Table I
Comparison of Theoretical and Experimental Values of $(\partial \mathrm{pH}/\partial \mathrm{p}n_{\mathrm{p}})_{\alpha,X_+,X_{2+}}$ for PAA-NaCl-QED(I)$_2$ Systems[a]

				$(\partial \mathrm{pH}/\partial \mathrm{p}n_{\mathrm{p}})_{\alpha,X_+,X_{2+}}$		
α	$(X_+, X_{2+})^d$	added salts	Y	expt	this calcn	M-H[b]
		PAA-Na$^+$ System				
0.4	(1, 0)	NaCl	0	0.76	0.85	1.00
			1	0.63	0.77	1.00
			10	0.59	0.64	1.00
0.7	(1, 0)	NaCl	0	0.80	1.00	1.00
			1	0.69	0.92	1.00
			10	0.66	0.80	1.00
		PAA-QED^{2+} System				
0.4	(0, 1)	QED(I)$_2$	0	0.44	0.52	0.50
			1	0.38	0.47	0.50
			10	0.32	0.42	0.50
		PAA-Na$^+$-QED^{2+} System				
0.4	(1, 0)	QED(I)$_2$	0	0.76	0.85	
			1/3	0.61	0.67	
			2/3	0.46	0.56	
			1	0.40	0.52	

[a] [PAA] = 0.005 N – 0.1 N. The pure solution of PAA was neutralized by NaOH or QED(OH)$_2$. The values of $(X_+,X_{2+})^d$ were the values for the partly neutralized PAA. We measured the pH of the solution after NaCl or QED(I)$_2$ was added to the solution of PAA that was partly neutralized. [b] Manning-Holtzer theory.

features agree well with the theoretically predicted features. However, the experimental values were always smaller (about 0.05–0.2) than the theoretical values. The reason for the deviation is unclear.

Finally, the disagreement between the present theory and experimental data at high ionic strengths and low charge density may be partly due to the failure of the parallel-rod cell model employed in this work.

Acknowledgment. The author thanks Professors N. Ise and M. Nagasawa for their criticism and discussion.

Supplementary Material Available: Determination of n_i^0 in solving the PB equation and a modified Dolar–Peterlin's method (Appendices I and II) (3 pages). Ordering information is given on any current masthead page.

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Distribution of Counterions around Polyions in Mixed Valency Counterion Systems

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ABSTRACT: The distribution of mono- and divalent counterions around polyions is discussed by use of the ionic activity coefficients of these ions calculated from the Poisson–Boltzmann equation appplied to rodlike polyion solutions. Our theoretical values of mean activity coefficients of simple salts are larger than the experimental values of Kwak et al. The calculated values assuming that the coion activity coefficient corrected for the salt term is 0.9–1.0 agree well with the experimental values in mixed valency counterion systems as well as in single counterion systems. Part of the "bound" divalent counterions become "free" by the addition of a large excess of monovalent counterions. For the case of an excess of monovalent salts on the binding of divalent counterions, the agreement between the experimental values by Krakauer and those calculated here is qualitatively satisfactory. Our calculated results are also compared with Manning's theory in mixed valency counterion systems. We conclude that the calculation based on the Poisson–Boltzmann equation for a rodlike model is better in treating mixed valency counterion systems than is Manning's theory.

Solutions of polyelectrolytes of biological interest and ion-exchange resins often contain not only mono- but also divalent counterions. Manning[1] applied his limiting laws, which incorporate both condensation and Debye–Hückel type effects, to mixed valency counterion systems in the absence of added salts. In Manning's theory, divalent counterions are assumed to condense preferentially on polyions with the charge parameter $\zeta > {}^1/_2$, where $\zeta = e^2/D_0kTb$ and e is the charge on a proton, D_0 is the bulk dielectric constant of the solvent, k is the Boltzmann constant, T is the absolute temperature, and b is the distance between the neighboring charges on a polyion. However, this assumption is not valid for the case of a large excess of 1-1 salts. For example, it was reported[17] that the amount of bound Mg^{2+} to polyions decreases with addition of NaCl. Kwak et al.[2] showed that Manning's treatment was not applicable to their experimental data measured in the systems of Na$^+$, Ca^{2+}, Cl$^-$, and poly(styrene sul-

