in paper 5 of this series;[4] from $\nu_X = 0.70 \times 10^{-4}$ mol/cm^3, the average number of cross-linked points per initial molecule (γ) is estimated to be 8.6, and T_e is found from Langley's graph (interpolated for $\bar{M}_w/\bar{M}_n = 1.7$) to be 0.62.

When the initial relaxation is slight, $T_{e,u}$ is independent of t_R and agrees with the Langley theory, as found previously.[4] After longer relaxation periods, the trapping probability of the unrelaxed entanglements increases. The trapping probability of the relaxed entanglements, $T_{e,r}$, is zero up to the point where $T_{e,u}$ begins to increase and then increases but remains smaller than the Langley prediction.

This behavior can be understood qualitatively in terms of the alternative tube model for the topological restraints of an entangled molecule as treated in detail recently by Doi and Edwards.[7,15,16] The final stage of relaxation in an uncross-linked polymer involves the escape of a molecule from its tube by diffusing back and forth along its contour.[17] In a state of strain, the ends regain a random configurational distribution finding new tube paths, progressing from the ends inward, while a steadily shrinking central portion remains confined in the deformed tube. The relaxed and unrelaxed entanglements can be identified with constraints on the ends and center, respectively. Whereas the Langley theory provides an average trapping probability, it is evident that the probability will be greater near the center of a molecule than near the ends. In fact, there is essentially no chance of trapping a relaxed entanglement until the randomized ends become longer than the average entanglement spacing and also longer than the average spacing between cross-linked points.

The average number of cross-linked points on a randomized end can be estimated as $(\gamma/2)(1 - \nu_e(t)/\nu_e^0)$. For the experiments of Figures 3 and 7, this becomes greater than 1 only for log t_R (s) $\simeq$ 3.5, in agreement with the first appearance of trapped relaxed entanglements. This description ignores the possibility that some constraints even near the center of the molecule can be relieved by escape of other molecules from *their* tubes, but no attempt is made to take their complication into account at the present time.

Acknowledgment. This work was supported in part by the National Science Foundation, Grant No. DMR 76-09196, Polymers Program. We are indebted to Professor J. E. Willard for the use of the ^{60}Co source for irradiation, to Dr. G. G. A. Böhm for the polymer, to Dr. N. R. Langley, Dr. O. Kramer, and Mr. S. Hvidt for comments, and to Mr. D. Deubler for help with calculations.

References and Notes

(1) O. Kramer, R. L. Carpenter, V. Ty, and J. D. Ferry, *Macromolecules*, **7**, 79 (1974).
(2) R. L. Carpenter, O. Kramer, and J. D. Ferry, *Macromolecules*, **10**, 117 (1977).
(3) R. L. Carpenter, O. Kramer, and J. D. Ferry, *J. Appl. Polym. Sci.*, **22**, 335 (1978).
(4) R. L. Carpenter, H.-C. Kan, and J. D. Ferry, *Polym. Eng. Sci.*, in press.
(5) H.-C. Kan, R. L. Carpenter, and J. D. Ferry, *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(6) N. R. Langley, *Macromolecules*, 1, 348 (1968).
(7) M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. 2*, 74, 1802 (1978).
(8) C. R. Taylor and J. D. Ferry, *J. Rheol.*, in press.
(9) J. D. Ferry and H.-C. Kan, *Rubber Chem. Technol.*, **51**, 731 (1978).
(10) J. W. M. Noordermeer and J. D. Ferry, *J. Polym. Sci., Polym. Phys. Ed.*, 14, 509 (1976).
(11) H.-C. Kan, Ph.D. Thesis, University of Wisconsin, 1979.
(12) O. Kramer, R. Greco, J. D. Ferry, and E. T. McDonel, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1675 (1975).
(13) S. Hvidt and O. Kramer, private communication; S. Hvidt, Cand. Scient. Thesis, University of Copenhagen, Denmark, 1978.
(14) J. D. Ferry, "Viscoelastic Properties of Polymers", 2nd ed., Wiley, New York, 1970, p 406.
(15) M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1818 (1978).
(16) M. Doi, personal communication.
(17) P. G. de Gennes, *J. Chem. Phys.*, **55**, 572 (1971).

