

Interpretation with a Donnan-Based Concept of the Influence of Simple Salt Concentration on the Apparent Binding of Divalent Ions to the Polyelectrolytes Polystyrenesulfonate and Dextran Sulfate

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It has been shown that the apparent enhancement of divalent metal ion binding to polyions such as polystyrenesulfonate (PSS) and dextran sulfate (DS) by decreasing the ionic strength of these mixed counterion systems (M^{2+} , M^+ , X^- , polyion) can be anticipated with the Donnan-based model developed by one of us (J.A.M.). Ion-exchange distribution methods have been employed to measure the removal by the polyion of trace divalent metal ion from simple salt ($NaClO_4$)-polyion ($NaPSS$) mixtures. These data and polyion interaction data published earlier by Mattai and Kwak for the mixed counterion systems $MgCl_2$ - $LiCl$ -DS and $MgCl_2$ - $CsCl$ -DS have been shown to be amenable to rather precise analysis by this model.

Introduction

In a recent publication of Mattai and Kwak¹ interpretation of a detailed investigation of polyion-counterion interactions in the mixed counterion systems $M^{2+}/M^+/X^-/polyion$ (where $M^{2+} = Mg^{2+}$, Ca^{2+} ; $M^+ = Li^+$, $(CH_3)_4N^+$, Na^+ , K^+ , or Cs^+ ; $X^- = Cl^-$; polyion = dextran sulfate) at various ionic strengths and polymer concentrations was sought with the "two-variable theory" developed by Manning.² This approach, a direct outgrowth of Manning's counterion "condensation model",³ while qualitatively predicting the observed properties of these systems, could not anticipate the differences in behavior that were determined to be a function of the particular metal ion employed. This result, of course, was not unexpected since the theoretical estimates which are solely determined by the structural charge density parameter of the polymer, ξ , yield one kind of behavior for all systems and must necessarily be completely insensitive to the effect of the nature of the univalent counterion present in excess. The qualitative aspects of this application do not, however, detract from the value of the "counterion condensation" concept. Instead they confirm the validity of the model and lead to the following reasoned observation. If a "condensed" volume is indeed encountered in charged polyelectrolyte systems it must be permeable to the diffusible components, excess salt and water of the system. The higher counterion density of the "condensed" volume must, as a consequence, lead to a Donnan potential resistant to salt entry. The Donnan model deduced from this kind of reasoning is believed to provide additional insight with respect to the properties of polyelectrolyte-excess neutral salt mixtures.

In an earlier publication by one of us (J.A.M.)⁴ it was shown that the distribution of counterions in polyelectrolyte-salt mixtures is indeed controlled by a Donnan potential. Use of this concept facilitated quantitative interpretation of polyelectrolyte equilibria to document fully this conclusion. Further confirmation of the applicability of a Donnan model to polyelectrolyte-salt mixtures has been sought in this paper by examining the use of this approach to anticipate counterion patterns of partition between a polyion domain, assumed to be identical with the "condensed" volume available from Manning's two-variable theory, and the solution in equilibrium with it.

We have analyzed by our approach⁴ the data obtained by us in a study of the interaction of several trace metal ions (Ca^{2+} , Zn^{2+} , and Co^{2+}) with sodium polystyrenesulfonate as a function of polyelectrolyte concentration and the concentration of excess salt. We have also examined by our approach additional data obtained by Mattai and Kwak for two systems ($MgCl_2$ - $LiCl$ -dextran

sulfate and $MgCl_2$ - $CsCl$ -dextran sulfate). The behavior of the first of these two systems was well anticipated by the Manning theoretical treatment while the properties of the other were not.

In this model, the electrochemical potential of the diffusible components, MX_2 and MX , in the presence of a fully dissociated polyelectrolyte, M^{2+} , M^+ polystyrenesulfonate ($(PSS^-)_n$), is at equilibrium at every point in the system. By dividing the system into regions large enough to buffer disturbance by ion fluctuations in the system but small enough to be representative of differential volume elements of the system, one can equate the electrochemical potential of the diffusible components in the volume element at the surface of the polymer which is representative of the polymer domain with any other differential volume element throughout the solution which in turn can be equated with the average macroscopic electrochemical potential measured for these components.^{4,5} With this approach

$$\bar{a}_{M^{2+}}/(\bar{a}_{M^+})^2 = \bar{a}_{M^{2+}}/(\bar{a}_{M^+})^2 \quad (1)$$

where the symbol \bar{a} and the bar placed over the activity, a , assigned to each of the two counterions represent the polyion surface (domain) and the solution itself.