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fonate)$^-$ ions. In order to fit the theoretical values of Manning to their experimental values, they needed a semiempirical modification of the limiting laws, based on the assumption that a certain fraction of Ca^{2+} remained uncondensed. Iwasa[3] presented a theory of polyelectrolyte solutions interpreting the counterion condensation as the free-energy minimum with respect to the number of condensed counterions instead of using the simple assumption by Manning. These theoretical treatments are based on the assumption that the polyelectrolyte solution can be divided into two phases—the condensed and uncondensed phases of counterions.

On the other hand, the Poisson–Boltzmann equation for a cell model of a polyelectrolyte solution has been applied to various systems by some investigators: (i) the salt-free systems containing either mono- or divalent counterions by Fuoss et al.[4] and Alfrey et al.;[5] (ii) the salt-free systems containing both mono- and divalent counterions by Dolar and Peterlin;[6] and (iii) the salt-containing systems containing 1–1 salts by Kotin and Nagasawa[21] and by Alexandrowicz[7] and Nitta and Sugai.[8] The author recently reported two kinds of numerical methods of solving the Poisson–Boltzmann (PB) equation in salt-containing systems containing multivalent ions and discussed the pH of weak polyacids in the presence of added salts.[9] In this paper, we calculate the activity coefficients of salts and ions from the solution of the PB equation and compare the calculated results with the experimental data in literature, in reference to Manning's theory.

Numerical Calculation

Our model of the polyelectrolyte solution is the same as that proposed by Fuoss et al.[4] The polyion is replaced by an infinite cylindrical rod of radius a and charge spacing b. The counterions are distributed symmetrically around the polyion in a cylinder with radius R. The radius R is inversely proportional to the square root of the polyion concentration. The electrostatic potential ψ is assumed to be determined by the solution of the Poisson–Boltzmann equation which is expressed as

$$\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(Dr\,\frac{\mathrm{d}\psi}{\mathrm{d}r}\right) = -\frac{4\pi eN_A}{10^3}\sum_i Z_i n_i(R)\exp\left(-Z_i\frac{e\psi}{kT}\right) \qquad (1)$$

where Z_i is the signed valency of ion i, D is the integral dielectric constant, r is the radial distance from the axis of the polyion rod, N_A is the Avogadro number, and $n_i(R)$ is the concentration in (mol/L) of ion i at $r = R$. The product, $|Z_i|n_i$, is termed the equivalent concentration of ion i in this paper. Conway et al.[18] pointed out that the activity coefficient of ion i, when the dielectric constant was assumed to be uniform throughout the solution, was in fact negligibly different from the values when the dielectric constant was assumed to be a function of the field intensity in salt-free polyion solutions. This point holds also in salt-containing systems, and hence we can neglect dielectric saturation in calculating the activity coefficients. Equation 1 was solved by the Runge–Kutta–Gill method, which was described in detail in our previous paper.[9]

The single ionic activity coefficient of ion i, denoted by f_i, is expressed by Marcus[23] and by Alexandrowicz[7] as follows,

$$f_i = (n_i(R)/n_i)f_i^0 \qquad (2)$$

where n_i is the average concentration in (mol/L) of ion i and f_i^0 expresses the relative secondary deviation from ideality which is caused by the interactions between microions in a solution at $r = R$. Since the equivalent concentration of counterions at $r = R$ is always higher than that of coions, it is difficult to evaluate f_i^0 precisely. We estimate the approximate values of f_i^0 by the values of the activity coefficients of ion i measured in the absence of polyion. Furthermore, we use the values of activity coefficients corrected for the salt term when comparing theory with experiments.

