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Interactions of Sodium Ions with the Sodium Salts of Poly(acrylic acid/acrylamide) Copolymers of Varying Charge Density

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ABSTRACT: Sodium ion activity coefficients in aqueous solutions of fully neutralized poly(acrylic acid/acrylamide) copolymers, whose charge spacing varied from 2.5 to 415 Å, were determined at 25 °C in both the absence and the presence of added simple electrolyte, NaBr. The results are compared with those predicted from additivity and from the theories of Manning and of Iwasa et al. A new empirical linear relationship between the square root of the polyelectrolyte charge density and measured counterion activity coefficients is demonstrated.

Introduction

Single-ion activity coefficients have been used extensively to study the interactions of small ions with polyelectrolytes. While coion activity coefficients generally are unaltered in the presence of polyelectrolytes,[1,2] counterion activity coefficients[1-12] are significantly lower in polyelectrolyte solutions than in simple salt solutions of comparable concentrations. The higher the charge density of the polyelectrolyte, the greater is the counterion–polyion interaction, and consequently, the lower is the activity coefficient.

In recent years attention has been focused on the Manning[13-18] theory of polyelectrolyte solutions, in which the polyelectrolyte is represented as an infinite line charge and limiting laws are derived for thermodynamic and transport properties of the small ions in solution. Since the theory is purely electrostatic, the limiting laws are derived in terms of the counterion charge Z_1, coion charge Z_2, and a dimensionless parameter ξ, which is a measure of the polyion charge density

$$\xi = e^2/\epsilon kTb \qquad (1)$$

where e is the protonic charge, ϵ is the dielectric constant of the solvent, k is the Boltzmann constant, T is the Kelvin temperature, and b is the average axial spacing between charged groups on the polyion.

Two modes of counterion–polyion interaction are incorporated into the theory, depending on whether ξ is above or below a critical value ξ_c defined as $|Z_1|^{-1}$. For $\xi < \xi_c$, counterion–polyion interactions are treated by the Debye–Hückel approximation, which results in the following expression for univalent counterion activity coefficients γ_1 for salt-containing polyelectrolyte solution

$$\gamma_1 = e^{-0.5\xi X/(X+2)} \qquad \xi \leq \xi_c \qquad (2)$$

where $X = n_p/n_s$, the concentration ratio of polyelectrolyte n_p to simple salt n_s, in equivalents. For salt-free solution ($X = \infty$) eq 2 simplifies to

$$\gamma_1 = e^{-0.5\xi} \qquad \xi \leq \xi_c \qquad (3)$$

When $\xi > \xi_c$ counterions condense onto the polyion until $\xi = \xi_c$, and the remaining uncondensed counterions interact with the polyion, whose charge density now equals ξ_c, by Debye–Hückel forces. The resulting expression for γ_1, incorporating both these concepts, for monovalent counterions is

$$\gamma_1 = \frac{\xi^{-1}X + 1}{X + 1} e^{-0.5\xi^{-1}X/(\xi^{-1}X+2)} \qquad \xi \geq \xi_c \qquad (4)$$

where the exponential term, due to the Debye–Hückel approximation, is multiplied by the fraction of uncondensed ions in solution. For a salt-free solution eq 4 becomes

$$\gamma_1 = \xi^{-1}e^{-0.5} \qquad \xi \geq \xi_c \qquad (5)$$

New limiting laws for counterion and coion activity coefficients were derived by Iwasa et al.[19,20] For the line charge model with its attendant counterion condensation, cluster theory was used to show that uncondensed counterions interact more strongly with the line charge than in the Manning treatment. For monovalent counterions in polyelectrolyte solutions containing salt

$$\gamma_1 = \exp\left\{\frac{\xi X}{X + 2}\left[-0.5 + 0.39\xi\left(\frac{X}{X + 2} - 1\right)\right]\right\} \qquad (6)$$

$$\xi \leq 1$$

$$\gamma_1 = \frac{\xi^{-1}X + 1}{X + 1} \times \exp\left\{\frac{\xi^{-1}X}{\xi^{-1}X + 2}\left[-0.5 + 0.39\left(\frac{\xi^{-1}X}{\xi^{-1}X + 2} - 1\right)\right]\right\} \qquad (7)$$

$$\xi \geq 1$$

In the absence of salt the Iwasa expressions are identical with those obtained by Manning (eq 3 and 5).