The pH of Weak Polyacid Solutions in the Presence of Mono- and Divalent Counterions

Masaaki Ishikawa

Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.
Received October 4, 1978

ABSTRACT: The pH of weak polyacid solutions containing mono- and/or divalent counterions has been treated by use of the solution of the Poisson–Boltzmann equation applied to the parallel-rod cell model. The dielectric saturation effect is taken into account in the calculation. Agreement between the theory and experimental data is generally satisfactory, particularly if the comparison is carried out at a constant charge density. If the charge density of the polyelectrolyte is low and the ionic strength is high, however, the agreement between the theory and experiments is not satisfactory, probably because the parallel-rod cell model fails.

The pH of weak polyacid solutions is related to the surface electric potential of the polymer skeleton.[1] The surface electric potential can be numerically and analytically calculated from the Poisson–Boltzmann (PB) equation if we assume a parallel-rod cell model for the polyion.[2-8] Some investigators[6-8,10-13] have discussed the potentiometric titration curves of weak polyacids in the presence of 1–1 salts using the surface potential of the polymer thus calculated. However, there have been few studies in the presence of divalent counterions. In this work, we used quaternized ethylenediamine as the divalent counterion and compared the experimental potentiometric titration results with the surface electric potential calculated from the PB equation. Ordinary divalent cations such as Ca^{2+} and Ba^{2+} show site binding to polyacrylic acid (PAA) causing precipitation. Such precipitation is not observed in the titration with quaternized ethylenediamine.

Based on the counterion condensation concept of Manning, Manning and Holtzer[14] derived a theory of

0024-9297/79/2212-0498$01.00/0

potentiometric titration of linear polyelectrolytes. Merits and demerits of the theory of Manning and also of the theories based on the PB equation were carefully discussed in comparison with experimental results. In their paper, they pointed out that the dielectric saturation is ignored in the theories based on the PB equation, i.e., the solvent is usually treated as a dielectric continuum that retains its bulk properties right up to the surface of the polyion. In this paper, the dielectric saturation effect is taken into account in solving the PB equation.

Experimental Section

A commercially available polyacrylic acid was obtained from Wako Pure Chemicals. The degree of polymerization of the polymer reported from the company is 700. The solution of the polymer was deionized by passing it through a mixed bed ion-exchanged column of Amberlite IR 120B and IRA 400 before measurement. Quaternized ethylenediamine iodide (QED(I)$_2$: $[(CH_3)_3N^+(CH_2)_2N^+(CH_3)_3](I^-)_2$) was prepared in a manner similar to that described in ref 15. The purity of QED(I)$_2$ was confirmed by conductometric titration with $AgNO_3$ and ^{13}C NMR. The quaternization was satisfactory. The quaternized ethylenediamine base (QED(OH)$_2$) was prepared by treating QED(I)$_2$ with porous anion-exchange resin Amberlite IRA 401. NaCl was of a reagent grade. Hitachi-Horiba pH meter F7 was used with NBS standard buffers. The measurements of pH were carried out in nitrogen atmosphere at 25 ± 0.02 °C.

Numerical Calculation

Our model of the polyelectrolyte is the same as that proposed by Fuoss et al.[2] and by Alfrey et al.[3] The polyion is represented by a cylindrical rod of radius a and length h having ν charges uniformly distributed axially on the surface and stretching along the axis of a cylinder of radius R. The polyions are considered to be essentially parallel. The length of the polyion is assumed to be large compared to R so end effects may be neglected. The counterions are distributed symmetrically around the polyion in a cylinder of radius R. The electrostatic potential ψ is determined by solving the following PB equation

$$\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(D_i r\frac{\mathrm{d}\psi}{\mathrm{d}r}\right) = -\frac{4\pi e N_A}{10^3}\sum_i Z_i n_i^0 \exp\left(-Z_i\frac{e\psi}{kT}\right) \quad (1)$$

