z_{2p}$)-type polyelectrolytes having ξ larger than Z_{2g}^{-1}.

$$\Delta G = RT \ln (m_2\gamma_2/m_2{}^*\gamma_2{}^*) = \frac{RT}{2Z_{2g}^2\xi}\ln (m_2/m_2{}^*) \tag{11}$$

$$\Delta H = -\Delta H_{\text{dil}} = -\frac{RT}{2Z_{2g}^2\xi}\left(1 + \frac{T}{D}\frac{\partial D}{\partial T}\right)\ln (m_2/m_2{}^*) \tag{12}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = -\frac{R}{Z_{2g}^2\xi}\left(1 + {}^1\!/_2\frac{T}{D}\frac{\partial D}{\partial T}\right)\ln (m_2/m_2{}^*) \tag{13}$$

The ΔS values are estimated from existing ΔG and ΔH_{dil} data of NaPAA[33,36,45] and are shown in Figure 9 (solid curve 1), poly(sytrenesulfonic acid) (HPSS)[5,34] (curve 2), and hydrochloride of polyethylenimine (PEI·HCl)[35,46] (curve 3). These observed values were compared with the theory (broken lines). The agreement between the theory and the experiment is not always good, since the experimental error is fairly large. However, both experimentally and theoretically, ΔS is negative and decreases with increasing m_2, whereas both ΔG and ΔH increase, though this is not shown in the figure. We note that the negative ΔS is not inconsistent with "regular" ionic distribution formed by the strong intermacroion linkage through the intermediary of gegenions which was proposed earlier by us.[3] The tendency for ΔS to decrease with increasing m_2 is not inconsistent with the sharp decrease of the macroion activity (Figure 2).[47]

Table III
The Changes of the B_2/Donnan Term with ξ Estimated by Manning's Theory[a]

ξ	0.1	0.3	0.6	1	2	2.85	4	5
B_2/Donnan term	0.98	0.96	0.90	0.74	0.68	0.73	0.78	0.81

[a] Z_{2p} and m_3 are taken as (ξ/2.85) × 3000 and 0.001 M, respectively.

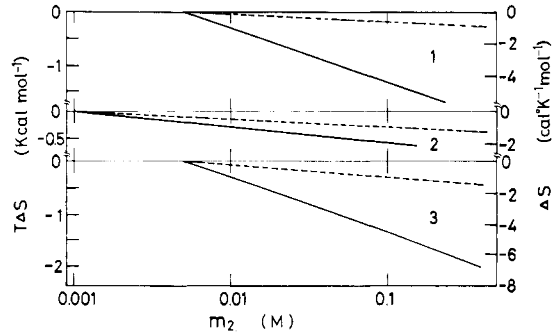

Figure 9. Comparison of the observed $T\Delta S$ with the calculated value for NaPAA (1), HPSS (2), and PEI·HCl (3) at 25 °C: (—) observed, (- - -) Manning's theory.

Agar and Lobo measured for the first time the Soret coefficient, σ, of aqueous sodium polyacrylate.[50] They estimated the heat of transport, Q, from the σ values by using the thermodynamic relation (eq 14) and by assuming that the term $[\partial \ln \gamma_2/\partial \ln m_2]$ equals zero.

$$Q = (1 + Z_{2p})[1 + \partial \ln \gamma_2/\partial \ln m_2]RT^2\sigma \tag{14}$$

According to Manning's theory the term $[\partial \ln \gamma_2/\partial \ln m_2]$ is not zero as was also experimentally confirmed,[12] but −0.825. Thus the Q values given by Agar and Lobo seem to be an overestimation.

Recently, application of Manning's theory to the surface phenomena was carried out by us. The excess concentrations (Γ_2) at the air–solution interface were determined for poly(4-vinyl-*N*-alkylpyridinium) halides and other hydrophobic polyelectrolytes[51] using eq 15.

$$\Gamma_2 = -\frac{2\xi Z_{2g}^2 Z_{2p}}{RT(Z_{2g} + Z_{2p})}\,\frac{\mathrm{d[surface\ tension]}}{\mathrm{d}\ln m_2} \quad \text{for } \xi \geq 1/Z_{2g} \tag{15}$$

The Γ_2 of the polyelectrolytes at high concentrations was found to be larger than that found for low molecular weight surfactants such as cetyltrimethylammonium bromide.[51]