To test the Manning and Iwasa theories significantly, experiments should be performed by utilizing a polyelectrolyte whose charge density can be varied over an extensive range of ξ values, on both sides of ξ_c, without altering the primary structure. With such a polyelectrolyte, specific effects remain constant and electrostatic effects can be focused upon. With this in mind, sodium ion activity coefficients have been determined for aqueous solutions containing fully neutralized poly(acrylamide/acrylic acid) copolymers, whose ξ values ranged from 0.02 to 2.85, in the presence and absence of sodium bromide.

Experimental Section

Copolymers of acrylamide/acrylic acid were prepared by hydrolyzing polyacrylamide (PAM) under alkaline conditions.[21] PAM of molecular weight (5–6) × 10^6 was obtained from Polysciences. Since aqueous solutions of this polymer were very viscous and difficult to handle, the polymer was sheared in a Waring blender until a significant decrease in viscosity was observed, prior to further treatment. Accurate control of the molecular weight in the shearing procedure was not undertaken since it is well established that electrochemical properties are independent of polyelectrolyte molecular weight.[22]

All acrylamide/acrylic acid copolymers were prepared by hydrolyzing PAM with NaOH at 60 °C at the conditions described in Table I. Following hydrolysis, the solutions were acidified to a pH below 1 and then purified by exhaustive dialysis against doubly distilled water. Concentrations of the resulting polyacid stock solutions were determined by drying several aliquots of the stock to constant weight in a vacuum oven at 60 °C. The error

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Table I
Conditions for Hydrolysis of PAM[a] and Several Properties of the Resulting Sodium Polyelectrolytes

sample	NaOH concn, N	hydrolysis time, min	mol % hydrolyzed	$[\eta]$,[b] dL/g	b,[c] Å	ξ
NaPAM-0.6			0.6	3.5	417	0.02
NaPAM-10	0.1	15	10	4.9	25	0.29
Na-PAM-14	0.1	30	14	4.3	18	0.40
Na-PAM-42	1.0	15	42	3.7	6.0	1.20
Na-PAM-57	1.0	120	57	6.4	4.4	1.62
NaPA			100	2.6	2.5	2.85

[a] Hydrolysis temperature 60 ± 2 °C, PAM concentration 16.5 g/L. [b] Measured at 25 ± 0.05 °C in 0.5 N NaBr. [c] Based on a spacing of 2.5 Å for vinyl groups.

in this determination is approximately ±0.3%. Equivalent weights (degree of hydrolysis) of the purified samples were determined by potentiometric titration of the purified polyacids with NaOH. One the basis of replicate determinations, the error in the determined equivalent weights is ±0.5%.

The purified polyacids were converted to their sodium salts with NaOH. All polymer samples are labeled as NaPAM-y, where y denotes the degree of hydrolysis as mol % (i.e., acrylic acid content of the copolymer). Intrinsic viscosities $[\eta]$ of the sodium salts of the copolymers were determined in 0.5 M NaBr at 25.0 ± 0.05 °C in an Ubbelohde viscometer and are reported in Table I. Since the molecular weight of the starting PAM for each hydrolyzed sample was different, no relationship between degree of hydrolysis and $[\eta]$ can be deduced from these data. A systematic study of the relationship between these two variables is currently in progress. Sodium polyacrylate (NaPA) was prepared from 2×10^6 molecular weight poly(acrylic acid) purchased from Polysciences. Purification and concentration determinations were carried out according to the procedures described above for the hydrolyzed PAM samples.

Analytical grade NaBr was used without further purification. All solutions were prepared by volumetric dilution of the stock NaBr and appropriate sodium polyelectrolyte solutions.

Orion solid-state sodium ion selective electrodes were used in conjunction with Orion double-junction reference electrodes (with NH_4Cl filling solution) for the measurement of activity coefficients. All measurements were carried out in stirred solutions thermostated at 25.0 ± 0.05 °C. Calibration curves were determined both before and after every series of measurements on the polyelectrolyte solutions. Electrode slopes were Nernstian and were never found to differ by more than 1 mV/decade (usually less) between the two calibrations. Activity coefficients of the standardizing NaBr solutions were calculated by the extended Debye–Hückel equation.

