Evaluation of the Counterion Condensation Theory from the Metal Ion Distributions Obtained by Ultrafiltration of a System Poly(sodium 4-styrenesulfonate)/Cd^{2+}/Na^{+}

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Received: July 2, 1998; In Final Form: September 6, 1998

The metal ion distributions of a solution of poly(sodium 4-styrenesulfonate) in the presence of Cd^{2+} and Na^{+} ions are obtained by ultrafiltration. The results are used to evaluate the Manning's two-variable counterion condensation theory concerned with long-range interactions. The original theory results are insufficient to explain the metal ion distributions obtained, and short-range interactions have to be included. We also propose the inclusion of the influence of the polymer conformations in the theory.

1. Introduction

Ultrafiltration through a known exclusion rating membrane allows the detection of polymer metal ion interactions when using water soluble polymers of high molecular weight.[1-7] These polymers are previously fractionated by the same method, and the highest molecular weight fractions may be used. Metal ions with high interaction rates with the polymer stay retained by the polymer, which is not able to pass through the ultrafiltration membrane, while other ions are eluted through the membrane. When solutions of mixtures of metal ions are put in contact with the polymer solution, a profile for the retention of the different metal ions by the polymer during filtration can be obtained. The features about the pattern of these profiles have been recently discussed.[1] Crucial information may be extracted from these profiles, as the value of the dissociation constants or the concentration of ions bound to the polymer and free in the solution in every instant. This technique also provides some analytical and technological potential applications.

The analysis of the retention profiles of the polyelectrolyte poly(sodium 4-styrenesulfonate) in combination with certain amounts of Cd^{2+} and Na^{+} has been described,[1] and it has been shown that some consequences of the Manning's two-variable counterion condensation theory are accomplished. It was noted that at the limit of infinite elution, a remaining fraction of metal ions keeps bound to the polymer. The metal ion distribution at these conditions accomplished the Manning's limiting law that $\xi = (1 - \theta_1 - 2\theta_2)^{-1}$ and, for different ionic strength conditions, it was found that $d \ln K_2^{\text{diss}}/d \ln C_1 = 2$. Manning's theory is concerned with the long-range electrostatic interactions between the counterions and the polyion.[8] This theory points out that counterions will nonspecifically bind to the polyion chain. They accumulate around the polyion skeleton within a volume V^p where they are able to move. A large experimental and theoretical literature indicates that this condensed layer of counterions on polyelectrolytes prevents the contourlength charge density of the polyionic chain from exceeding a definite critical value. The central parameter of the theory is the dimensionless charge-density parameter ξ. A number of other theoretical approches on territorial binding have been developed,[9] including analysis of the cylindrical Poisson−Boltzmann

equation, hypernetted chain theory, and Monte Carlo computer simulations, and have reached qualitatively similar conclusions and found reasonable agreement with experiment.

However, other experiments have indicated the influence of short-range site-specific interactions. For example, it is impossible to explain, only invoking the long-range effects, the species selectivity among similar valence counterions in binding on the polyion. Manning[10] has included a $\delta\mu°$ parameter in his theory to account for short-range interactions, and Hao and Harvey[11] have developed a lattice theory to incorporate the short-range interactions into the counterion theory. On the other hand, comparison between experimental results and theoretical predictions demand the effective calculations of parameters such as the condensation volume, or the fitting of the effective condensation volume or the charge density parameter.[9,12-17]

In this paper, the results of the experiment previously described[1] concerning the distributions of counterions bound and free in the solution are analyzed under the scope of Manning's and Hao−Harvey's theories, to evaluate their validity.