III. Kinetic Aspects of Polyelectrolyte Dilute Solutions

Connected with understanding the mechanism of enzyme action, intensive studies have been carried out on the catalytic influence of synthetic polyelectrolytes on various kinds of reactions.[3,52–55] Interionic reactions between cationic species were found to be enormously accelerated by anionic polyelectrolytes, and reactions between cations and anions were strongly hindered by both cationic and anionic polyelectrolytes. Though the phenomena are highly interesting, theoretical analysis, which can account for simultaneously not only

Table IV
Comparison of the Observed k_2/k_2^* with that Calculated from the Observed Activity Data for the Ammonium Cyanate–Urea Conversion

[NaPAA], M	log (k_2/k_2^*) Obsd	log (k_2/k_2^*) Calcd from the obsd activity data
0	0	0
0.056	−0.140	−0.145
0.112	−0.253	−0.251
0.223	−0.421	−0.408

the kinetic properties but also other thermodynamic aspects of polyelectrolyte solutions, was lacking. We wished to develop such an interpretation by using Manning's theory and Brønsted–Bjerrum theory,[56,57] which reads for reaction $A + B \rightleftarrows X \rightarrow C + D$

$$k_2 = k_{20}(\gamma_A \gamma_B/\gamma_X) \qquad (16)$$

where X is the activated complex, γ the (single-ion) activity coefficient of the reactants and the activated complex, and k_{20} the rate constant at zero ionic strength. For reactions between monovalent cations and anions, we have

$$\log k_2/k_2^* = 2 \log \gamma_{AB}/\gamma_{AB}^* - \log \gamma_X/\gamma_X^* \qquad (17)$$

where γ_{AB} is the mean activity coefficient of the hypothetical electrolyte AB and zero polymer concentration is chosen as a reference (denoted by asterisk). It was proposed[58] earlier to evaluate k_2/k_2^* by introducing the "observed" values of the γ's into eq 17 for ammonium cyanate–urea conversion, which was decelerated by addition of polyelectrolytes. The agreement with experiment is excellent (Table IV), suggesting that the polyelectrolyte influence is the primary salt effect. This type of argument is however stricly restricted to such cases where γ_X can be assumed to be unity, and to interionic reactions between ions of the same amount of charge with different sign, because γ_X cannot generally be obtained experimentally.

In order to overcome this difficulty, we need to evaluate the activity terms in eq 16 by using appropriate theories on electrolyte solutions. In the case of simple electrolytes, the Debye–Hückel theory is used and, as is well-known, the final result is

$$\log k_2 = \log (kTK^{\ddagger}/h) + 1.018 Z_A \cdot Z_B I^{1/2} (25\ {}^\circ\mathrm{C, water}) \qquad (18)$$

where $K^{\ddagger}$ is the equilibrium constant between X and the reactants, Z's are the valencies of the reactants, I is the ionic strength, and k, T, and h have the usual meanings. The excellent agreement is proverbial.

Obviously, the Debye–Hückel theory is not valid for polyelectrolyte-containing systems. Instead, we use Manning's theory on polyelectrolyte solutions to calculate the γ's. The results are described below.

A. A^+–B^- Reactions.[59] An example is the ammonium cyante–urea conversion. In this case ionic species contained in solutions are $NH_4^+(A^+)$, $OCN^-(B^-)$, polyions, and their gegenions. The mean activity coefficient γ_{AB} of the ammonium cyanate is given by Manning's theory as follows

$$\gamma_{AB}^2 = \frac{\xi^{-1} m_2 + m_3}{m_2 + m_3} \exp\left(\frac{-\xi^{-1} m_2}{\xi^{-1} m_2 + m_3}\right) \qquad (19)$$

where m_2 and m_3 are the concentrations (equivalent or mol ions per L) of polyions and the salt. By combining eq 17 and 19, we have

$$\ln k_2/k_2^* = \ln \frac{1 + \xi^{-1} X}{X + 1} - \frac{X}{X + 2\xi} \qquad (20)$$

where $X = m_2/m_3$. Equation 20 is very satisfactorily compared with experiment in Figure 10.