Results and Discussion

Sodium ion activity coefficients have been measured at 25 °C in aqueous solutions of the sodium poly(acrylate/acrylamide) polyelectrolytes listed in Table I. Each polyelectrolyte was studied at two polyelectrolyte concentrations, 0.018 and 0.0045 N, both in the presence of NaBr and in salt-free solutions. The NaBr concentration was varied so that X, the equivalent concentration ratio of polyelectrolyte to simple salt, ranged from 0.5 to 12.5 at each polyelectrolyte concentration. In the absence of simple salt $X = \infty$. The dependence of the measured activity coefficient γ_{Na^+} on X is shown in Figures 1 and 2, where γ_{Na^+} is corrected for small ion–small ion interactions by $\gamma_{Na^+}{}^{\circ}$, the sodium ion activity coefficient of the added NaBr in the absence of polyelectrolyte. Values of $\gamma_{Na^+}{}^{\circ}$ were obtained from the extended Debye–Hückel equation. For salt-free solution ($X = \infty$), $\gamma_{Na^+}{}^{\circ}$ is equal to unity. Also shown in Figures 1 and 2 are the theoretical curves obtained from the Manning and the Iwasa limiting laws. The plotted data demonstrate that, for the concentration range studied, $\gamma_{Na^+}/\gamma_{Na^+}{}^{\circ}$ is independent of the concentration of polyelectrolyte at any given value of X. This is in accord with both theories, which predict that the extent of counterion–polyion interaction is governed by the ratio of polyelectrolyte to simple salt and *not* by the concentration of either component individually.

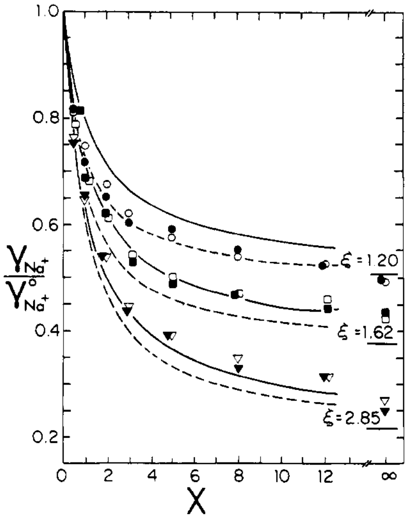

Figure 1. Dependence of $\gamma_{Na^+}/\gamma_{Na^+}{}^{\circ}$ on X at 25 °C in aqueous solutions of NaPAM-42 ($\xi = 1.20$), NaPAM-57 ($\xi = 1.62$), and NaPA ($\xi = 2.85$) containing NaBr. Open and closed symbols are for 0.018 and 0.0045 N polyelectrolyte, respectively. The solid and broken lines are from the Manning and Iwasa theories, respectively.

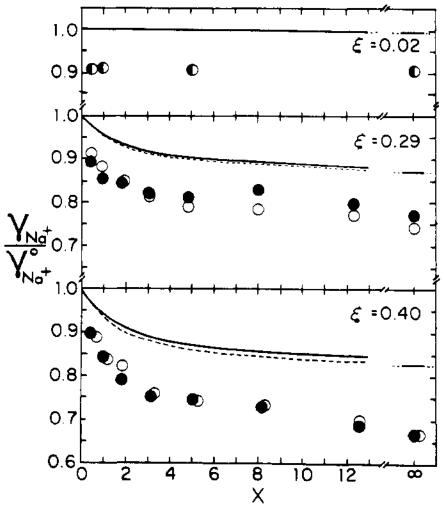

Figure 2. Dependence of $\gamma_{Na^+}/\gamma_{Na^+}{}^{\circ}$ on X at 25 °C in aqueous solutions of 0.018 (○), 0.0045 (●), and 0.003 N (◐) NaPAM-0.6 ($\xi = 0.02$), NaPAM-10 ($\xi = 0.29$), and NaPAM-14 ($\xi = 0.40$) containing NaBr. Solid and broken lines are from the Manning and Iwasa theories, respectively.