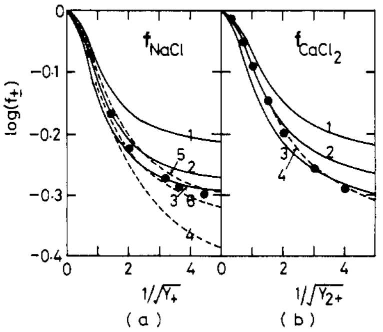


Figure 1. Comparison of calculated and experimental values of mean activity coefficient for single counterion systems: (a) KCl–KPSS, n_p = 0.01 N; (b) $CaCl_2$–CaPSS, n_p = 0.009 N. a = 6.8 Å, ζ = 2.8. Solid lines, this calculation; broken lines, Manning's theory. The curve number shows: 1, this calculation; 2, this calculation, assuming $f_{Cl^-}/f_s^0 = 1.0$; 3, this calculation, assuming $f_{Cl^-}/f_s^0 = 0.9$; 4, Manning's theory; 5, Manning's theory, assuming $f_{Cl^-}/f_s^0 = 1.0$; 6, Manning's theory assuming $f_{Cl^-}/f_s^0 = 0.9$. The experimental data are from ref 20.

Comparison with Experiment

The following notation is used: n_p is the concentration in equiv/L of polyion; n_c^{add} is the concentration in mol/L of the counterions from added salts; $X_+ \equiv n_+/n_p$, $X_{2+} \equiv 2n_{2+}/n_p$; $Y_+ \equiv n_+^{add}/n_p$, $Y_{2+} \equiv 2n_{2+}^{add}/n_p$. Then, the polyion solution is salt free when $X_+ + X_{2+} = 1$ or $Y = 0$.

Figure 1 shows a comparison between theoretical and experimental values for KCl–KPSS and $CaCl_2$–CaPSS systems[20] (PSS = poly(styrene sulfonate)). For the KCl–KPSS system, our theoretical values (curve 1) are larger than the experimental values, while the values calculated from Manning's theory (curve 4) are less than the experimental values. For the $CaCl_2$–CaPSS system, our theoretical values are larger than the experimental values, while the theoretical values of Manning agree well with the experimental values.

Kwak et al.[2] reported mean activity coefficients of NaCl and $CaCl_2$ in aqueous polyion solutions containing Na^+, Ca^{2+}, Cl^-, and PSS ions. These measurements were performed with a series of solutions at constant polyion and chloride ion concentration while the ratios of Na^+ to Ca^{2+} were varied. Figure 2 shows a comparison between calculated values and their experimental values. Our theoretical values are slightly larger than the experimental values but give better agreement with experimental values than the theory of Manning.

Krakauer,[17] using a dye-colorimeter method, measured the "bound to unbound" ratios for Mg^{2+} in Na^+, Mg^{2+}, Cl^-, and polynucleotide mixtures which contained a considerable excess of NaCl. Figure 3 shows a comparison of the calculated and experimental values of the concentration ratio of "bound" Mg^{2+} to polyion. The experimental ratios are larger than the theoretical ones. This discrepancy may be partly explained as follows: The conformation of the polymer is somewhat "coiled" in the presence of a large excess of NaCl, and the actual charge spacing is smaller than the stretched one, increasing the "bound" ratio. Although the experimental data obtained with a dye-colorimeter method may not necessarily be identical with the theoretical ratios calculated from f_{2+}, the agreement between experimental data and the calculated data is qualitatively satisfactory. Figure 3 also shows the theo-