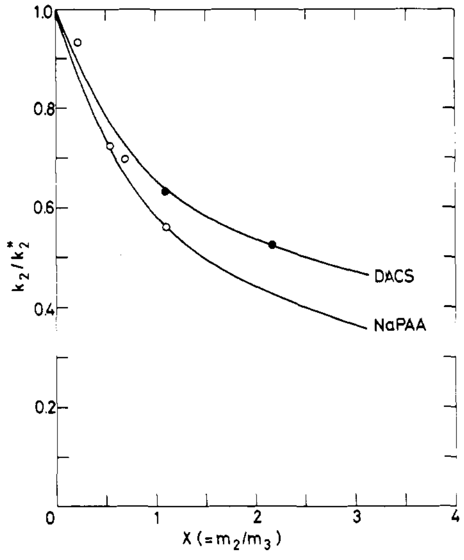

Figure 10. Comparison of the observed k_2 of ammonium cyanate–urea conversion with those predicted by Manning's theory (50 °C): (○) NaPAA added, $[NH_4OCN] = 0.0205$ M (ref 58); (●) DACS added, $[NH_4OCN] = 0.1025$ M (ref 58); (—) eq 20 from Mita et al. (ref 59) by permission of the Chemical Society].

Likewise satisfactory results are obtained for an addition reaction of CN^- to (monovalent cationic) derivatives of nicotinamide.[60]

The activation parameters were also calculated by using eq 20. The increase in the free energy of activation for the ammonium cyanate–urea conversion by addition of polyelectrolytes was well reproduced by the theory.[59]

B. A^{Z_A+}–B^{Z_B+} Reactions with Polyanions[61] ($Z_A > Z_B$, $Z_A \geq 2$, $Z_B \geq 1$). The Bjerrum–Brønsted–Manning treatment for this and the following cases is not so straightforward as for the previous one, because an assumption regarding competitive condensation of the reactant ions by polyions has to be introduced. In the present case A^{Z_A+} is assumed to condense on the polyion in preference to B^{Z_B+} until either the net value of ξ is reduced to $1/Z_A$ or A^{Z_A+} is depleted. For convenience, we discuss only the cases where the ξ value is larger than $1/Z_A$, A^{Z_A+} condenses on a polyion until ξ is lowered to $1/Z_A$, and "uncondensed" A^{Z_A+} exists. When A^{Z_A+} exists in excess over B^{Z_B+}, the reaction is assumed to occur between condensed A^{Z_A+} and uncondensed B^{Z_B+}. The single-ion activity coefficients of these ionic species are derived and the rate constant ratio is given approximately by

$$k_2/k_{2R} = X_A/X_{AR} \qquad (21)$$

when $X_A = m_2/m_A$ and the subscript R denotes a reference state (the lowest polymer concentration used). (This choice is necessary because of the assumption that reactions between uncondensed A^{Z_A+} and B^{Z_B+} are negligible.) Equation 21 is compared with experiments for electron-transfer reactions[62] in Figure 11. The linear concentration dependence of the rate constant is successfully substantiated. The following reactions are found to be in accord with eq 21: CH_2BrCOO^-–$S_2O_3^{2-}$ with poly(ethylenimine hydrochloride) (PEI·HCl),[63] CH_2ClCOO^-–$S_2O_3^{2-}$ with a copolymer of dimethyldiallylammonium chloride and SO_2 (a cationic polymer, DACS),[64] and Ag^+- or Tl^{3+}-induced aquation of $Co(NH_3)_5Br^{2+}$ with NaPSS.[65] Equation 21 is not valid for electron-transfer reactions between Co complexes and Cr^{2+} [66] or $Ru(NH_3)_6^{2+}$ [67] and between $Co(phen)_3^{3+}$ and $Co(phen)_3^{2+}$ [68] in the presence of anionic polyelectrolytes probably because the polymer concentration employed was high.

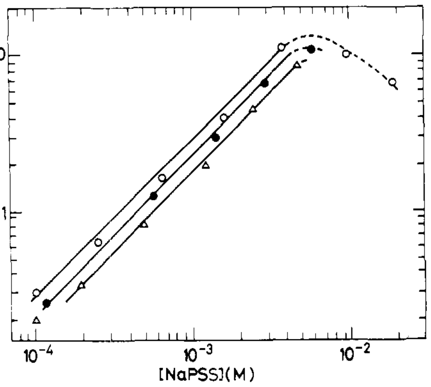

Figure 11. Electron-transfer reaction between Fe^{2+} and $Co(NH_3)_4(N_3)_2^+$ in the presence of NaPSS of three different degrees of solfonation ((○) 0.62, (●) 0.78, (△) 1) [from Shikata et al. (ref 62) by permission of the Royal Society]: (—) Manning's theory (eq 21), $[Fe^{2+}] = 1.5 \times 10^{-5}$ M, [Co complex] $= 3 \times 10^{-5}$ M, $[H^+] = 10^{-3}$ M.