For each of the polyelectrolytes investigated, the measured activity coefficient ratios qualitatively follow theoretical predictions; i.e., $\gamma_{Na^+}/\gamma_{Na^+}{}^{\circ}$ decreases with increasing X for low X values and levels off approaching the

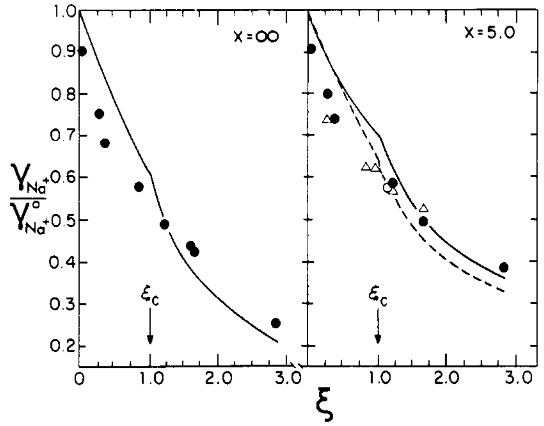

Figure 3. Dependence of $\gamma_{Na^+}/\gamma_{Na^+}{}^{\circ}$ on ξ at 25 °C in salt-containing ($X = 5$) and salt-free ($X = \infty$) solutions of NaPAM-*y* (●), NaPEC (△), and NaCMC (○). The solid and dashed curves are from the Manning and Iwasa limiting laws, respectively. (At $X = \infty$ both theoretical curves coincide.) NaPEC and NaCMC data are from ref 2.

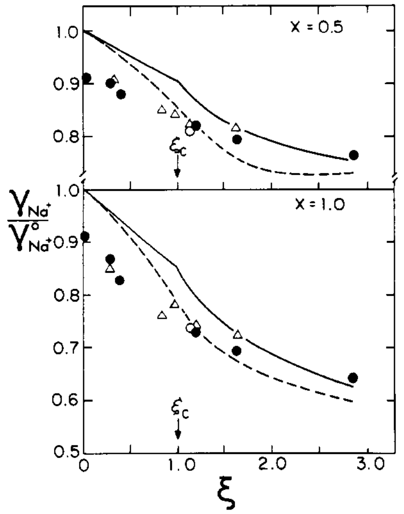

Figure 4. Dependence of $\gamma_{Na^+}/\gamma_{Na^+}{}^{\circ}$ on ξ at 25 °C in salt-containing aqueous solutions of NaPAM-*y* (●), NaPEC (△), and NaCMC (○). The solid lines are from the Manning and Iwasa limiting laws, respectively. NaPEC and NaCMC data are from ref 2.

salt-free value with increasing X. With the higher charge density polyelectrolytes, i.e., $\xi > 1$, the observed activity coefficients are in reasonable quantitative agreement with theory (Figure 1). For $\xi = 1.2$ the measured activity coefficients are consistently in agreement with the Iwasa predictions and below the Manning predictions over the whole range of X values studied. At higher charge densities, $\xi = 1.62$ and 2.85, the observed activity coefficient ratios are in good agreement with the Manning predictions and above the Iwasa predictions, except in salt-free solution, where both theories overestimate the extent of counterion–polyion interactions. When the charge density is below the critical value, $\xi = 0.02$, 0.29, and 0.40, both theories greatly underestimate the extent of interaction between counterions and polyions over the entire range of X values, as seen in Figure 2.

To examine the relationship between the measured and predicted counterion activity coefficients and ξ more closely, our experimental data and the theoretical curves are plotted in Figures 3 and 4 as a function of ξ for four different conditions: salt-free ($X = \infty$), excess polyelectrolyte ($X = 5$), equal concentrations of polyelectrolyte and simple electrolyte ($X = 1$), and excess simple salt ($X = 0.5$).

