less on molecular weight when we take into account the variation of the specific volume $\bar{v}_2$ of the pure liquid polymer vs. their molecular weight. It is then obvious that relation 14 describes very well the behavior of the excess volume over the entire range of molecular weight. Concerning the behavior of the ASV, Figure 7 shows that the scatter of the experimental points is also less for high molecular weight than previously and that the agreement between calculation and the experimental data of the ASV is excellent.

Conclusion

We have presented a modified version of the bifluid theory using the nonrandom mixing approximation to fit the ASV behavior of polystyrene vs. concentration and molecular weight in the dilute and semidilute regimes. Introducing the local organization of the solvent driven by the expansion coefficient α and by the length of the conformer sequences,[20] we were able to describe our data with only two parameters, X_2 and k'. This modification does not affect Flory's equation of state for pure components but that of the mixture. Some restrictions of these calculations are due to the determination of the crossover concentration or c^*, where the expansion α of the coil has a different scaling law vs. molecular weight. These variations of α with the molecular weight was computed as in the asymptotic region and may explain the discrepancy observed for the excess volume ΔV in the concentrated regime.

Registry No. Polystyrene (homopolymer), 9003-53-6.

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Counterion Condensation in Polyelectrolyte Solution: A Theoretical Prediction of the Dependences on the Ionic Strength and the Degree of Polymerization

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ABSTRACT: As an extension of Manning theory, we propose, without explicit consideration of the condensed phase, a free energy minimization treatment for the estimation of the degree of counterion condensation in polyelectrolyte solutions. The theory is compared with those of Manning, Iwasa et al., Ramanathan et al., and Delville and with experimental data on counterion activity coefficients. The agreement with the data is satisfactory.

Introduction

Manning theory, which first appeared in 1969[1] based on Mayer's cluster theory, predicts the degree of counterion condensation, θ, of polyelectrolyte assumed as an infinitely long linear charge array

$$\nu\theta = 1 - \xi_0/\xi \tag{1}$$

$$\xi = e^2/DkTb \tag{2}$$

where ν is the valence of the counterion, e the electronic charge, D the dielectric constant of the bulk solvent, T the Kelvin temperature, b the axial charge spacing of the polyelectrolyte, and ξ the nondimensional charge density parameter. When $\xi > \xi_0$ counterions will condense to reduce the effective polymer charge density to ξ_0. This critical charge density is expressed as ν^{-1}. Manning has obtained eq 1 also based on a two-phase model[2] in which electrostatic energy of polyelectrolyte and mixing entropy of counterions in the condensed and the bulk phases are taken into account. In this model, a free energy minimization method was applied to infinitely long polyelectrolytes in the limit of infinite dilution under an assumption that the volume of the condensed phase V_p is a constant independent of the ionic strength. The limiting law and the two-phase model of Manning have been referred to for elucidation of colligative and other physicochemical properties of polyelectrolyte solutions.[3-8]

On the other hand, criticisms about the model adopted by Manning have also appeared. For instance, Guéron et al.[9] have shown, based on calculation of the Poisson–Boltzmann distribution of counterions around a rodlike polyelectrolyte, that the volume corresponding to V_p, in which condensed counterions reside, depends on the ionic strength and becomes infinitely large in the limit of infinite dilution. Recently, Le Bret and Zimm[10] have compared the Poisson–Boltzmann equation and Manning theory and concluded that a large fraction of counterions which are predicted by Manning to be condensed lies within a finite volume even in the limit of infinite dilution. Woodbury and Ramanathan[11] have discussed end effects on the counterion condensation phenomenon using the Mayer cluster theory and showed that the higher order cluster terms for rigid polyion with finite length are insignificant in the limit of infinite dilution, which means no occurrence of condensation in the limit. They have reported a statistical mechanical study of polyelectrolyte[12] and expressed their main results as

$$\xi_0 = 1 \qquad \text{when } \kappa L/2 \gtrsim 1 \tag{3}$$

$$\xi_0 = \frac{\log (\kappa r)^{-1}}{\log (L/2r)} > 1 \qquad \text{when } \kappa L/2 \ll 1 \tag{4}$$

where ξ_0 is the critical value for the condensation of single-valent counterion, κ the Debye parameter, L the length of the polyion, and r the distance of the closest approach to the polyion. These equations were derived under the conditions of $L \gg r$ and $\kappa e^2/DkT \ll 1$, the latter of which means high dilution of the added salts. According to eq 3 and 4, Manning theory is valid only when L is larger than or comparable to κ^{-1}; otherwise the degree of condensation, which is expressed to be smaller than that by Manning theory, decreases with the decrease in the ionic strength.