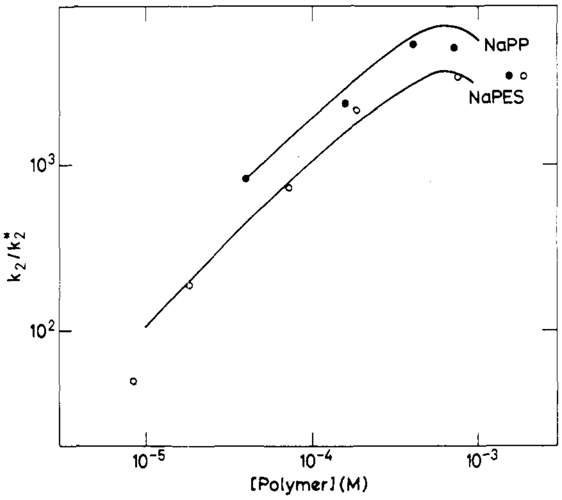

Figure 12. Hg^{2+}-induced aquation of $Co(NH_3)_5Br^{2+}$: (○) NaPES; (●) NaPP (ref 65); (—) Manning's theory (eq 22),$[Hg^{2+}] = 5 \times 10^{-4}$ M, $[Co(NH_3)_5Br^{2+}] = 6 \times 10^{-5}$ M [from Mita et al. (ref 61), by permission of the Chemical Society].

C. A^{Z_A+}–B^{Z_B+} Reactions with Polyanions[61] ($Z_A = Z_B \geq 2$). In this case, four types of reactions were considered, i.e., (i) between uncondensed A^{Z_A+} and uncondensed B^{Z_B+}, (ii) between uncondensed A^{Z_A+} and condensed B^{Z_B+}, (iii) between condensed A^{Z_A+} and uncondensed B^{Z_B+}, and (iv) between condensed A^{Z_A+} and condensed B^{Z_B+}. The reactions i and iv may be assumed to be negligible compared with the reactions ii and iii due to electrostatic repulsion and immobility of condensed gegenions. Since the reactions ii and iii are symmetrical with each other, we may discuss either ii or iii. With an assumption that the ratio of the fractions of A^{Z_A+} and B^{Z_B+} condensed on a polyion is proportional to the ratio of their initial concentrations, the activity coefficients are evaluated and the rate constant ratio is approximately

$$k_2/k_{2R} = \left[X - \frac{1}{Z_A}\left(1 - \frac{1}{Z_A\xi}\right)X^2\right] \Big/ \left[X_R - \frac{1}{Z_A}\left(1 - \frac{1}{Z_A\xi}\right){X_R}^2\right] \quad (22)$$

with $X = m_2/(m_A + m_B)$. In Figure 12, eq 22 is compared with observed data for Hg^{2+}-induced aquation of $Co(NH_3)_5Br^{2+}$ in the presence of sodium polyphosphate (NaPP) and sodium poly(ethylenesulfonate) (NaPES). Agreement is reasonably good. It is to be noted that eq 22 gives a maximum in the rate–concentration curve (as is often observed), as a result of a balance of an increasing tendency of the fraction of condensed A (with polymer concentration) and a decreasing trend of the fraction of uncondensed B.

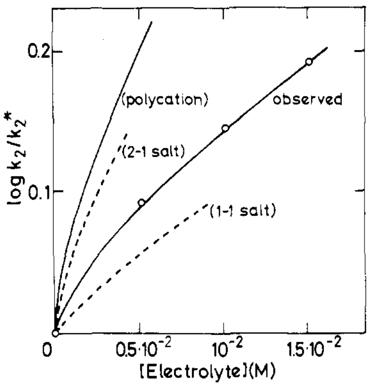

Figure 13. Electron-transfer reactions in the presence of a cationic polyelectrolyte: (○) observed (ref 62), (—) Manning's theory (eq 23), (- - -) Debye–Hückel theory for (2–1) and (1–1) salts [from Shikata et al. (ref 62) by permission of the Royal Society].