where e is the electronic charge, Z_i is the signed valency of ion i, r is the radial distance from the axis of the polyion rod, D_i is the integral dielectric constant of the solvent at r, n_i^0 is the concentration (mol/L) of ion i at $r = R$, k is the Boltzmann constant, T is the absolute temperature, and N_A is the Avogadro number. The first boundary conditions are expressed as

$$(\mathrm{d}\psi/\mathrm{d}r)_{r=R} = 0, \qquad \psi(R) = 0 \quad (2)$$

and the second boundary condition is expressed as

$$(D_i\,\mathrm{d}\psi/\mathrm{d}r)_{r=a} = -2e\nu/ah \quad (3)$$

The parameter n_i^0 is related to the average concentration of ion i, n_i, by

$$n_i = \frac{R^2 - a^2}{R^2}\frac{n_i^0}{V}\int_V \exp(Z_i\phi)\,\mathrm{d}V \quad (4)$$

where $V = \pi h(R^2 - a^2)$ and $\phi = -e\psi/kT$.

The dielectric saturation effect on the pH was evaluated using the same method as that of Conway et al.[17] The differential dielectric constant (D_d) and the integral one (D_i) were expressed as a function of the electric field intensity ($E = \mathrm{d}\psi/\mathrm{d}r$) by Graham[18] and Laidler[19] such as

$$D_d = \frac{\mathrm{d}Q}{\mathrm{d}E} = \frac{D_0 - n^2}{1 + mE^2} + n^2 \quad (5)$$

$$D_i = \frac{Q}{E} = \frac{D_0 - n^2}{m^{1/2}E}\arctan(m^{1/2}E) + n^2 \quad (6)$$

where Q is the electric displacement, D_0 is the dielectric constant in the bulk phase, the square of the optical refractive index n^2 is equal to 1.78, and the constant m is found to be equal to 1.08×10^{-8} esu^{-2}. Equation 1 is transformed into

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}t^2} = \frac{1}{D_d}\left[\frac{4\pi kTa^2N_A}{10^3 e}\sum_i Z_i n_i^0 \exp(Z_i\phi + 2t) - (D_i - D_d)\frac{\mathrm{d}\phi}{\mathrm{d}t}\right] \quad (7)$$

where $t = \ln(r/a)$. The boundary conditions are also transformed into

$$(\mathrm{d}\phi/\mathrm{d}t)_{t=\ln(R/a)} = 0, \qquad \phi(\ln(R/a)) = 0 \quad (8)$$

$$\left(D_i\frac{\mathrm{d}\phi}{\mathrm{d}t}\right)_{t=0} = -2e^2\nu/kTh \quad (9)$$

Equation 7 was solved by the Runge–Kutta–Gill method. The interval $0 \le t \le \ln(R/a)$ was divided into N subdivisions ($N = 100$ here). In the system of mixtures of mono- and divalent counterions whose concentrations are n_+ and n_{2+} (the concentration of coion is n_-), it is not easy to determine the parameters n_i^0 to satisfy the boundary condition of eq 9. Our procedure was that values of n_+^0 and n_{2+}^0 are kept as constants and n_-^0 is varied under the condition of $n_-^0 < n_+^0 + 2n_{2+}^0$ so as to satisfy eq 9. After a solution with a set of n_+^0 and n_{2+}^0 was obtained, the average concentration n_i was calculated from eq 4 by use of the Lagrange interpolation formula through three points. The surface electric potential $\phi(0)$ at a given concentration of n_+, n_{2+} can be obtained from a family of calculated results by use of appropriate interpolation methods. The details of the calculation are given in Appendix I (supplementary material). The convergent condition of the calculation was $[(D_i\ \mathrm{d}\phi/\mathrm{d}t)_{t=0} - (-2e^2\nu/kTh)] < 10^{-6}$. The numerical solutions for salt-free polyion solutions were found to agree with the analytical solutions of Fuoss et al.[2] within 0.01%. If the concentration ratio of added salt to polyion is high, we need to use a computer which can compute with higher precision otherwise the calculation cannot converge.