2. Theory

2.1. Ultrafiltration Process and the Retention Profiles. The ultrafiltration is carried out in a steady state mixed flow reactor in which the binding and elution processes may be formulated as a chemical reaction, where reversible reaction in combination with an irreversible transfer of the metal ions across the membrane is responsible for metal retention, following Scheme 1:

SCHEME 1

$$M_Z^{b} \text{ (bound)} \quad \Leftrightarrow \quad M_Z \text{ (free)}$$
$$\downarrow$$
$$M_Z^{f}$$
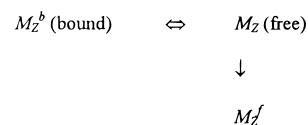
where M_Z^{b} is the amount of metal ions bound to the polymer and M_Z is the free or nonbound metal ions of valence Z in the cell solution. The uniformly mixed system attains in every instant during filtration an equilibrium situation. The retention R_Z is defined for each species of metal ions as the fraction per unit of metal ion remaining in the cell. The filtration factor F is defined as the volume ratio of the filtrate, V^f versus the volume

in the cell V^c. The metal ion remaining in the cell during filtration consists of the sum of the metal ion bound to the polymer chain and the metal ion free in the solution. These values are function of F. Then, the retention may be formulated as follows:

$$R_Z(F) = \frac{C_Z(F) + \theta_Z(F)c_p}{c_Z^{\text{init}}} \qquad (1)$$

where C_Z is the molarity in excess counterion of valence Z, θ_Z is the equilibrium binding fraction of the bound counterions per fixed polyion charge, c_p is the polyion concentration expressed in mole of polyion charge units per liter, and c_Z^{init} is the initial total metal ion concentration of valence Z.

The retention can be plotted versus the filtration factor, and a retention profile is obtained. The experimental profiles obtained by the authors correspond to functions of the type:

$$R_Z = u_Z + v_Z \exp(-k_Z F) \qquad (2)$$

where u_Z, v_Z, and k_Z are experimental parameters.

The subscript Z always refers to the valence of the metal ion concerned. If k_Z is greater than 1, it holds that, in every instant during filtration, a new equilibrium state is achieved with a characteristic dissociation constant. An expression of K_Z^{diss} as a function of F may be obtained:

$$K_Z^{\text{diss}}(F) = \frac{1}{\dfrac{k_Z^m}{k_Z} + \dfrac{u_Z k_Z^m}{v_Z k_Z \exp(-k_Z F)} - 1} \qquad (3)$$

where k_Z^m is the coefficient of membrane retardation, defined as $k_Z^m = c_Z^f/C_Z$, where c_Z^f is the concentration of metal ions in the filtrate in every instant. During filtration, all the variables θ_1, θ_2, C_1, and C_2 are changing. From eqs 1 and 3, the values of these variables can be calculated as a function of F, yielding

$$\theta_Z(F) = \frac{R_Z c_Z^{\text{init}}}{[1 + K_Z^{\text{diss}}]c_p} = \frac{c_Z^{\text{init}}}{c_p}[u_Z + (1 - k_Z)v_Z \exp(-k_Z F)] \qquad (4)$$

$$C_Z(F) = \frac{R_Z c_Z^{\text{init}} K_Z^{\text{diss}}}{[1 + K_Z^{\text{diss}}]} = c_Z^{\text{init}} k_Z v_Z \exp(-k_Z F) \qquad (5)$$

where the assumption that the influence of the membrane in the retention is negligible, that is to say, $k_Z^m = 1$, has been made.

2.2. Manning's Original Theory. Manning's theory[8] represents the solution as composed by a polyelectrolyte domain, in which counterions are nonspecifically bound (territorially bound or condensed) to the polyion and by uncondensed mobile ions diffused in the zone outside the polyion domain. The real polyelectrolyte chain is modeled as an infinite regular linear array of infinite fixed univalent point charges of spacing b. In the two-variable condensation theory, where the existence of two species of counterions of different valence is supposed, the formulation of the free energy of the system G_{sys}, taking in account the mixing of free counterions, bound counterions, and solvent molecules, yields in equilibrium conditions the following two expressions:

$$1 + \ln[10^3\theta_1/(V^pC_1)] = $$
$$-2\xi(1 - \theta_1 - 2\theta_2)\ln[1 - \exp(-\kappa b)] \qquad (6)$$

$$\ln[10^3\theta_2/(V^pC_2)] = 1 + 2\ln[10^3\theta_1/(V^pC_1)] \qquad (7)$$

where the subscripts 1 or 2 represent the mono- or divalent metal ion, respectively, V^p is the condensation volume within which the condensed ions are able to move, and ξ is the charge-density parameter given by the formula:

$$\xi = e^2/\epsilon k_B Tb \qquad (8)$$

where ϵ is the dielectric constant of the solvent, e is the elemental charge, T is the Kelvin temperature, and k_B the Boltzmann constant. Here it is supposed that $\theta_1 \gg \theta_2$.