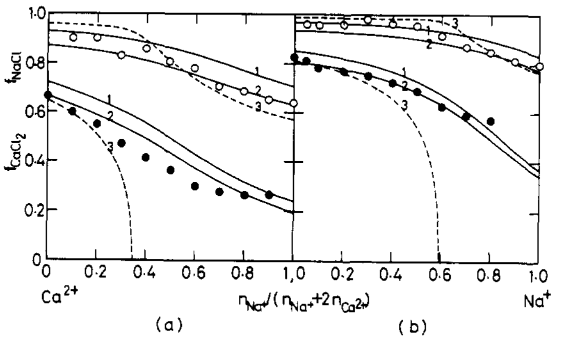


Figure 2. Comparison of calculated and experimental values of the mean activity coefficient for mixed-valency counterion systems (Ca^{2+}, Na^+–PSS) [a = 6.8 Å, ζ = 2.8, n_p = 0.02 N]: (a) $Y = {}^1/_4$; (b) Y = 1.0; (○) f_{NaCl}; (●) f_{CaCl_2}. Solid lines, this calculation; broken lines, Manning's theory. The curve number shows: 1, this calculation; 2, this calculation, assuming f_{Cl^-}/f_s^0 = 1.0; 3, Manning's theory.

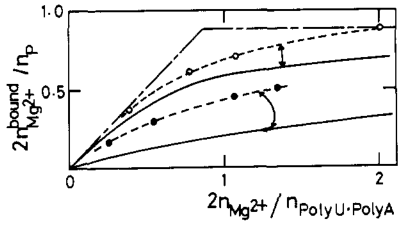


Figure 3. Comparison of theoretical and experimental values of the concentration ratios of "bound" Mg^{2+} to the PolyA–PolyU complex (a = 12 Å, b = 1.68 Å): (○) n_{Na^+} = 0.01 N, n_p = 1.96 × 10^{-3} N; (●) n_{Na^+} = 0.06 N, n_p = 1.8 × 10^{-3} N, (---) experimental curves; (—) this calculation; (— —) Manning's theory. The experimental data are from ref 17.

retical curve calculated from Manning's theory assuming that the amount of condensed counterions is equal to that of "bound" Mg^{2+}. If we calculate the theoretical values of amount of "bound" Mg^{2+} from the activity coefficient, the values are very slightly larger than the values calculated from condensation only, and increase but hardly vary with the concentration of monovalent counterions. Accordingly, we can consider that the amount of "bound" Mg^{2+} predicted by Manning's theory hardly varies with the concentration of monovalent counterions, and the curve in Figure 3 then represents the theoretical curve. The curve greatly deviates from the experimental data at large values of X_{Na^+}.[22] This shows that Manning's condensation assumption for the mixed valency counterion system is invalid at large values of X_+.

Discussion

Disagreement between Theory and Experiments for Mean Activity Coefficients. Table I shows comparisons between the experimental values of f_+ and f_{2+} by Lyons and Kotin[12] and by Vasilescu et al.[16] and the calculated values. The calculated values are generally in good agreement with the experimental data. The difference between the values calculated from Manning's theory and the present one may be insignificant considering that the meaning of the single ionic activity coefficient is not well defined and the electrode, the salts bridge, the calibration, and the extrapolation procedures can seriously affect the experimental values.

Table I
Comparison of Theoretical and Experimental Values of f_+ and f_{2+} for Single-Counterion Systems

n_p × 10^3 N	$\lvert Z_c\rvert n_c^{add}$ × 10^3 N	f^{exptl}	$f^{theor,1}$ (this)	$f^{theor,2}$ (Manning)
(NaPVS; NaCl) b = 3.04 Å, a = 5.5 Å				
1.55	0.329	0.35[a]	0.37	0.41
1.53	1.74	0.62[a]	0.61	0.68
(NaPSS; NaCl) b = 2.52 Å, a = 8 Å				
0.293	0.0864	0.47[a]	0.42	0.49
1.97	0.570	0.46[a]	0.43	0.47
(NaDNA (E, Coli); NaCl) b = 1.68 Å, a = 12 Å				
1.04	2	0.73[b]	0.70	0.72
1.87	2	0.61[b]	0.57	0.60
(NaDNA (V.378); NaCl) b = 1.68 Å, a = 12 Å				
1.2	2	0.66[b]	0.67	0.69
(MgPVS; $MgCl_2$) b = 3.04 Å, a = 5.5 Å				
1.34	0.159	0.14[a]	0.21	0.23
1.34	0.317	0.21[a]	0.28	0.30
(MgDNA; $MgCl_2$) b = 1.68 Å, a = 12 Å				
1.31	0.107	0.14[a]	0.14	0.14
1.28	0.521	0.33[a]	0.32	0.34

[a] From ref 12. [b] From ref 16. f^{exptl} and f^{theor} are experimental and theoretical values of f, respectively. The following abbreviations are used: PVS = poly(vinyl sulfate); PSS = poly(styrene sulfonate); DNA = deoxyribonucleic acid.