As shown above, Manning theory, which was obtained for infinitely long polymer in infinitely dilute solution, is inadequate for discussing the dependences of counterion condensation on the ionic strength and on the polymer chain length. Equation 4 may be of use for such purposes, although this equation is valid under rather restricted conditions and contains an unknown parameter, r.

In this paper, we estimate the degree of counterion condensation and the counterion activity coefficient of polyelectrolyte solution, based upon the free energy minimization proposed by Manning or Iwasa,[13] but with no explicit reference to the condensed phase. In other words, V_p is not assumed for the calculation of the free energy to estimate the degree of counterion condensation of a polyelectrolyte with finite length in solution of finite dilution. The degrees of condensation and activity coefficients thus derived are compared with those predicted by other theories or obtained experimentally.

Model

We treat a system consisting of polyion, salt composed of common counterion and single-valent co-ion, and solvent (water).

We use the following polymer model and assumptions in the free energy calculation.

(1) The polymer chain is expressed by a linear array of unit charges with a finite length.

(2) Condensed counterions reside just around the polymer chain, the effective charge density of which is reduced to $(1 - \nu\theta)^2\xi$. Such counterions do not contribute to the mixing entropy of counterions in the bulk phase.

(3) Only long-range electrostatic interaction is taken into account for small ion–polyion interaction. Effects of the short-range interactions are implicitly included in the reduction of the effective polymer charge by the counterion condensation.

(4) Effects of solvation (hydration) of small ions and polyions on the condensation are neglected.

Equations for the Free Energy Calculation. The free energy of the system, ΔG, can be expressed by using the terms that contain θ as follows

$$\Delta G/RT = C_+(\ln C_+ + \ln \gamma_+) + C_- \ln \gamma_- + C_p \ln \gamma_p + C_w \ln a_w \tag{5}$$

where C means molar concentration, γ means activity coefficient, and a is activity. Subscripts +, −, p, and w mean counterion, co-ion, polyion, and water (solvent), respectively. C_+, C_-, and a_w are given by the following equations

$$C_+ = C_s + (1 - \nu\theta)C_p/\nu \tag{6a}$$

$$C_- = \nu C_s \tag{6b}$$

$$a_w = C_w/(C_w + (1 - \nu\theta)C_p/\nu + (1 + \nu)C_s) \tag{6c}$$

where C_s is the salt concentration and a_w is expressed by the mole fraction in which the contribution of polyion is neglected. Equation 5 and the equations of Manning or of Iwasa differ in a few points. For example, in eq 5, the entropy term for counterions in the condensed phase is not considered, and the activity coefficients of small ions and the activity of solvent water are taken into account. For the cases of counterions with which no dehydration is concerned upon condensation, the water activity term does not contribute much to the free energy. However, when dehydration does take place upon condensation of counterions, e.g., divalent cations, the inclusion of this term becomes essential.

Excess free energy, which is necessary for the estimation of activity coefficients γ_i, is expressed by summing the electrostatic energy between charges on the polyion via the Debye–Hückel screened Coulombic potential as

$$F_{ex}/RT = C_p\xi(1 - \nu\theta)^2 \sum_{m=1}^{N-1} (1 - m/N) \exp(-\kappa m b)/m \tag{7a}$$

$$\kappa^2 = 8\pi \times 10^{-3} N_{Av}(e^2/DkT)I \tag{7b}$$

$$I = \tfrac{1}{2}(\nu^2 C_s + \nu C_s + \nu(1 - \nu\theta)C_p) \tag{7c}$$

N is the number of charges on a polyion, N_{Av} is the Avogadro number, and the ionic strength I contains a contribution of "free" counterions of the polyion. Equation 7a gives $\ln \gamma_{+,-}$ and $\ln \gamma_p$ at 25 °C as

$$\begin{aligned} \ln \gamma_{+,-} &= (\partial(F_{ex}/RT)/\partial C_{+,-})_{C_{-,+},C_p,\theta} \\ &= -0.830\nu^2 A C_p(1 - \nu\theta)^2/I^{1/2} \end{aligned} \tag{8}$$

$$\ln \gamma_p = (\partial(F_{ex}/RT)/\partial C_p)_{C_+,C_-,\theta} = 7.14 \times 10^{-8}(1 - \nu\theta)^2 \sum_{m=1}^{N-1} (1 - m/N) \exp(-\kappa m b)/mb \tag{9}$$