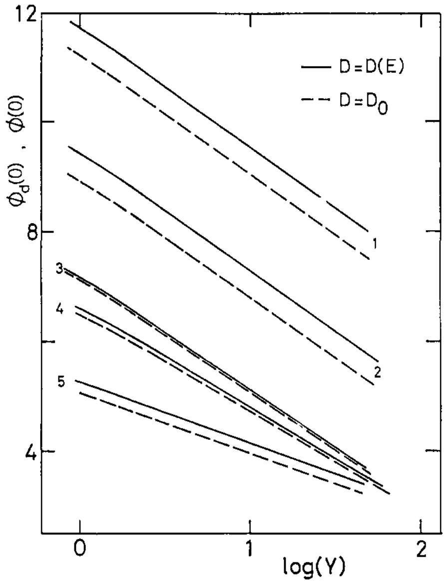
If the dielectric saturation effect need not to be taken into account, the above numerical solution can more easily be carried out by a modified method of Dolar and Peterlin[4] without assuming parameters n_i^0. It was confirmed that both methods give the same results. However, the modified method takes a longer time for computation than the Runge–Kutta–Gill method. Our method applying the theory of Dolar and Peterlin to added salt systems is explained in Appendix II (supplementary material).

Results and Discussion

The following notations are used: n_p is the equivalent concentration of polyion and n_c^{add} is the concentration (mol/L) of counterion added to a salt-free polyion solution; $Y \equiv |Z_c|n_c^{add}/n_p$; $X_+ \equiv n_+/n_p$, $X_{2+} \equiv 2n_{2+}/n_p$. Then, the polyion solution is salt-free when $Y = 0$ or $X_+ + X_{2+} = 1$. The pH of weak polyacid solution is related to $\phi(0)$ by

$$\mathrm{pH} = \mathrm{p}K_0 - \log\left(\frac{1-\alpha}{\alpha}\right) + 0.434\,\phi(0) \quad (10)$$

where pK_0 is the negative logarithm of the intrinsic dissociation constant and is assumed to be approximately



number of curve	n_p (N)	h/ν (Å)	a (Å)	valency of counterion
1	10^{-4}	2.52	4	+1
2	10^{-3}	2.52	4	+1
3	10^{-3}	2.52	10	+1
4	10^{-3}	5.2	4	+1
5	10^{-3}	2.52	4	+2

Figure 1. Comparison of $\phi_d(0)$ and $\phi(0)$.

independent of n_c^{add}, n_p, and the degree of ionizaton of ionizable group α. The definitions of pK and ΔpK are

$$\mathrm{p}K \equiv \mathrm{pH} + \log\left(\frac{1-\alpha}{\alpha}\right) \tag{11}$$

$$\Delta\mathrm{p}K \equiv \mathrm{p}K - \mathrm{p}K_0 = 0.434\phi(0) \tag{12}$$

If the value of pK_0 is determined empirically by extrapolating the experimental data to $\alpha = 0$, it may contain the free energy of the conformational change of polyions and, therefore, cannot always be reasonable when comparing the experimental data and the values calculated under the assumption that the conformation does not vary with α and salt concentration. The values of pK_0 therefore have to be chosen to achieve the best agreement between the calculated and experimental curves.[11] However, when we discuss the dependence of pH on n_c^{add} or n_p at constant α, the comparison between theory and experiments is not influenced by the choice of pK_0.

(1) Effect of the Dielectric Saturation Effect on the Potentiometric Titration Curves. The reduced electric surface potential calculated with and without taking into consideration the dielectric saturation is denoted by $\phi_d(0)$ and $\phi(0)$, respectively. Figure 1 shows a comparison between $\phi_d(0)$ and $\phi(0)$, which were calculated from eq 7. $\phi_d(0)$ is always larger than $\phi(0)$. This means that the pH of weak polyacid solution increases as the dielectric saturation effect increases. Figure 2 shows a comparison of theoretical and experimental values of ΔpK for a PAA–NaCl system. The theoretical curves calculated without taking into account the dielectric saturation effect more markedly deviate from the experimental data as the degree of neutralization increases. On the other hand, the theoretical curves calculated taking into consideration the dielectric saturation agree well with the experimental curves in $\alpha > 0.5$. Accordingly, the difference of ΔpK between experimental values and theoretical values calculated without taking into consideration the dielectric saturation[7,10] may be due to the dielectric saturation.