Lyons and Kotin[12] examined experimentally the additivity rule for the counterions. They defined the deviation from additivity as

$$\Delta a_c = (f_c^{adt} - f_c)/f_c \qquad (3)$$

where f_c^{adt} is the value calculated from the additivity rule. According to their data, Δa_c was usually positive, e.g., 1–8% at $Y < 0.9$ for the NaCl–NaPVS system and 13–22% at $Y < 0.5$ for the $MgCl_2$–MgPVS system. According to the experimental data by Podlas and Ander,[13] Δa_c was 0.3–13% at $Y < 11$ for the NaCl–Na-alginate system. The theoretical value of Δa_c is positive and about 0–10% and approximately agrees with the above experimental data.

Thus, it is concluded that the activity coefficient for counterions is predicted well by both our calculation and Manning's theory in the case of a single counterion system. Accordingly, the disagreement between theory and experiment for mean activity coefficients may be due to the poorly predicted activity coefficient of the coion. Our theoretical values of coion activity coefficients are larger than unity. Nagasawa et al.[14] reported that the experimental activity coefficient of the coion is 0.80–0.95 in the NaCl–NaPVS system. The experimental values corrected for the salt term are 0.9–1.0. If we calculate mean activity coefficients using the experimental values (0.9–1.0) instead of $n_{coion}(R)/n_{coion}$ for coion activity coefficients and the theoretical values for counterion activity coefficient, the calculated values agree well with the experimental values in single-counterion systems as well as in mixed-valency counterion systems, as seen in Figures 1 and 2.

The disagreement between our theoretical and experimental values for the coion activity coefficient is qualitatively interpreted as follows. The equivalent concentration of counterion and coion at $r = R$ is always larger than that of added salts, and that of the counterion is larger than that of the coion at $r = R$; that is, $|Z_c|\cdot n_{counterion}(R) > n_{coion}(R) > n_s^{add}$. Therefore, the activity coefficient may be expressed as

$$f_i = (n_i(R)/n_i)f_i^0 = (n_i(R)/n_i)f_i'f_s^0 \qquad (4)$$

where f_s^0 is the activity coefficient of the added salts in the absence of polyion and has often been used for the evaluation of the salt term, and f_i' is the contribution of the concentration difference between coion and counterion at $r = R$ to f_i^0. As the concentration ratio of added salt to polyion (Y) decreases, $n_{counterion}(R)$ becomes much larger than $n_{coion}(R)$. Accordingly, the counterions are poorly screened by coions, i.e., $f'_{counterion} \sim 1$; on the other hand,

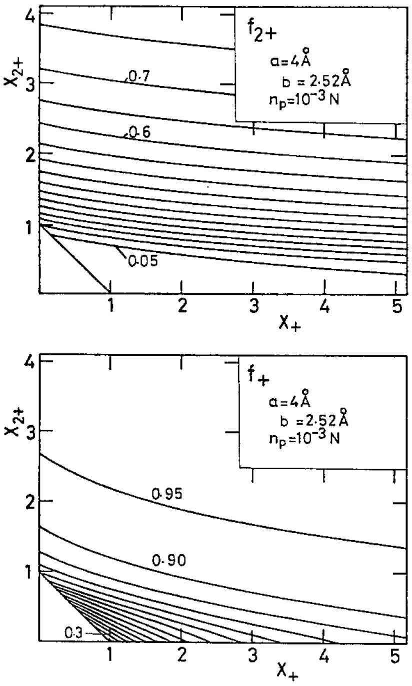
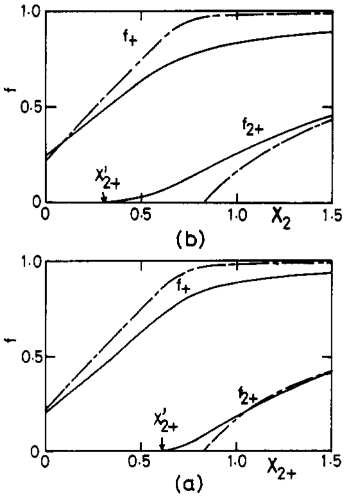