ν^2 is replaced by 1.0 for $\ln \gamma_-$. A in eq 8 is given as $A = ((N - 1)B + B^{N+1} - NB^2)/(1 - B)^2 N$, where $B = \exp(-\kappa b)$. It should be noted here that F_{ex} obtained by eq 7a estimates only polyion–small ion interaction; i.e., when $\gamma_{+,-}$ values are compared with experimental values, correction should be made by using activity coefficients of small ions in the absence of the polyion, as shown in the next section. The θ value, with which ΔG assumes the minimum value,

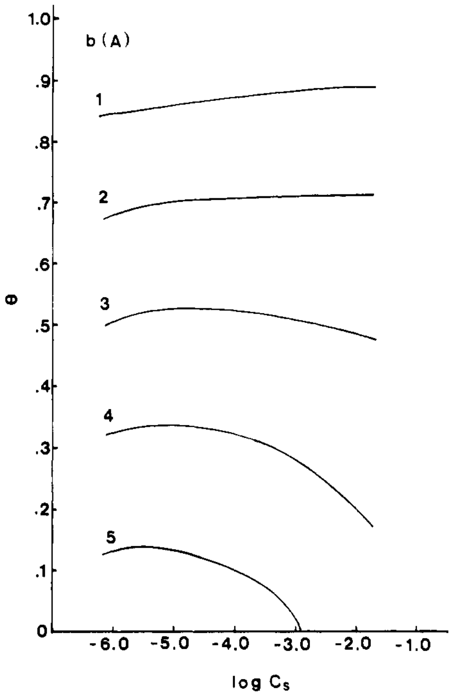

Figure 1. C_s dependence of θ estimated by eq 5. $X = 10^{-2}$ and $N = 1000$.

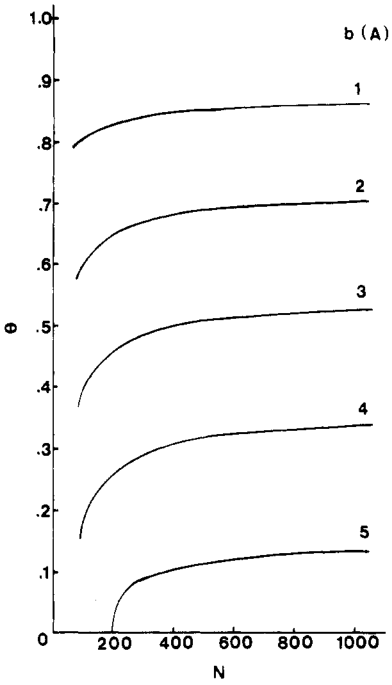

Figure 2. N dependence of θ estimated by eq 5. $X = 10^{-2}$ and $C_s = 1 \times 10^{-5}$ M.

was searched numerically between 0 and $1/\nu$ by using eq 5–9.

Results and Discussion

Dependences of θ Estimated by Eq 5–9 on C_s and N. Figure 1 shows the dependence of θ on C_s for $C_p/C_s \equiv X = 10^{-2}$ and $N = 1000$. θ values estimated for $b = 1 \times 10^{-8}$ to 5×10^{-8} cm decrease with the decrease in C_s at least in the lowest C_s region shown in the figure. This trend corresponds to the prediction by Woodbury and Ramanathan[11,12] that counterion condensation will not occur for a polyelectrolyte with a finite length in the limit of infinite dilution. In fact, we obtained C_s values below which counterion condensation does not occur, or $\theta = 0$, as 1×10^{-30} and 1×10^{-9} M for $b = 1 \times 10^{-8}$ and 5×10^{-8} cm, respectively.

Another interesting trend in the figure is found in the curves for $b \geq 3 \times 10^{-8}$ cm, where θ decreases with increasing C_s at the relatively high-C_s region. A literal explanation for this is that for polyelectrolyte with relatively low charge densities, the entropy loss due to condensation predominantes over the energy gain at the C_s region. Such C_s dependence is not limited to the particular value of $N = 1000$: the same behavior was observed for θ of polyelectrolytes with N both greater than and less than 1000, though the smaller N, the more markedly decreases θ with decreasing C_s.