Equations 6 and 7 represent a 2×4 equation system, where the four variables are θ_1, θ_2, C_1, and C_2.

2.3. Manning's Extended Theory. Manning extended his theory[10] with the introduction of a parameter, $\delta\mu°$, that accounts for short-range interactions of a territorially bound counterion with its local environment. Manning's interpretation of these short-range interactions is consistent with the notion of a highly mobile binding mode for the counterions: if a counterion A interacts more attractively with its local bound-state environment than does B, then A cannot wander as far from the polyion as its B counterpart. The new equations derived for the system considered above, i.e., a mixture of a monovalent counterion in excess with a divalent spieces, are

$$\frac{10^3 e\theta_1 \exp(Z_1\{\theta_1,\theta_2\})}{C_1 V_1^p \exp(-\delta\mu_1^0/RT)} = [1 - \exp(-\kappa b)]^{-2\xi(1-\theta_1-2\theta_2)} \qquad (9)$$

$$\frac{10^3 e\theta_2 \exp(Z_2\{\theta_1,\theta_2\})}{C_2 V_2^p \exp(-\delta\mu_2^0/RT)} = [1 - \exp(-\kappa b)]^{-4\xi(1-\theta_1-2\theta_2)} \qquad (10)$$

where $Z_1(\theta_1, \theta_2)$ and $Z_2(\theta_1, \theta_2)$ are defined in ref 10.

2.4. The Hao−Harvey Theory. The Hao−Harvey theory[11] is another extension of Manning's theory that includes considerations about short-range interactions. The counterions are admitted to bind in some extent site specifically. Then, the contribution to the free energy of the counterions site-specifically bound to the polymer is considered, including the corresponding binding constant K_Z for a single site of the polyion. The equilibrium binding fractions for the mixture of a monovalent and a divalent counterion are given by the expressions:

$$\frac{\theta_1}{C_1(1 - \theta_1 - \theta_2)} = K_1[1 - \exp(-\kappa b)]^{-2\xi(1-\theta_1-2\theta_2)} \qquad (11)$$

$$\frac{\theta_2}{C_2(1 - \theta_1 - \theta_2)} = K_2[1 - \exp(-\kappa b)]^{-4\xi(1-\theta_1-2\theta_2)} \qquad (12)$$

3. Experimental Section

3.1. Reagents. Commercialy available poly(sodium 4-styrenesulfonate), 20 wt % solution in water (Aldrich, synthesized from the para-substituted monomer), was fractionated by ultrafiltration over three membranes with an exclusion rating of 3000, 10000, or 100000 g/mol (Filtron), respectively, and the fractions were washed with water and lyophilized. Three fractions were obtained corresponding to the following molecular weight range: 3000−10000, 10000−100000, and over 100000 g/mol. Metal nitrates were used to prepare metal solutions.

3.2. Equipment. The unit used for retention studies consisted of a filtration cell with a magnetic stirrer, a membrane
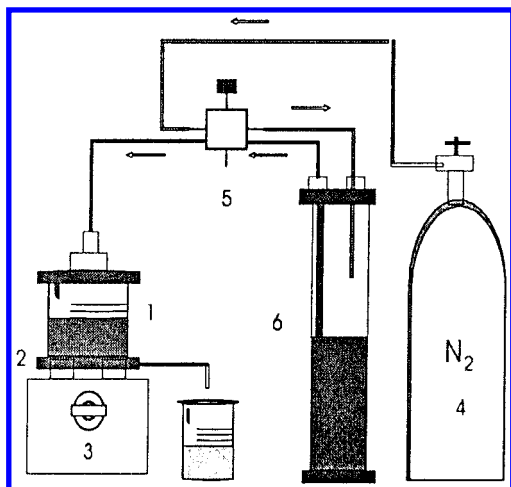
Figure 1. Retention unit. (1) Filtration cell containing the polymer−metal solution. (2) Membrane filtrate. (3) Magnetic stirrer. (4) Pressure trap. (5) Selector. (6) Reservoir.

with an exclusion rating of 3000, 10000, or 100000 g/mol (Filtron), a reservoir, a selector, and a pressure source (see Figure 1).