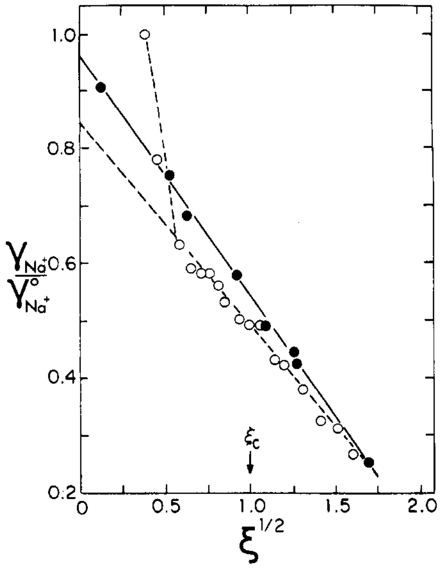

Figure 5. Linear relationship between $\gamma_{Na^+}/\gamma_{Na^+}{}^{\circ}$ and $\xi^{1/2}$ at 25 °C for aqueous salt-free solutions of NaPAM-*y* (●) and NaPMA (○). The NaPMA data are from ref 7.

In the absence of simple electrolyte ($X = \infty$, Figure 3) identical activity coefficients are predicted by the Manning and Iwasa limiting laws for each value of ξ. The measured values of $\gamma_{Na^+}/\gamma_{Na^+}{}^{\circ}$ are below the theoretical curve at low charge densities, intersect the theoretical curve at $\xi = 1.2$, and continue above the theoretical curve at higher charge densities.

In the presence of simple salt ($X = 5$, 1, and 0.5, Figures 3 and 4), the theoretical values obtained from the Iwasa limiting law are lower than from the Manning limiting law, over the whole range of ξ. The relationship of the experimental results to the theoretical curves is the same for all three conditions: at low charge densities the experimental results show that the counterion–polyion interactions are much stronger than dictated by either theory, at $\xi = 1.2$ the measured activity coefficients fall on the Iwasa curve, and at higher charge densities the experimental data are best described by the Manning theory.

Included in Figures 3 and 4 are the counterion activity coefficients reported by Joshi and Kwak[2] for sodium (carboxymethyl)cellulose (NaCMC) and a series of sodium pectinates (NaPEC) of varying charge density ($\xi = 0.25$–1.63), above and below ξ_c, in NaCl solution. Their results are in excellent agreement with those obtained in the present study at all charge densities. It was proposed by these authors that the poor agreement with theory at low charge densities might be the result of folding of the polyelectrolyte chain and thus a breakdown of the linear model employed in both theories. The use of conformational arguments to explain the discrepancy between experiment and theory does not seem justified in view of the excellent agreement in experimental results for the stiff polysaccharide polyelectrolytes and the much more flexible vinylic polyelectrolytes. It is highly unlikely that these two types of polyelectrolytes at equal charge densities would coil to the same extent in solution to give identical activity coefficients. In view of the results of these two studies it must be concluded that for polyelectrolytes whose ξ values are less than unity, the electrostatic interactions between counterions and polyions are more significant than predicted by either theory. Perhaps condensation takes place below ξ_c, as well as above.

While neither the Manning nor Iwasa theory adequately describes the behavior of counterions over the entire range of charge densities investigated, a new empirical rela-

Table II
Experimental and Predicted[a] Values for S and I in Equation 8

X	I_{exptl}	S_{exptl}	$S_{\text{pred}}{}^a$
0.5	0.96	0.13	0.14
1.0	0.96	0.19	0.21
2.0	0.97	0.27	0.28
3.0	0.97	0.32	0.31
5.0	0.97	0.36	0.35
8.0	0.99	0.40	0.37
12.5	0.96	0.40	0.39
∞	0.96	0.42	

[a] Predicted from eq 9.

tionship between the measured activity coefficients and polyelectrolyte charge density has been found. This is demonstrated in Figure 5, where the experimentally determined values of $\gamma_{\text{Na}^+}/\gamma_{\text{Na}^+}{}^\circ$ obtained in salt-free solution are seen to decrease linearly with $\xi^{1/2}$ according to the relationship