Figure 2 shows the dependence of θ on N. θ increases with N and apparently approaches constant values in the limit of infinitely large N. This trend is also consistent with that predicted by Ramanathan and Woodbury[12] through eq 3 and 4. Experimentally, physicochemical properties of polyelectrolyte solution have been established to be independent of the degree of polymerization.[14,15] However, most of the pertinent experiments have been carried out with polyelectrolytes with relatively large N and in aqueous solution of moderate salt concentrations. The estimated values of θ in this study vary largely for $N < 200$ and become relatively insensitive to N when C_s is as high as 10^{-2} M, frequently used as an experimental condition: e.g., $\theta = 0.476$ and 0.487 for $N = 100$ and 1000 with $b = 3 \times 10^{-8}$ cm, respectively. Miyamoto[16] and several workers[17,18] reported that equivalent conductivities of polyelectrolyte solutions decrease with N when $N < 200$. Although conductivity is a dynamic property, this behavior may be qualitatively consistent with our results.

Table I
Comparison of Eq 5 with Manning Theory for θ Values

ν	$10^8 b$, cm	eq 5[a]	Manning (eq 1)
1	1.0	0.862	0.860
	2.0	0.703	0.720
	5.0	0.137	0.300
	10.0	0.0	0.0
	20.0	0.0	0.0
2	1.0	0.464	0.465
	2.0	0.419	0.430
	5.0	0.258	0.325
	10.0	0.0	0.150
	20.0	0.0	0.0
3	1.0	0.316	0.318
	2.0	0.295	0.302
	5.0	0.217	0.256
	10.0	0.051	0.178
	20.0	0.0	0.022

[a] $N = 1000$, $C_s = 1 \times 10^{-5}$ M, and $C_p = 1 \times 10^{-7}$ equiv/L.

Comparison with Other Theories. In Table I, θ values estimated by our method (eq 5) and Manning theory (eq 1) are compared for $N = 1000$, $X = 10^{-2}$, and $C_s = 1 \times 10^{-5}$ M. Both theories predict nearly the same θ values for high charge densities. This trend is independent of the valence of the counterion, N, C_s, and C_p, at least used here. As can be seen in Table II, a similar behavior is observed for activity coefficients of counterion, too. γ values listed in the table were calculated by the following three equations.

$$\gamma_+' = (\xi^{-1}X + 1)(X + 1)^{-1} \exp\left[-\frac{1}{2}\xi^{-1}X/(\xi^{-1}X + 2)\right] \tag{10}$$

$$\gamma_+' = (\xi^{-1}X + 1)(X + 1)^{-1} \exp[(-0.5 - 0.3906) \times (\xi^{-1}X/(\xi^{-1}X + 2)) + 0.3906(\xi^{-1}X/(\xi^{-1}X + 2))^2] \tag{11}$$

$$\gamma_+' = [(1-\theta)X+1](X+1)^{-1}\gamma_+ \tag{12}$$

Here eq 10–12 are those of Manning,[1] Iwasa et al.,[19] and the present study, respectively. Values of θ and γ_+ in the last equation can be obtained from eq 5–9. In eq 11 of Iwasa et al., the higher order cluster terms are taken into account, but no marked differences in the estimated activity coefficients of single-valent counterion were found among the three equations under the conditions used here (the largest difference was about 20% between eq 11 and eq 12 for $b = 5 \times 10^{-8}$ cm and $X = 5$).

It may be interesting for comparison purposes to see how θ values estimated by eq 4 with eq 1 depend on L and C_s through κ, especially in the higher C_s region. In Table III, however, the θ values are given only for $C_s = 1 \times 10^{-6}$ M, because eq 4 is valid under the condition of $\kappa e^2/DkT \ll 1$ and $\kappa L/2 \ll 1$. At a given r and b, θ increases with L, showing satisfactory agreements with our results. Quantitative comparison, however, may be meaningless because the closest approach distance, r, of counterion to polyion is not explicitly considered in our model.

In a recent study of Bratko and Dolar,[20] where the Poisson–Boltzmann equation was applied to a linear polyion modeled by a prolonged ellipsoid of revolution in a cell of ellipsoidal symmetry, the influences of the degree of polymerization and of the concentration on thermodynamic behavior of polyelectrolyte solutions were discussed. They have obtained qualitatively similar results on dependences of polyion–counterion interaction on N and C_p: e.g., in Figure 4 of ref 20, osmotic coefficients of polyelectrolyte solution were shown to increase with the decrease in N and to assume a minimum as a function of C_p. Our results, shown in Figures 1, 2, and 6, agree with these predictions.