Figure 4. Contour maps of f_+ and f_{2+}.



(b)

(a)

Figure 5. Plots of f_+ and f_{2+} vs., X_{2+} at $X_+ = 1.0$ for $b = 2.52$ Å, $a = 4$ Å, and the following: (a) $n_p = 10^{-4}$ N; (b) $n_p = 10^{-2}$N; (-) this calculation; (—-) Manning's theory.

the coions are well screened by an excess of counterions, i.e., f'_{coion} is less than unity and decreases with decreasing Y. On the other hand, $n_{\mathrm{coion}}(R)/n_{\mathrm{coion}}$ is larger than unity and increases with decreasing Y. The two effects tend to cancel each other and the coion activity coefficient corrected for the salt term $(=f_{\mathrm{coion}}/f_s^0)$ may be nearly unity.

Comparison with Manning's Theory for the Mixed-Valency Counterion System. Figure 4 is a contour map of f_+ and f_{2+}. The figure shows that f_+ and f_{2+} depend on X_{2+} much more than X_+. In order to discuss the more detailed features of f_+ and f_{2+}, we calculate f_+ and f_{2+} for two cases: X_{2+} is a variable and X_+ is unity; and X_+ is a variable and X_{2+} is a constant. The plots of f_+ and f_{2+} vs. X_{2+} are shown in Figure 5. The value of f_{2+} is zero in the region of $X_{2+} \leq (1 - (2\zeta)^{-1})$ in Manning's theory but is nearly zero in the region of $X_{2+} \leq X_{2+}'$ in the present calculation. The value of X_{2+}' is different from $(1 - (2\zeta)^{-1})$, and moreover it depends on the polyion concentration. The difference between two theoretical curves of f_{2+} decreases with decreasing polyion concentration. This may relate partly to the fact that Manning's theory is rigorous in the limit of zero polyion concentration. The value of $\mathrm{d}f_+/\mathrm{d}X_{2+}$ is always about 1.0 in the region of $X_{2+} \leq (1 - \zeta^{-1})$ in Manning's theory, while it is less than unity in our calculation. Condensed monovalent counterions are displaced equivalently by the added divalent counterions in Manning's theory, while bound monovalent counterions are not equivalently displaced by them in the present calculation.

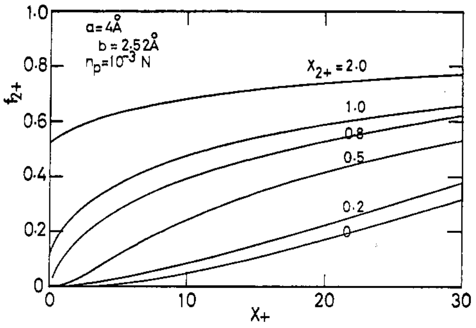


Figure 6. Plots of f_{2+} vs. X_+.

Figure 6 shows f_{2+} as a function of X_+. The values of f_{2+} increase with X_+, e.g., $f_{2+} = 0.01$ for $X_+ = 1$ and $X_{2+} = 0.5$, while $F_{2+} = 0.53$ for $X_+ = 30$ and $X_{2+} = 0.5$. The "bound" divalent counterions are considerably repelled from the polymer domain by a large excess of monovalent counterions. This aspect differs from that predicted by Manning's theory. Our calculated results explain the experimental fact that bound divalent ions in an ion exchange resin are displaced into the water phase by addition of excess 1–1 salts.

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