Metal ion concentrations were measured by atomic absorption on a Perkin-Elmer 3100 spectrometer. The pH was controlled on a pH meter H. Jürgens & Co.

3.3. Procedure. Polymer (molecular weight fraction over 100000 g/mol, 83 mg, 0.4 mmol sulfonate groups) and $NaNO_3$ (255 mg) were dissolved in bidistilled water, and $Cd(NO_3)_2$ 3.4 10^{-4} M solution (4 mL) was added. The solution was brought to 23 mL of total volume, and the pH was adjusted. The pH of the cell solutions and the reservoir containing only water were adjusted to pH 5. The filtration runs were carried out over a membrane with an exclusion rating of 3000 g/mol under a total pressure of 3 bar, keeping constant the total volume in the cell to 23 mL by creating a continuous flux of liquid through the cell solution from the reservoir. Filtration fractions were collected and the metal concentrations analyzed.

4. Results and Discussion

4.1. Equilibrium distributions of Cd^{2+} and Na^+. From the retention profiles obtained in the ultrafiltration experiment, the values of θ_2, θ_1, C_2, and C_1 may be calculated as a function of F. Then it was shown that the retenton profiles obtained,[1] in the experiment described, adjust very well with the functions $R_2 = 0.55 + 0.45 \exp(-1.90\ F)$ for Cd^{2+} and $R_1 = 0.064 + 0.936 \exp(-0.95F)$ for Na^+. The values of θ_2, θ_1, C_2, and C_1 calculated for these metal ions with eqs 4 and 5 from these retention profiles are shown in Table 1.

4.2. Problem of V^p. The experimental data shown in Table 1 may be used for comparison with the theoretical Manning's predictions. This demand the effective calculations of the condensation volume and the charge density parameter. However, there is no general accepted theoretical expression for V^p. Expressions of V^p have been developed upon the assumption of relative low ionic strengths.[9,12−14] An expression of V^p for sufficient diluted solutions is given by

$$V^p = 2718.28[(1 - \xi^{-1})(\kappa b)^2]/C_1 \qquad (13)$$

If the experimental θ_2, θ_1, C_2, and C_1 obtained by ultrafiltration are substituted in eqs 6 or 7, the condensation volume should be calculated. The results of these substitutions are shown in Table 2 as well as the condensation volumes calculated from

TABLE 1: Values of the Binding Fractions of Na^+ and Cd^{2+} and the Concentrations of Free Metal Ions in the Solution as a Function of F Calculated From the Ultrafiltration Experimental Results

F	$\theta_1{}^a$	$\theta_2{}^a$	$C_1{}^b$ (mol l^{-1})	$C_2{}^b$ (mol l^{-1})
0	0.949	0.014	0.132 447	0.001 456 4
0.87	0.724	0.046	0.05 798	0.000 279 1
1.74	0.625	0.052	0.025 381	5.348×10^{-5}
2.61	0.582	0.054	0.011 111	1.025×10^{-5}
3.48	0.563	0.054	0.004 864	1.964×10^{-6}
4.35	0.555	0.054	0.002 129	3.764×10^{-7}
5.22	0.551	0.054	0.000 932	7.213×10^{-8}
6.09	0.549	0.054	0.000 408	1.382×10^{-8}
6.96	0.549	0.054	0.000 179	2.649×10^{-9}
7.83	0.548	0.054	7.82×10^{-5}	5.076×10^{-10}
8.7	0.548	0.054	3.42×10^{-5}	9.727×10^{-11}
9.57	0.548	0.054	1.5×10^{-5}	1.864×10^{-11}
10.4	0.548	0.054	6.56×10^{-6}	3.572×10^{-12}

^{a} Calculated from eq 4. ^{b} Calculated from eq 5.