Comparison with Experimental Data. Theories of Manning and Iwasa and the Poisson–Boltzmann equation have been brought into comparison with the observed counterion activity coefficients of several polyelectrolytes in aqueous salt solutions. Figures 3 and 4 show experimentally obtained plots of γ/γ_0 against X for sodium polyphosphate (NaPP)[5] and ι-carrageenan (NaCarr)[5] in aqueous salt solutions, respectively. Here γ_0 means the counterion activity coefficient of the salt solution in the absence of the polyelectrolyte. γ_+' given by eq 12 corresponds to the ratio γ/γ_0, because γ_+ in eq 5 takes account of interactions between polyion and small ions only. Since wide ranges of C_s, X, and ξ ($C_s = 5 \times 10^{-4}$ to 1×10^{-2} M, $X = 0.1$–8, and $\xi = 1.6$ for NaCarr; $C_s = 1 \times 10^{-3}$ to 1×10^{-2} M, $X = 0.1$–15, and $\xi = 2.8$ for NaPP) were covered in the study, the results may be most appropriate to scrutinize eq 12.

With NaPP in Figure 3, slight dependences of the coefficient on the salt concentration are found at any X value; i.e., γ/γ_0 for $C_s = 1 \times 10^{-3}$ M is higher than those for $C_s = 5 \times 10^{-3}$ and 1×10^{-2} M, while between the latter two C_s's, no appreciable trend in γ/γ_0 is found. The upper curve in Figure 3 is drawn by eq 12 for $C_s = 1 \times 10^{-3}$ M and the middle one is for both $C_s = 5 \times 10^{-3}$ and 1×10^{-2} M. All these curves show a qualitative agreement with the experimental results. However, with NaCarr (Figure 4), large dependences on C_s are found. The two theoretical curves by eq 12 (the upper one is for $C_s = 1 \times 10^{-2}$ M and the middle one for $C_s = 5 \times 10^{-4}$ M) can qualitatively predict the observed enhancement of the activity coefficient with C_s. Theories of Manning and Iwasa et al., which give the lowest curves in the figures (eq 11 of Iwasa et al. gives slightly lower curves than those by Manning theory), give no explanation for such dependences. However, in a quantitative sense, no preference to any of the three theories is evinced in these figures.

Table II
Comparison of Eq 12 with Equations of Manning and of Iwasa et al. for γ_+'

		present study (eq 12)		Manning (eq 10)	Iwasa et al. (eq 11)
$10^8 b$, cm	X	θ	γ_+'	γ_+'	γ_+'
1.0	0.1	0.890	0.917	0.919	0.916
	0.5	0.883	0.698	0.701	0.692
	1.0	0.881	0.548	0.552	0.539
	5.0	0.878	0.247	0.249	0.231
	∞	0.876	0.094	0.085	0.085
3.0	0.1	0.488	0.942	0.938	0.930
	0.5	0.509	0.781	0.769	0.744
	1.0	0.516	0.667	0.651	0.616
	5.0	0.527	0.421	0.400	0.363
	∞	0.531	0.280	0.255	0.255
5.0	0.1	0.0	0.969	0.956	0.944
	0.5	0.0	0.874	0.835	0.795
	1.0	0.018	0.795	0.747	0.693
	5.0	0.055	0.607	0.546	0.499
	∞	0.064	0.495	0.425	0.425

[a] $\nu = 1$, $N = 1000$, and $C_p = 1 \times 10^{-3}$ equiv/L.

Table III
Comparison of Eq 5 with Eq 4 of Ramanathan et al. for θ Values

				θ	
$10^8 b$, cm	$10^8 L$, cm	$10^8 r$, cm	ξ_0[a]	eq 1, 4	eq 5[a]
1.0	200	1.0	1.74	0.756	0.800
		5.0	2.14	0.700	0.800
		10.0	2.48	0.652	0.800
1.0	600	1.0	1.41	0.803	0.834
		5.0	1.57	0.781	0.834
		10.0	1.68	0.765	0.834
1.0	1000	1.0	1.29	0.819	0.845
		5.0	1.39	0.805	0.845
		10.0	1.46	0.795	0.845
3.0	600	1.0	1.41	0.409	0.387
		5.0	1.57	0.342	0.387
		10.0	1.68	0.294	0.387
5.0	1000	1.0	1.29	0.097	0.0
		5.0	1.39	0.025	0.0
		10.0	1.46	0.0	0.0

[a] $C_s = 1 \times 10^{-6}$ M and $C_p = 1 \times 10^{-8}$ equiv/L.