The contribution of the dielectric saturation effect to ΔpK, i.e., $0.434(\phi_d(0) - \phi(0))$, is denoted by ΔpK_d. The following are features of ΔpK_d: (i) ΔpK_d increases with the charge density of the polyion. At low charge density, e.g., at $\alpha < 0.4$ for PAA, ΔpK_d is negligibly small. (ii) ΔpK_d decreases with rod radius of the polyion, e.g., 0.22 for a = 4 Å and 0.02 for a = 10 Å in the case of h/ν = 2.52 Å. From (i) and (ii), we can neglect the dielectric saturation effect for helical poly(glutamic acid)[8] (α = 0.2–0.3, a = 12.5 Å, and h/ν = 1.68 Å for α = 1) and carboxymethylcellulose[11] (a = 7.8 Å,[20] h/ν = 3.37 Å for α = 1). In fact, the agreement between the experimental data and the theoretical values calculated by neglecting the dielectric saturation was fairly good, as seen in Figure 2 of ref 7 and Figure 1 of ref 11, respectively. (iii) The values of ΔpK_d for divalent counterions are about half the values of ΔpK_d for monovalent counterions. (iv) However, ΔpK_d hardly varies either with the concentration of added salts at constant n_p and α or with the concentration of the polyion at constant X_+, X_{2+}, and α. If the experiments are carried out at constant n_p or at constant X_+ and X_{2+}, therefore, we may discuss the dependence of pH on n_c^{add} and n_p without taking into consideration the dielectric saturation effect.

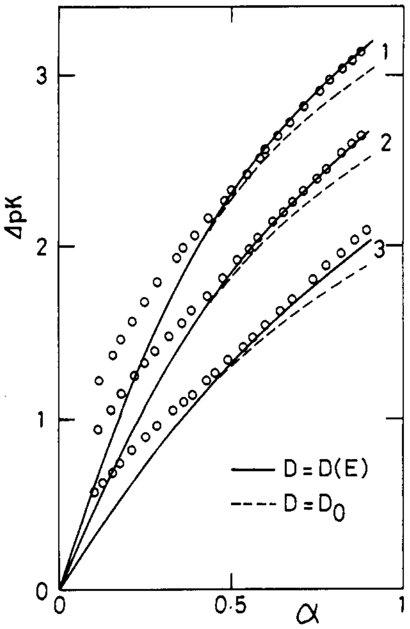


Figure 2. Comparison of the calculated and experimental values of ΔpK of Nagasawa et al.[10] on PAA. NaCl concentration: 1, 0.005 N; 2, 0.02 N; 3, 0.1 N. The circles show the experimental values at [PAA] = 0.00829 N. The theoretical values was calculated for a = 4 Å, h/ν = 2.52 Å at α = 1 (pK_0 = 4.06).

(2) Potentiometric Titration of PAA with QED^{2+}. Figure 3a shows a comparison between theoretical and experimental curves for the potentiometric titration of PAA with QED(OH)$_2$ in the presence of QED(I)$_2$. Agreement was found to be unsatisfactory. On the other hand, Figure 3b shows a comparison between theoretical and experimental values of $[(\mathrm{pH})_Y - (\mathrm{pH})_{Y=5}]$, where $(\mathrm{pH})_Y$ is the pH at Y. Good agreement was found. From eq 10, we have

$$\left(\frac{\partial \mathrm{pH}}{\partial \mathrm{p}Y}\right)_{n_p,\alpha} = 0.434\left(\frac{\partial\phi(0)}{\partial \mathrm{p}Y}\right)_{n_p,\alpha} \tag{13}$$

where pY = −log (Y). Figure 4 shows a comparison of experimental values of $(\partial\mathrm{pH}/\partial\mathrm{p}Y)_{n_p,\alpha}$ with theoretical values of $0.434(\partial\phi(0)/\partial\mathrm{p}Y)_{n_p,\alpha}$. The agreement between theory and experiment is satisfactory even in the case of QED^{2+} salt. In Figure 4, comparison between the theory and experimental results with monovalent cations reported in the literature is also shown. At low degrees of neutralization, the experimental data are somewhat larger than