TABLE 2: Values of the Condensation Volumes Calculated from Different Equations as a Function of F and their Corresponding Total Volumes in the Solution

F	V^{pa} (cm^3/mol)	V^{pb} (cm^3/mol)	V^{pc} (cm^3/mol)
0	16227.2	14310.0	1175.2
0.87	5137.1	2553.9	1154.1
1.74	2260.2	1681.7	1144.9
2.61	1398.8	1425.3	1140.8
3.48	1080.3	1328.5	1139.1
4.35	944.1	1288.7	1138.3
5.22	879.6	1271.7	1138.0
6.09	845.9	1264.4	1137.8
6.96	825.9	1261.1	1137.7
7.83	811.9	1259.8	1137.7
8.7	800.6	1259.2	1137.7
9.57	790.4	1258.9	1137.7
10.4	780.7	1258.8	1137.7

^{a} Calculated from eq 6. ^{b} Calculated from eq 7. ^{c} Calculated from eq 13.

eq 13. For diluted solutions, the condensation volumes calculated from eq 13 take values that are in the range between the values calculated from eqs 6 and 7. But it is noted that these two last condensation volumes calculated are not coincident. That means that our experimental results do not satisfy Manning's equation system 6 and 7; that is to say, there is no V^p that may allow the experimental set of θ_2, θ_1, C_2, and C_1 be a solution of this equation system. The combination of these equations yields

$$\frac{C_1\theta_2}{C_2\theta_1} = [1 - \exp(-\kappa b)]^{-2\xi(1-\theta_1-2\theta_2)} \qquad (14)$$

which is not dependent on V^p. Evaluating both sides of this equation with the experimental results, they differ in a factor which is also a function of F. This factor can be calculated by the following expression:

$$g(F) = \frac{C_1\theta_2}{C_2\theta_1}[1 - \exp(-\kappa b)]^{2\xi(1-\theta_1-2\theta_2)} \qquad (15)$$

The values of $g(F)$ are shown in Figure 2. They show that both sides of eq 14 differ in a factor that varies from 0.5 to 2. A reason of this inaccuracy may be found invoking extended theories.

4.3. The short-range interactions. Hao−Harvey and Manning's extended theories include the effect of the short-range interactions on the free energy of the system. Manning's

Counterion Condensation Theory

J. Phys. Chem. B, Vol. 102, No. 52, 1998 **11027**
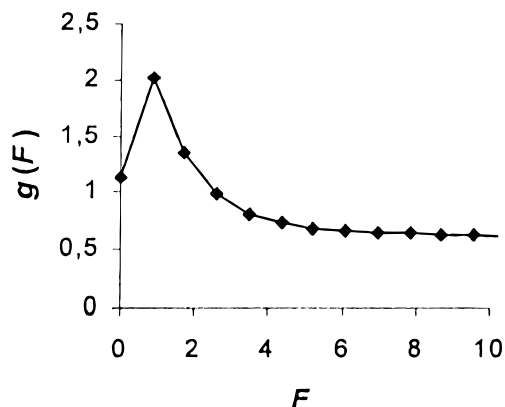
Figure 2. Plot of $g(F)$ from the experimental θ_2, θ_1, C_2, and C_1 obtained by ultrafiltration.

eqs 9 and 10 may be combined, and the same can be done with Harvey's eqs 11 and 12, to obtain expressions very similar to eq 14 that include $g(F)$, so that

$$g(F) = \frac{V_2^{\mathrm{p}}}{V_1^{\mathrm{p}}} e^{Z_2(\theta_1,\theta_2)-Z_1(\theta_1,\theta_2)} e^{-(\delta\mu_0^2-\delta\mu_1^0)/RT} \qquad (16)$$

and

$$g(F) = \frac{K_2}{K_1} \qquad (17)$$

applying for Manning's and Hao−Harvey expressions, respectively. The factor $\exp[Z_2(\theta_1,\theta_2) - Z_1(\theta_1,\theta_2)]$ is 1 in this case. From Hao−Harvey expression it can be interpreted that the values of the function $g(F)$ in every point are direct measurements of the relative short-range interactions of the polyion with the two counterion species. These relative short-range interactions are function of F as shown in Figure 2. This point may be discussed from many points of view. Hao and Harvey pointed out that the short-range interactions are basically independent of the ionic strength, and the long-range interactions are strongly dependent on it. From our results it is noted that both K_1 and K_2 are changing as well with F, and so does their ratio. However, here, the main property changing with F is the concentration of free metal ions in the solution, as well as the distributions of metal ions bound to the polymer. Then from the Hao−Harvey equation it has to be concluded that the binding constants increase as the ionic strength increases. The values of the constants are calculated from the experimental data and they are shown in Table 3. Upon analyzing Manning's expression, the dependence of $g(F)$ with F could be interpreted as an effect of the local concentrations.[10] The assumption of independence of V^{p} with the concentrations could also be reviewed. The values of $V_Z^{\mathrm{p}} \exp(-\delta\mu_Z^\circ/RT)$ calculated from eqs 9 and 10 are also shown in Table 3.