The slight and the marked dependences of γ/γ_0 on C_s for NaPP and NaCarr, respectively, appear to have an origin in the dependence of θ on C_s shown in Figure 1. However, the validity of this interpretation should be reserved at this moment, because no additional reports are available on such dependences of counterion activity coefficients on the ionic strength. One of the reasons for the lack of such data may be that in most studies polyions with rather high charge densities are used and/or the range of the ionic strength is narrower than in the study cited above. As expected from Figure 1, measurements of counterion activity coefficients in wide ionic strength ranges, especially for polyelectrolytes with low charge densities ($\xi = 1$–2), will be necessary to test eq 12 thoroughly. This is now being undertaken.

Two other examples to compare the prediction of the present study with experimental data are given in Figure 5, where the points represent the corrected counterion activity coefficients of sodium pectate and sodium pectinate in aqueous NaCl solutions,[21] respectively. The solid curves drawn by eq 12 are in satisfactory agreement with the data, especially in Figure 5A. In the figures compar-

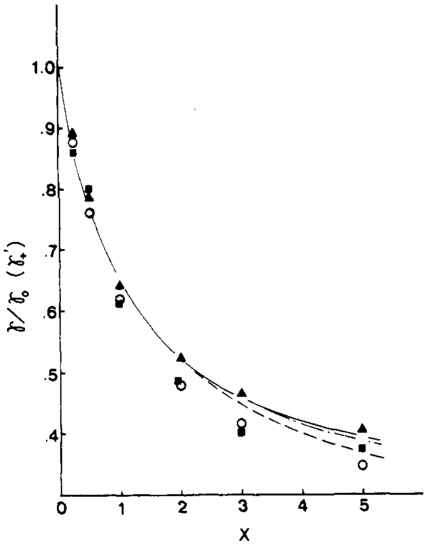

Figure 3. Comparison of γ/γ_0 obtained by Kowblansky et al. for NaPP–NaCl with the theoretical curves of eq 10 and 12. $N = 206$ and $b = 2.55 \times 10^{-8}$ cm. (▲) $C_s = 1 \times 10^{-3}$ M; (■) 5×10^{-3} M; (○) 1×10^{-2} M; (—), (- - -) theoretical curves by eq 12 for $C_s = 1 \times 10^{-3}$ M, and $C_s = 5 \times 10^{-3}$ and 1×10^{-2} M, respectively; (— - —): theoretical curve by eq 10.

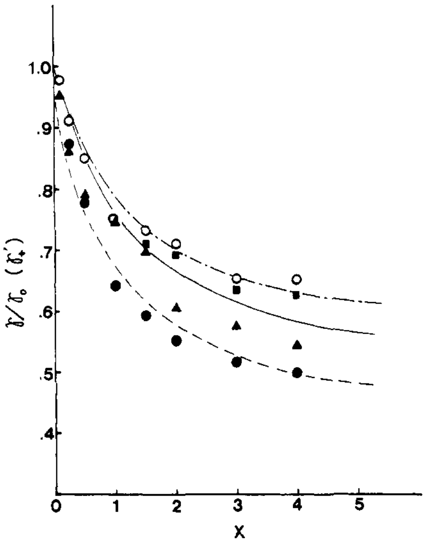

Figure 4. Comparison of γ/γ_0 obtained by Kowblansky et al. for NaCarr–NaCl with the theoretical curves of eq 10 and 12. $N = 1116$ and $b = 4.463 \times 10^{-8}$ cm. (●) $C_s = 5 \times 10^{-4}$ M; (▲) 1×10^{-3} M; (■) 5×10^{-3} M; (○) 1×10^{-2} M; (—), (- - -) theoretical curves by eq 12 for $C_s = 5 \times 10^{-4}$ M and 1×10^{-2} M, respectively; (— - —) theoretical curve by eq 10.