D. A^{Z_A+}–B^{Z_B+} Reactions with Polycations.[62] The catalytic influence has often been suggested to be due to the so-called concentration effect. (This is understood to imply that the reactant concentration around polyions is raised by high electrostatic field of the oppositely charged polyions, causing enhanced collision frequency and hence reaction rate.) This interpretation was, however, not consistent with observed thermodynamic parameters, though the argument was not cogent enough.[55]

If the concentration effect is a main factor for the observed catalysis, we may expect that reactions between cations should be hindered or unaffected by addition of cationic polyions. Kinetic study on electron-transfer reactions between Fe^{2+} and $Co(NH_3)_4(N_3)_2^+$ shows[62] that the reaction is unexpectedly accelerated by addition of a cationic polymer, DACS, though slightly. Independently the Bjerrum–Brønsted–Manning treatment is found to give the following equation for the present case

$$\ln k_2/k_2{}^* = Z_A \cdot Z_B\xi^{-1}m_2/ [\xi^{-1}m_2 + ({Z_A}^2 + Z_A)m_A + ({Z_B}^2 + Z_B)m_B + 2m_3] \quad (23)$$

The right-hand side of eq 23 contains only positive quantities so that $k_2/k_2{}^* > 1$. In Figure 13, the experimental data are compared with eq 23. The acceleration is substantiated, through qualitatively, by eq 23, confirming that the catalytic influence by polyelectrolytes is basically the primary salt effect.

In this aspect, three points are to be noted. First, the Bjerrum–Brønsted–Debye–Hückel theory (for the primary salt effect) also predicts acceleration by salts of multivalent cation and monovalent anion for reactions between cations [see eq 18]. Experimentally, Olson and Simonson found that the $Co(NH_3)_5Br^{2+}$–Hg^{2+} reaction was accelerated by $NaClO_4$ or $La(ClO_4)_3$.[69] Acceleration was also noticed for the nitrourethane–OH^- reaction in the presence of salts of monovalent cations and polyvalent anions.[70] Second, the acceleration in Figure 13 is not due to an exclusion volume effect toward reactant by DACS, which is negligibly small at the polymer concentrations employed. Third, eq 23 shows that $k_2/k_2{}^*$ decreases with increasing ξ (charge density), indicating that the acceleration predicted by eq 23 is not due to electrostatic exclusion between the reactants and the polyions.

E. Kinetics of Helix Formation of DNA. Equation 16 was originally derived for chemical reactions taking place between simple reactants in the presence of simple electrolytes. As stated above, we tried to extend the equation to chemical reactions in the presence of polyelectrolytes by using Manning's theory. This approach was recently further extended to a physical process proceeding between polyions in the presence of simple electrolytes by Manning.[71] The first target of this interesting study was the association reaction of complementary polynucleotide strands which was schematized as

$$A + A' \rightleftarrows C_0 \rightarrow \text{nucleation} \rightarrow \text{zippering} \qquad (24)$$

where A and A′ are the separated strands and C_0 is the nonbonded precursor to the nucleated form. With the assumption that C_0 is in equilibrium with A and A′ with the equilibrium constant K and that nucleation is rate limiting, the measured rate constant k_2 was claimed to be written as

$$k_2 \sim K(\gamma_A \cdot \gamma_{A'}/\gamma_{C_0}) \qquad (25)$$

where γ is the single-ion activity coefficient of polyionic reactants and activated complex. After taking into account the ionic strength dependence of K and γ (by Manning's theory), the following equation was obtained

$$k_2 = \beta(T;T_m)\gamma_{Na^+}{}^{Q/\xi}[Na^+]^{Q/2\xi} \qquad (26)$$

where $\beta(T;T_m)$ is a proportionality factor, T_m is the melting temperature, Q is the number of phosphate groups in each of the two approximately aligned single-stranded segments which constitute C_0, and γ_{Na^+} and $[Na^+]$ are the activity coefficient and concentration of Na^+ (gegenions). From comparison of eq 26 with the observed ionic strength dependence of k_2, Q/ξ was found to be 7.4, which gave 13–16 nucleotides for Q using a ξ value of 1.7–2.2 for the single-stranded chain. The stability measurements by Niyogi et al.[72,73] show that nucleation formation must be followed by zippering of about 10 or 15 more neighboring base pairs. The close correspondence of Q to this measurement indicates that Q is the minimum length required to stabilize the complex and allow reaction completion and substantiate the validity of Manning's theory.