On the other hand, another change associated with the change of the amounts of metal ions in polyelectrolyte solutions is the conformation of the chain. In the next section it will be discussed how the conformation effects could be included in the theory.

4.4. The Conformation. Manning's theory relates the concentration of counterions bound and not bound to the polymer with the charge-density parameter assuming the polymer as a straight linear arrange. In salt-free solutions of polyelectrolytes, the conformation of the polymer is rodlike due to charge repulsions in the chain. But as the ionic strength

TABLE 3: Values of the Site-Specific Binding Constants Calculated from Hao-Harvey's Equations as a Function of F, and the Parameters $V_Z^{\mathrm{p}} \exp(-\delta\mu_Z^\circ/RT)$ Calculated from Manning's Equations, Considering $b = 2.42$ Å

| F	$K_1{}^a$	$K_2{}^b$	$V_1^{\mathrm{p}} \exp(-\delta\mu_1^\circ/RT)^c$	$V_2^{\mathrm{p}} \exp(-\delta\mu_2^\circ/RT)^d$
0	162.1	183.8	16227.2	18401.2
0.87	8.212	16.51	5137.1	10333.1
1.74	2.577	3.464	2260.2	3037.8
2.61	1.411	1.385	1398.8	1372.9
3.48	1.037	0.843	1080.3	878.5
4.35	0.887	0.650	944.1	691.6
5.22	0.819	0.566	879.6	608.4
6.09	0.784	0.525	845.9	565.9
6.96	0.764	0.501	825.9	540.8
7.83	0.751	0.484	811.9	523.3
8.7	0.740	0.471	800.6	509.0
9.57	0.731	0.459	790.4	496.3
10.4	0.722	0.448	780.7	484.2

^{a} Calculated from eq 11. ^{b} Calculated from eq 12. ^{c} Calculated from eq 9. ^{d} Calculated from eq 10.
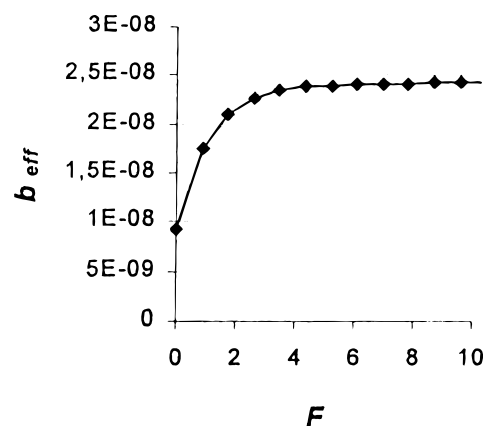
Figure 3. Evolution of the effective average distance between the charges in the polymer b_{eff} with the filtration factor F.