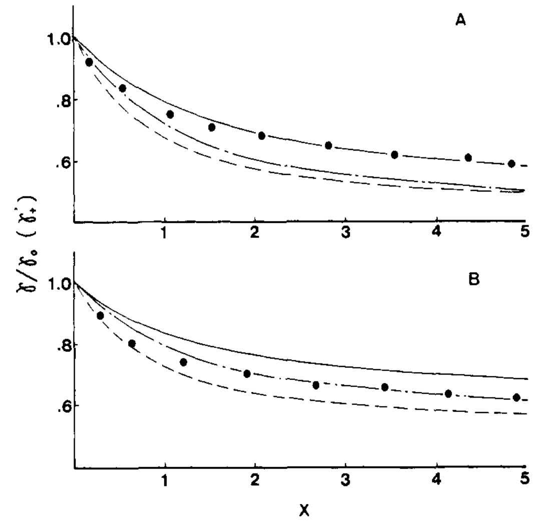

Figure 5. Comparison of γ/γ_0 obtained by Joshi and Kwak with the theoretical curves of eq 10 and 12 and the modified Poisson–Boltzmann equation by Delville. (—) eq 12; (- - -) eq 10; (— - —) modified Poisson–Boltzmann equation.[22] (A) Sodium pectate in aqueous NaCl solution. $N = 162$, $b = 4.38 \times 10^{-8}$ cm, and $C_p = 1 \times 10^{-2}$ equiv/L. (B) Sodium pectinate in aqueous NaCl solution. $N = 160$, $b = 5.95 \times 10^{-8}$ cm, and $C_p = 1 \times 10^{-2}$ equiv/L.

isons are also made with a modified Poisson–Boltzmann equation of Delville[22] and with that of Manning. Again, there seems to be no preference for any of the three theories in their reproducibility of the experimental variations.

A lot of data are also available for activity coefficients of polyelectrolyte solutions under salt-free conditions.[14,23-25] It should be recollected here that eq 10–12 were derived without consideration for the contribution of polymer charges to the ionic strength. In our model the Debye parameter κ is obtained by eq 7c, which assumes that "free" counterions contribute to the ionic strength I in the absence of added salts. Both in the Manning theory and the Iwasa one, all counterions were assumed to contribute to I. The applications of eq 10–12 to salt-free systems, therefore, is justified only at low-C_p conditions, such as $C_p < 10^{-3}$ equiv/L, where the polyion–polyion interaction can be neglected. Few studies, however, have been made at such low C_p. Nagasawa et al.[14,24] have determined counterion activity coefficients of sodium poly(vinyl alcohol sulfate) (NaPVS) and some other polyelectrolytes for $C_p \geq 10^{-3}$ equiv/L and found a common increasing trend of the counterion activity coefficients with C_p. Kagawa et al.[23] have measured counterion activity coefficients of the silver salt of (carboxymethyl)cellulose (AgCMC) also for $C_p > 10^{-3}$ equiv/L, and they observed a decreasing trend of the coefficients with C_p. On the other hand, Oman and Dolar[25] have determined counterion activity coefficients of several kinds of salts of poly(methylstyrenesulfonic acid) (H-, Na-, Ag-, Tl-, Zn-, Cd-, and PbPMSS) for C_p between 10^{-4} and 10^{-1} equiv/L and found that the coefficients of the polyelectrolyte systems except H- and PbPMSS show minima near $C_p = 10^{-3}$–10^{-2} equiv/L. These three examples suggest that a minimum of counterion activity coefficients in the plot against C_p is a common feature for polyelectrolyte solutions. A similar behavior has been observed for self-diffusion coefficients of counterions in polyelectrolyte solutions such as sodium and silver poly(styrenesulfonates),[26,27] sodium dextran sulfate, sodium carrageenan, and sodium alginate.[28] Minima of the diffusion coefficients in these cases are found in the region $C_p = 10^{-3}$–10^{-2} equiv/L, corresponding to that for the activity coefficient minima. In Figure 6, some data selected from the studied cited above are plotted against log C_p, together with theoretical curves calculated by eq 12. As shown in the figure, eq 12 predicts that γ_+' of polyelectrolytes with relatively low charge densities assume a minimum as a function of C_p. This is consistent with the experimental results of Oman and Dolar and those of diffusion coefficients and with the theoretical prediction of Bratko and Dolar.[20] Quantitative agreement with the data of Oman and Dolar is, however, poor as can be seen from the comparison with the theoretical curves for $b = 2 \times 10^{-8}$ and 3×10^{-8} cm (because the b value of the NaPMSS sample is 2.6×10^{-8} cm). A more detailed discussion on eq 12 for salt-free systems requires that experimental data be obtained under low-C_p conditions.