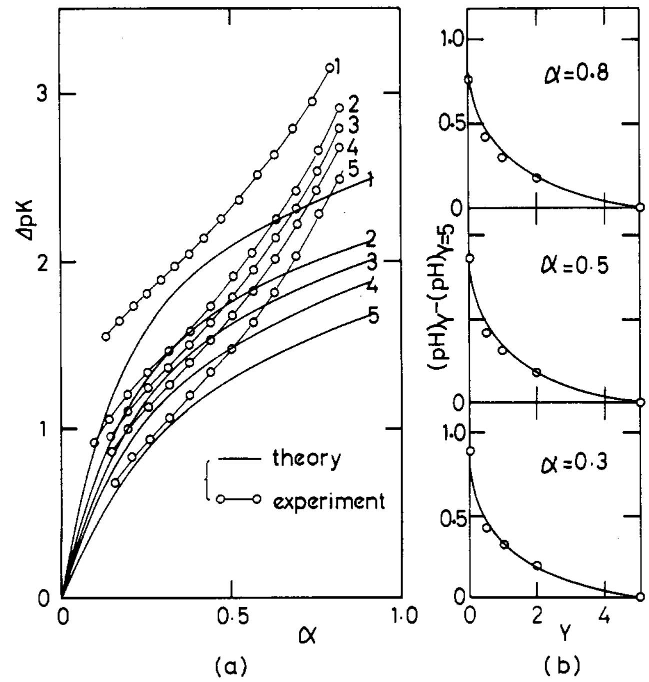


Figure 3. Comparison of the calculated and experimental values of ΔpK and $[(\mathrm{pH})_Y - (\mathrm{pH})_{Y=5}]$ for the PAA–QED(I)$_2$ system; [PAA] = 0.0025 N. QED(I)$_2$ concentration: 1, 0 N; 2, 0.00125 N; 3, 0.0025 N; 4, 0.005 N; 5, 0.0125 N (pK_0 = 4.06).

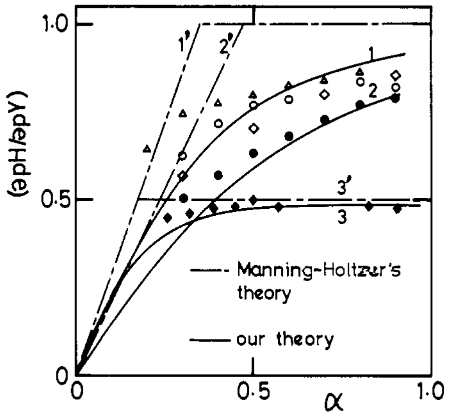


Figure 4. Comparison of the theoretical and experimental values of (∂pH/∂pY). The plots are the experimental data: (△) PAA–NaCl system by Nagasawa et al.,[10] [PAA] = 0.00827 N, [NaCl] = 0.02–0.05 N; (○) PAA–NaCl system by Nagasawa et al.,[10] [PAA] = 0.00827 N, [NaCl] = 0.02–0.1 N; (◇) PAA–NaCl system by Kondo and Ikegami,[16] [PAA] = 0.0071 N, [NaCl] = 0.02–0.5 N; (●) CMC–NaCl system by Muroga et al.,[11] [CMC] = 0.0051 N, [NaCl] = 0.01–0.1 N; (◆) PAA–QED(I)$_2$ system (this work), [PAA] = 0.0025 N, [QED(I)$_2$] = 0.005–0.0125 N. The theoretical curves correspond to the experimental data: 1, PAA–NaCl; 2, CMC–NaCl; 3, PAA–QED(I)$_2$.

our calculated values. This may be due to the fact that the polyions are more tightly coiled at low α so that the actual charge density of the polyion may be larger than that for the stretched chain and also the fact that the parallel-rod cell model fails at low α. Data from the theory of Manning were also compared with the same experimental data at infinite dilution in a form similar to eq 13 by Manning and Holtzer.[14] Comparison between Figure 2 in ref 14 and Figure 4 in this paper appears to indicate that the present theory shows better agreement with experimental data than the theory of Manning and Holtzer.