$$\gamma_{\text{Na}^+}/\gamma_{\text{Na}^+}{}^\circ = I - S\xi^{1/2} \tag{8}$$

where $I = 0.96$, $S = 0.42$, and $\gamma_{\text{Na}^+}{}^\circ$, as defined previously for salt-free solutions, equals unity. Since the measured activity coefficients were found to be independent of the polyelectrolyte concentration, only average measured values are plotted for clarity. What is most important about the linearity is that the same continuous relationship extends over both sides of ξ_c. As a consequence of this behavior, coupled with the large discrepancy between measured and theoretical activity coefficients below ξ_c, it is tempting to speculate that condensation not only occurs when $\xi > \xi_c$, where there is good agreement between experiment and theory, but below ξ_c as well. Although the physical significance of the linear relationship is not clear, it is not unreasonable that the intercept value of 0.96 for the sodium ion activity coefficient when $\xi = 0$ may be due to specific interactions between sodium ions and un-ionized polyacrylamide and that the slope is an interaction constant.

To determine if the linear relationship is unique for our series of polyelectrolytes, or more generally true, sodium ion activity coefficients reported by Costantino et al.[7] for salt-free aqueous solutions of partially neutralized poly(methacrylic acid) (PMA) are also plotted in Figure 5 for comparison. Between $\xi = 0.3$ and $\xi = 2.85$ good linearity is obtained, with $S = 0.35$ and $I = 0.84$. The rapid increase in the sodium ion activity coefficient below $\xi = 0.3$, which corresponds to 10% neutralization, may be an anomaly. This is supported by the fact that anomalous behavior has also been reported in viscosity[24] studies of PMA at low degrees of neutralization. It is most noteworthy that the linear relationship for NaPMA extends well above and below ξ_c, which is unity. When fully neutralized, the charge densities of poly(acrylic acid) and poly(methacrylic acid) are equal ($\xi = 2.85$). At this point the lines for the two polyelectrolyte systems intersect but they diverge with decreasing ξ. Since the charge density of PMA is varied by neutralization of carboxyl groups, with decreasing degree of neutralization (i.e., decreasing ξ) the self-ionization of unneutralized carboxyl groups becomes increasingly significant and, thus, may result in the divergence from the NaPAM-y series of polyelectrolytes, which were all fully neutralized. A systematic study comparing the behavior of partially and fully neutralized polyelectrolytes of comparable charge densities should be undertaken.

In the presence of NaBr, at any constant ratio of polyelectrolyte to simple salt, i.e., constant X, the linear relationship between $\gamma_{\text{Na}^+}/\gamma_{\text{Na}^+}{}^\circ$ and $\xi^{1/2}$ given by eq 8 is also obeyed as is shown in Figure 6. The numerical values of S and I in eq 8 for each X are given in Table II, where the correlation coefficients were all greater than 0.99. With increasing X, the values of S approach the salt-free value of 0.42; with decreasing X, they approach zero. If S, as suggested above, is a measure of the counterion–polyion interaction and if it is assumed that counterions from the added NaBr are not affected by the polyelectrolyte, then the slope for any value of X can be represented as an additivity rule

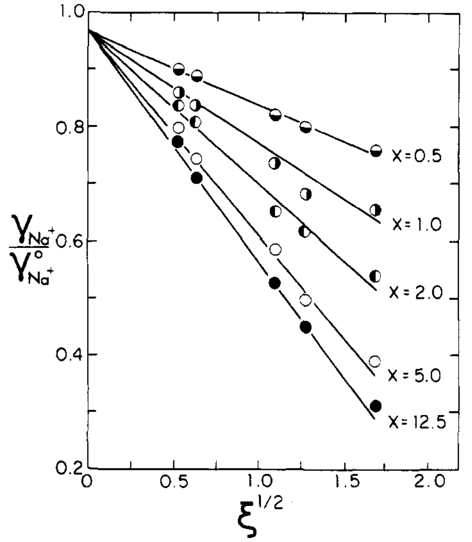

Figure 6. Linear dependence of $\gamma_{\text{Na}^+}/\gamma_{\text{Na}^+}{}^\circ$ on $\xi^{1/2}$ at 25 °C for aqueous solutions of NaPAM-y in the presence of NaBr.

$$S_X = \frac{X}{X+1}S_\infty + \frac{1}{X+1}S_s \tag{9}$$

where $X/(X + 1)$ and $1/(X + 1)$ are the dimensionless concentration weighting factors for polyelectrolyte and simple salt, respectively, S_∞ is the measured slope from salt-free polyelectrolyte solutions, and S_s is the slope for polyelectrolyte-free simple salt solutions. Since in formulating eq 9 it was assumed that S is an interaction constant and that the added simple electrolyte does not interact with the polyelectrolyte, $S_s = 0$, and the second term in eq 9 also equals zero. The experimental and predicted slopes agree remarkably well at all values of X, as is shown in Table II, confirming the assumptions that S is indeed an interaction constant and the added simple electrolyte does not interact with the polyelectrolyte to any significant extent.