IV. Concluding Remark

The above argument demonstrates that various thermodynamic properties of polyelectrolyte solutions and kinetic properties can be fairly satisfactorily discussed by using Manning's theory. It should be stressed again that the theory contains only one parameter, rendering us a great advantage. Naturally, there exists a limit to the theory. As was originally claimed by Manning, it is a limiting law, which is expected to be valid only at low ionic concentrations. The point-charge approximation adopted in the theory does not allow us to consider the specificity of simple ions within the framework of the theory. There exist, furthermore, experimental data of polyelectrolyte catalysis showing definitely the necessity to take into consideration nonelectrostatic factors such as dehydration of reactants.[74] In addition, the treatment of the simple-ion condensation in the vicinity of polyions raises a difficulty in quantitative discussion of the kinetic processes between similarly charged ionic species; only the concentration or ionic strength dependence of the rate constants could be discussed. Even with the deficiencies in mind, it may be said that the theory in question is a useful one at least to the first approximation.

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Note Added in Press. First it should be mentioned that the shift of chemical equilibria by addition of polyelectrolytes was also successfully discussed by the present treatment. [T. Okubo, T. Ishiwatari, K. Mita, and N. Ise, *J. Phys. Chem.*, **79**, 2108 (1975).] In other words, the phenomenon is a secondary salt effect.

Second, Mohan reported the presence of a peak in the correlation function of the small-angle neutron scattering on polyelectrolyte solutions, who ascribed it to "ordering" between the macroions. (M. Mohan, 4th International Conference on Small-Angle Scattering of X-Rays and Neutrons, Gatlinburg, Tenn., October 1977.) It is highly possible that what we described as the "regular" ionic distribution formed by the intermacroion linkage through the intermediary of gegenions (see sections IIB and IIG) is essentially the same as "ordering" discussed by Mohan. It would be worthy to point out that Imai proposed a "free-volume model" theory in which macroion–macroion interaction was considered by adopting a lattice-like regular distribution of macroions [N. Imai, IUPAC 26th Congress, Tokyo, September 1977, Preprint page 1365].

Third, we are glad to know that our earlier observation of the steep decrease of the single-ion activity of the macroion species with increasing concentration [N. Ise and T. Okubo, *J. Phys. Chem.*, **69**, 4102 (1965)] has recently been confirmed by Vesnaver et al. [G. Vesnaver, J. Span, and D. Dolar, *Makromol. Chem.*, **178**, 2429 (1977)]. However, it is difficult to admit their view that polyelectrolyte properties are "primarily determined by the interaction" between macroion and its gegenion and macroion–macroion interaction has not a similar importance as the macroion–gegenion interaction. The basis for our assertion is the magnitude of the interaction parameter β_{ij} (see section IIF). The measurement on the ternary system H_2O–sodium polyacrylate–NaCl [T. Okubo, N. Ise, and F. Matsui, *J. Am. Chem. Soc.*, **89**, 3697 (1973)] gives at [NaCl] = 0.1 M and at zero polymer concentration $\beta_{22} = -8.8 \times 10^4$ and $\beta_{23} = -3.7 \times 10^2$. Under the experimental condition Vesnaver et al. employed ([NaCl] = 0 M) the difference between β_{22} and β_{23} must be much larger. The reason why the Manning theory (which seemingly neglects the intermacroion interactions) was nonetheless successful in describing various polyelectrolyte properties considered in the present review and the activity coefficient data by Vesnaver et al. as well would be in the physical situation in which the intense intermacroion interactions cancel out partially or almost completely, depending on the quantity to be discussed. For example, no matter how strong the macroion–macroion interaction would be, the gegenions right in the middle between two macroions would behave "ideally" as a result of compensation of opposing influence from the two macroions. We note that the presence of the regular ionic distribution may allow such a compensation to occur in a much wider region in solutions. Therefore, it seems to us that the linear line charge model, Manning's theory based thereupon, the cube-root rule, and the regular ionic lattice structure have much deeper implications than Vesnaver et al. suggest.

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(1) The latter half of the present article (the kinetic aspect) is based on a paper delivered at the Faraday Informal Discussion, Cranfield, England, January 1976.
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