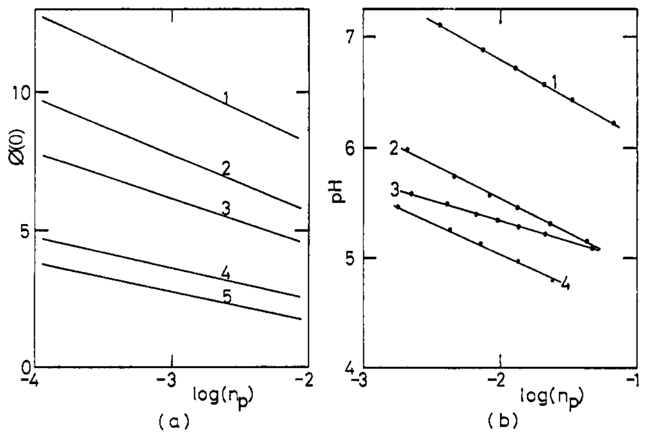


Figure 5. Linear relationship of $\phi(0)$ and pH with log (n_p) at constant X_+ and X_{2+}. (a) Theoretical curves for a = 4 Å: 1, $X_+ = 1$, $X_{2+} = 0$, h/ν = 2.52 Å; 2, $X_+ = 1.6$, $X_{2+} = 0.4$, h/ν = 2.52 Å; 3, $X_+ = 0.4$, $X_{2+} = 0.6$, h/ν = 5.2 Å; 4, $X_+ = 0$, $X_{2+} = 20$, h/ν = 2.52 Å; 5, $X_+ = 0$, $X_{2+} = 20$, h/ν = 5.2 Å. (b) The experimental curves for the PAA–NaCl–QED(I)$_2$ system: 1, $X_+ = 2$, $X_{2+} = 0$, $\alpha = 0.7$; 2, $X_+ = 2$, $X_{2+} = 0$, $\alpha = 0.4$; 3, $X_+ = 1$, $X_{2+} = 1$, $\alpha = 0.4$; 4, $X_+ = 11$, $X_{2+} = 0$, $\alpha = 0.4$.

The agreement in Figures 3b and 4 and the disagreement in Figure 3a may be explained as follows. (i) The hydrophobic atmosphere by QED^{2+} around the polymer chain increases with α since the counterion concentration in the immediate neighborhood of the polymer chain increases with α. Therefore, the average dielectric constant around –COOH on the polymer chain decreases largely with α, depressing the dissocation of H$^+$ from –COOH and increasing the pH of the solution. (ii) Since the distribution of the counterions hardly varies with Y in the immediate neighborhood of the polyions as is shown in the solution of the PB equation, the contribution of the hydrophobic effect to pH would hardly vary with Y. That is, the hydrophobic effect is not important for discussing (∂pH/∂pY) if α is kept constant. Furthermore, (∂pH/∂pY) is found to be insensitive to charge density of polyion, e.g., 0.5, 0.5, 0.48 for h/ν = 1.25, 2.5, 5.2 Å, respectively. This means that the increase in the actual charge density by coiling of the polyion with addition of QED^{2+} hardly contributes to (∂pH/∂pY). These may be the reasons why the values of $[(\mathrm{pH})_Y - (\mathrm{pH})_5]$ and [∂pH/∂pY] agreed well with the theoretical values, as seen in Figures 3b and 4. However, we need further data in order to discuss the hydrophobic effect of counterions on the pH of weak polyacid solutions in detail.