Concluding Remarks

In this paper an estimation of the degree of counterion condensation and activity coefficient for polyelectrolyte

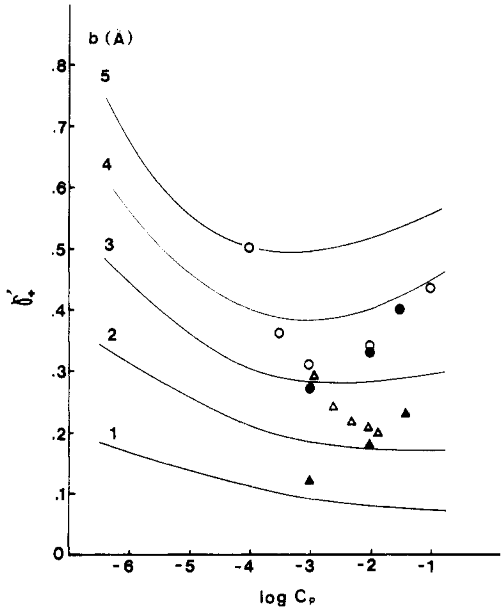

Figure 6. Comparison of experimental counterion activity coefficients for salt-free polyelectrolyte systems with the theoretical curves of eq 12. (○) NaPMSS,[25] $N = 761$ and $b = 2.66 \times 10^{-8}$ cm; (●) NaPVS,[14] $N = 293$ and $b = 5.8 \times 10^{-8}$ cm; (▲) NaPVS,[14] $N = 348$ and $b = 3.38 \times 10^{-8}$ cm; (△) AgCMC,[23] $N = 289$ and $b = 3.31 \times 10^{-8}$ cm. Theoretical curves: $N = 1000$.

solutions has been made without an explicit consideration of the condensed phase. Values of θ and γ thus obtained were compared with other theories and experimental data. The benefit of the present study may consist in that the dependences of θ and γ on C_s, C_p, and N can be predicted. Satisfactory agreements with the experimental data of Kowblansky et al.[5] were found for C_s and C_p dependences of γ/γ_0. A minor modification of our model[29] will extend the applicability to systems containing counterions with different valences and to those in which dehydrations from counterions and polyions are involved in the condensation process.

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Dye Binding Characteristics of Imidazole-Containing Polymers

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ABSTRACT: The interactions of methyl orange with methyl, hexyl, and benzyl quaternized poly(*N*-vinylimidazoles) were studied to assess the structural factors and the nature of the driving forces for dye binding. The stoichiometry of the polymer–dye complex is dictated by charge. The apparent binding constant increases with polymer charge density as well as polymer saturation r (where $r = [D_b]/[P_t]$, and $[D_b]$ and $[P_t]$ are the molar concentrations of bound dye and total polymer quaternary sites, respectively), but decreases in the presence of competing counterions, indicating that Coulombic forces operate. The van der Waals forces between the dye and the aromatic or long-chain hydrocarbon group at the polymer quaternary site also enhance binding strength. Cooperative dye binding was observed in the region $0 \leq r \leq 0.7$. This behavior is discussed in terms of the dimerization tendency of the dye molecules. In the high-saturation region ($0.7 \leq r \leq 1.0$), however, steric hindrance prevents further aggregation of the dye, and cooperativity was lost.

Two types of interactions can occur between an aromatic dye molecule and a polymer in aqueous solution, i.e., the nonspecific adsorption and the specific site interaction. The former interaction is a result of van der Waals attraction between molecules caused by dipole–dipole, dipole–induced dipole, and the London dispersion forces. The enthalpy of such an interaction is generally very small among nonpolar linear hydrocarbons, but the total free energy change in an aqueous medium can be significant because of an entropy gain resulting from the structural change of the "hydrophobic hydration"[1] shells surrounding the associated complex.[2,3] The second type of interaction involves specific sites on the polymer where a covalent bond, metal complex, charge-transfer complex, or ion-pair formation takes place. The enthalpy for this type of interaction is generally large, and the total free energy change may be enhanced by an entropy gain caused by the "hydrophobic effect"[2,3] described above for the nonspecific nonpolar association.

The interaction between anionic dye molecules and synthetic polycations has been investigated by several workers,[4-8] yet the nature of the driving forces for binding,

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