The latter conclusion has previously been drawn from the observed additivity of counterion activities[3,6,11,25]

$$a_{\text{Na}^+} = a^{\text{P}}{}_{\text{Na}^+} + a^{\text{S}}{}_{\text{Na}^+} \tag{10}$$

where $a^{\text{P}}{}_{\text{Na}^+}$ and $a^{\text{S}}{}_{\text{Na}^+}$ are the sodium ion activities in salt-free polyelectrolyte solution and in polyelectrolyte-free simple salt solution, respectively. However, when expressed in this form, the additivity rule is dependent on the concentration of simple salt, due to small ion–small ion interactions. To eliminate this dependency a new empirical additivity rule is formulated analogously to eq 9, in terms of the dimensionless concentration parameter X

$$\left(\frac{\gamma_{\text{Na}^+}}{\gamma_{\text{Na}^+}{}^\circ}\right)_X = \left(\frac{X}{X+1}\right)\left(\frac{\gamma_{\text{Na}^+}}{\gamma_{\text{Na}^+}{}^\circ}\right)_\infty + \left(\frac{1}{X+1}\right)\left(\frac{\gamma_{\text{Na}^+}{}^\circ}{\gamma_{\text{Na}^+}{}^\circ}\right)_X \tag{11}$$

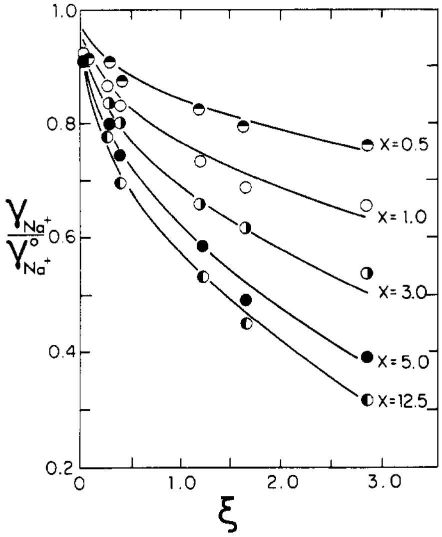

Figure 7. Comparison of experimental values of $\gamma_{Na^+}/\gamma_{Na^+}{}^\circ$ for NaPAM-*y* with predictions from additivity eq 11 (solid lines).

where the subscripts have the same meanings as in eq 9 and all other symbols have been previously defined. The first term on the right-hand side of eq 11 is the contribution from the polyelectrolyte; since its value is obtained from measurements in salt-free polyelectrolyte solution, $\gamma_{Na^+}{}^\circ$ equals 1. The second term is the simple salt contribution. A comparison of the experimental values with those predicted by additivity eq 11 is made in Figure 7, where again agreement is very good for all values of X, except at the very low charge density of $\xi = 0.02$. Thus from a knowledge of the activity coefficients in salt-free polyelectrolyte solution, the activity coefficients of salt-containing polyelectrolyte solutions can be quite accurately predicted, much more accurately than from either the Manning or Iwasa limiting laws.