(3) Dependence of pH on Polyion Concentration. From eq 10, we have

$$\left(\frac{\partial \mathrm{pH}}{\partial \mathrm{p}n_\mathrm{p}}\right)_{X_+,X_{2+},\alpha} = 0.434\left(\frac{\partial \phi(0)}{\partial \mathrm{p}n_\mathrm{p}}\right)_{X_+,X_{2+},\alpha} \equiv H \quad (14)$$

where pn_p = –log (n_p). Figure 5a shows the dependence of $\phi(0)$ on log (n_p) at constant X_+, X_{2+}, and α. From the figure, we find that $\phi(0)$ decreases approximately linearly with log (n_p). That is, the factor H is a constant. In the absence of divalent counterions, Nitta and Sugai[7] have already shown the linear relationship from the solution of the PB equation which was obtained by a numerical method different from ours. Thus, it can be predicted that pH is proportional to log (n_p) at constant X_+, X_{2+}, and α. In experiments, the linear relationship between pH and pn_p was reported in the salt-free solutions of poly(methacrylic acid).[21] We found that the linear relationship holds in salt-containing solutions of PAA. Some plots of pH vs. log (n_p) are shown in Figure 5b. In Table I, our experimental data for H are compared with the theoretical results. The experimental data show that: (i) H decreases with Y; (ii) H depends mainly on X_{2+} in the systems of mixed counterions; and (iii) H decreases with α. These

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

α	$(X_+, X_{2+})^d$	added salts	Y	$(\partial \mathrm{pH}/\partial p n_p)_{\alpha,X_+,X_{2+}}$ 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.

References and Notes

(1) A. Katchalsky and J. Gill, *Recl. Trav. Chim. Pays-Bas*, **68**, 879 (1949).
(2) R. M. Fuoss, A. Katchalsky, and S. Lifson, *Prov. Natl. Acad. Sci. U.S.A.*, **37**, 579 (1951).
(3) T. Alfrey, P. W. Berg, and H. Morawetz, *J. Polym. Sci.*, **7**, 543 (1951).
(4) D. Dolar and A. Peterlin, *J. Chem. Phys.*, **50**, 3011 (1969).
(5) Z. Alexandrowicz, *J. Polym. Sci.*, **56**, 97 (1962).
(6) Z. Alexandrowicz and A. Katchalsky, *J. Polym. Sci., Polym. Phys. Ed.*, 1, 3231 (1963).
(7) K. Nitta and S. Sugai, *J. Phys. Chem.*, **78**, 1189 (1974).
(8) L. Kotin and M. Nagasawa, *J. Chem. Phys.*, **36**, 873 (1962).
(9) M. Ishikawa, *J. Phys. Chem.*, 81, 2053 (1977).
(10) M. Nagasawa, T. Murase, and K. Kondo, *J. Phys. Chem.*, **69**, 4005 (1965).
(11) Y. Muroga, K. Suzuki, Y. Kawaguchi, and M. Nagasawa, *Biopolymers*, **11**, 137 (1972).
(12) A. D. MacGillivray, *J. Chem. Phys.*, **56**, 80 (1972); **57**, 4071 (1972).
(13) K. Nitta, M. Yoneyama, and N. Ohno, *Biophys. Chem.*, **3**, 323 (1975).
(14) G. Manning and A. Holtzer, *J. Phys. Chem.*, **77**, 2206 (1973).
(15) E. Tsuchida and Y. Osada, *Makromol. Chem.*, **175**, 593 (1974).
(16) N. Kondo and A. Ikegami, *Biopolymers*, **4**, 823 (1966).
(17) B. E. Conway, J. E. Desnoyers, and A. C. Smith, *Philos. Trans. R. Soc. London, Ser. A*, **256**, 389 (1964).
(18) C. D. Graham, *J. Chem. Phys.*, **18**, 903 (1950); **21**, 1054 (1953).
(19) J. K. Laidler, *Can. J. Chem.*, **37**, 138 (1959).
(20) The rod radii adopted here are different from those by Nagasawa et al.[10,11] Our method of estimating the rod radius was described in Appendix I of our previous paper (supplementary material).[9]
(21) H. Maeda and F. Oosawa, *J. Phys. Chem.*, **76**, 3445 (1972).

Distribution of Counterions around Polyions in Mixed Valency Counterion Systems

Masaaki Ishikawa

Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.
Received December 26, 1978

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-

0024-9297/79/2212-0502$01.00/0 © 1979 American Chemical Society