increases, the polymer coils as it is largely observed by viscosimetric studies.[17−19] Besides, it has been shown by Essafi et al. that hydrophobicity in the backbone of PSS affects its conformation, even if the chain is highly charged.[20] This polymer can build clusters in dilute solutions. All this can influence the "observed" value of the charge-density parameter, and some authors have used it as an adjustable parameter.[9,15,16] In this discussion we are assuming that $V_1^{\mathrm{p}} = V_2^{\mathrm{p}}$, an assumption that has previously been considered.[10] We are also interpretating the influence of the local concentrations in $\delta\mu_Z^\circ$ being negligible or at least equal for both counterion species, so that the value of the selectivity coefficient, $\alpha = \exp[-(\delta\mu_2^\circ - \delta\mu_1^\circ)/RT]$, and then $g(F)$ is constant. As the charge density parameter is related with the average spacing between the charges, we prefer to parametrize $b = b_{\mathrm{eff}}$. We have looked for the values of b_{eff} that make $g(F)$ constant and equal to the value obtained at infinite elution, also considering the change on ξ with b_{eff}. The results are given in Figure 3, where it can be seen that for low F values, the distance between the charges decreases notably. We model this fact visualizing the polymer projected over an imaginary straight line who will be responsible for the counterion condensation, as Manning's models are constructed on the basis of a straight linear arrange. The polymer coils and, in consequence, the charge-density parameter increases because b decreases in the proyection. Coiling is function of the concentration of metal ions in the solution and b is function of coiling. The dependence of b_{eff} with C_1 is plotted in Figure 4, and the result is a straight line, at least in this concentration range. The calculation of $V_Z^{\mathrm{p}} \exp(-\delta\mu_Z^\circ/RT)$ from eqs 9 and
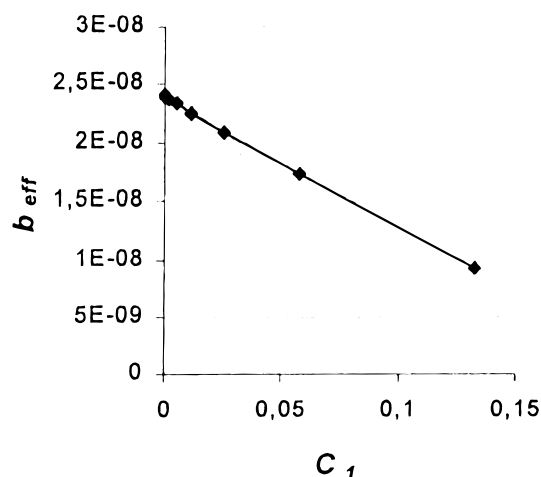
Figure 4. Evolution of the effective average distance between the charges in the polymer b_{eff} with the concentration of Na^+ in excess C_1.

TABLE 4: Values of the Site-Specific Binding Constants Calculated from Hao-Harvey's Equations as a Function of F, and the Parameters $V_Z^p \exp(-\delta\mu_Z°/RT)$ Calculated from Manning's Equations, Considering b_{eff} in angstroms

F	$K_1{}^a$	$K_2{}^b$	$V_1^p \exp(-\delta\mu_1°/RT)^c$	$V_2^p \exp(-\delta\mu_2°/RT)^d$
0	88.64	54.97	8875.1	5504.3
0.87	2.532	1.571	1584.1	982.5
1.74	1.189	0.738	1043.1	647.0
2.61	0.892	0.553	883.8	548.1
3.48	0.791	0.490	823.9	510.9
4.35	0.751	0.466	799.2	495.6
5.22	0.734	0.455	788.7	489.2
6.09	0.727	0.451	784.1	486.3
6.96	0.724	0.449	782.2	485.1
7.83	0.723	0.448	781.4	484.7
8.7	0.722	0.448	781.0	484.4
9.57	0.722	0.448	781.3	484.9
10.4	0.722	0.448	780.7	484.2

^{a} Calculated from eq 11. ^{b} Calculated from eq 12. ^{c} Calculated from eq 9. ^{d} Calculated from eq 10.

10 with the values of b_{eff} plotted in Figure 3 are shown in Table 4. Variations of these values with F are observed. If $\exp(-\delta\mu_Z°/RT)$ does not change with F, it should be V_Z^p which changes. The calculated K_Z values from eqs 11 and 12 with the new b_{eff} values are also shown in Table 4.

5. Conclusions

The data obtained from an ultrafiltration experiment concerning the distributions of Cd^{2+} and Na^+ bound to the polymer and free in the solution have been used to analyze the Manning's two-variable counterion condensation theory. The experimental data do not satisfy Manning's original equations, and invoking the inclusion of short-range interactions to the theory becomes necessary. Then, Manning's and Hao–Harvey's extended theories from Manning's original theory have been analyzed. The short-range interaction constants calculated from the Hao–Harvey theory are a function of F. Assuming that $V_1^p = V_2^p$, and that the selectivity coefficient is constant, the experimental values satisfy Manning's extended equations if we parametrize the average distance between the charges of the polyion. Parametrizing the values of b could have the physical meaning of introducing the effect of the polymer conformation in the theory.

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