References and Notes

(1) Kowblansky, M.; Tomasula, M.; Ander, P. *J. Phys. Chem.* **1978**, *82*, 1491.
(2) Joshi, Y. M.; Kwak, J. C. T. *J. Phys. Chem.* **1979**, *83*, 1978.
(3) Nagasawa, M.; Izumi, M.; Kagawa, I. *J. Polym. Sci.* **1959**, *37*, 375.
(4) Gubensek, F.; Lapanje, S. *Biopolymers* **1967**, *5*, 351.
(5) Oman, S.; Dolar, D. *Z. Phys. Chem.* **1967**, *56*, 1.
(6) Jordan, D. O.; Kurucsev, T.; Martin, M. L. *Trans. Faraday Soc.* **1969**, *65*, 598.
(7) Costantino, L.; Crescenzi, V.; Quadrifoglio, F.; Vitagliano, V. *J. Polym. Sci., Part A-2* **1967**, *5*, 771.
(8) Podlas, T. J.; Ander, P. *Macromolecules* **1970**, *3*, 154.
(9) Satake, I.; Fukuda, M.; Ohta, T.; Nakamura, K.; Fujita, N.; Yamauchi, A.; Kimizuka, H. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 2343.
(10) Ueda, T.; Kobatake, Y. *J. Phys. Chem.* **1973**, *77*, 2995.
(11) Archer, B. G.; Craney, C. L.; Krakauer, H. *Biopolymers* **1972**, *11*, 781.
(12) Rinaudo, M.; Milas, M. In "Polyelectrolytes and Their Applications"; Rembaum, A., Selegny, E., Eds.; Reidel Publishing Co.: Dordrecht, Holland, 1975; p 31.
(13) Manning, G. S. *Annu. Rev. Phys. Chem.* **1972**, *23*, 117.
(14) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(15) Manning, G. S. *J. Phys. Chem.* **1975**, *79*, 262.
(16) Manning, G. S. In "Polyelectrolytes"; Selegny, E., Ed.; Reidel Publishing Co.: Dordrecht, Holland, 1974; p 9.
(17) Devore, D. I.; Manning, G. S. *J. Phys. Chem.* **1974**, *78*, 1242.
(18) Manning, G. S. *Acc. Chem. Res.* **1979**, *12*, 443.
(19) Iwasa, K.; Kwak, J. C. T. *J. Phys. Chem.* **1977**, *81*, 408.
(20) Iwasa, D.; McQuarrie, D. A.; Kwak, J. C. T. *J. Phys. Chem.* **1978**, *82*, 1879.
(21) Moens, J.; Smets, G. *J. Polym. Sci.* **1957**, *23*, 931.
(22) Nagasawa, M. *J. Polym. Sci., Polym. Symp.* **1975**, *No. 49*, 1.
(23) Wells, J. D. *Proc. R. Soc. London, Ser. B* **1973**, *183*, 399.
(24) Noda, I.; Tsuke, T.; Nagasawa, M. *J. Phys. Chem.* **1970**, *74*, 710.
(25) Mock, R. A.; Marshal, C. A. *J. Polym. Sci.* **1954**, *13*, 263.

Active Transport and Selective Transport of Alkali Metal Ions through Poly(3-vinyl-1,4-butyrolactone-*co*-acrylonitrile) Membrane

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ABSTRACT: A membrane made of the lactone-containing polymer poly(3-vinyl-1,4-butyrolactone-*co*-acrylonitrile) exhibited active transport and selective transport of alkali metal ions. The active transport of metal ions was promoted by H^+. In the selective transport, the selectivity depended on both the affinity of the carrier fixed to the membrane for alkali metal ions and the hydrophobicity or hydrophilicity of the membrane.

The transport of specific ions is a common function of a biomembrane. It is observed in the active transport of ions through the cell wall, the proton transport in oxidative phosphorylation, and the selective transport of K^+ and Na^+ through the protoplasmic membrane. To develop synthetic membranes having such functions is an important objective of polymer chemistry.

Previously, active transport of metal ions through liquid membranes, such as the transport of alkali metal ions by monensin,[1] transport of Cu^{2+} by β-diketone,[2] and the transport of heavy-metal ions and anions by dithizone or trioctylamine,[2] has been investigated. Selective transport of metal ions through liquid membranes, such as the transport by crown ether[3] and macrocyclic ligands composed of tetrahydrofuran,[4] or through synthetic membranes[5,6] has been studied. With the liquid membrane, there is a membrane stability problem. Active and selective transport through a synthetic membrane carrying a fixed functional group has not been investigated.

We have synthesized several lactone-containing polymers.[7–9] Preliminary experiments showed that, among these polymers, the membrane made of poly(3-vinyl-1,4-butyrolactone-*co*-acrylonitrile) was capable of active and selective transport of metal ions.[10,11] In the present paper,

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