To facilitate assignments of activities to the pairs of ions (univalent and divalent) examined in our studies the ratio of $\bar{a}_{M^{2+}}/(\bar{a}_{M^+})^2$ has been obtained from the literature-based mean molal activity coefficients at the experimental ionic strength by expressing their ratio as

$$\frac{(\bar{a}_{M^{2+}})}{(\bar{a}_{M^+})^2} = \frac{m_{MX_2}(\gamma_{\pm}^0(MX_2))^3}{(m_{MX})^2(\gamma_{\pm}^0(MX))^4} \quad (2)$$

In those situations where the ionic strength of the system was 0.10 or less the single ion activity coefficients employed were based on their computation by Kielland.⁶ To obtain a similar evaluation of $\bar{a}_{M^{2+}}/(\bar{a}_{M^+})^2$ ion-exchange selectivity data available for the various pairs of ions⁷ were used to assign values of $\bar{\gamma}_{M^{2+}}/(\bar{\gamma}_{M^+})^2$ in the PSS systems studied. In our examination of the trace divalent metal- $NaPSS$ - $NaClO_4$ systems in this article, $\bar{\gamma}_{M^{2+}}/(\bar{\gamma}_{M^+})^2$ was obtained directly by simply extrapolating such ion-selectivity data, plotted as a function of resin molality, to the molality value deduced for the polymer domain. With the dextran sulfate system the same procedure was used for assignment of $\bar{\gamma}_{M^{2+}}/(\bar{\gamma}_{M^+})^2$ values. However, because of the absence of ion-selectivity data for resin analogues of dextran sulfate the ion-exchange data available for the poly(styrenesulfonate) system were

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substituted for estimate of this parameter. The presumption that dextran sulfate parallels the polystyrenesulfonate in its interaction with metal ions is not unreasonable but can be expected to detract somewhat from the unambiguous model substantiation sought in this article.

In this approach the effect of ion-ion interaction on the activity coefficient ratios in the polyion domain and in the overall solution as the relative content of M^{2+} and M^+ varied in both phases has been neglected.

To evaluate $\sum \bar{M}^+ / \sum S V_p$, the fraction of univalent metal ion apparently associated with the polymer domain volume, V_p , in the presence of trace metal ion, a correlation for site vacancy was made by multiplying the above term by $(1 - \phi_{P_{M^+}})$, where $\phi_{P_{M^+}}$ is the measured^{7,8} (or computed)³ practical osmotic coefficient of the M^+ ion form of the polyelectrolyte. In transposing the data of Mattai and Kwak site vacancy associated with the uptake of M^{2+} ion by the dextran sulfate also had to be taken into account as shown in eq 3 by multiplying its experimental fractional uptake, $\sum \bar{M}^{2+} / \sum S$, by $2(1 + \phi_{P_{M^{2+}}})$ where $\phi_{P_{M^{2+}}}$ is the measured^{7,8} (or calculated)³ practical osmotic coefficient of its M^{2+} ion form. Use of the ϕ_p parameter in the above manner for site vacancy estimates is justified, both experimentally and theoretically, by the fact that the fraction of polymer matrix surface charge neutralized by counterion condensation can be equated with $(1 - \phi_p)$.

$$\left[1 - \left(\frac{2 \sum \bar{M}^{2+}}{\sum S} \right) (1 + \phi_{P_{M^{2+}}}) \right] (1 - \phi_{P_{M^+}}) = \sum \bar{M}^+ / \sum S V_p \quad (3)$$

With eq 1 rearranged as shown:

$$\frac{\bar{a}_{M^{2+}}}{(\bar{a}_{M^+})^2} \frac{(\bar{a}_{M^+})^2}{(\bar{a}_{M^{2+}})^2} = 1 \quad (1a)$$

Substitution of the concentration and activity coefficient terms expressed as described above yields

$$\left(\frac{\sum \bar{M}^{2+}}{\sum S} \right) (V_p) (\bar{\gamma}_{M^{2+}}) (\bar{m}_{MX})^2 (\gamma_{\pm}^0(MX))^4 / \left[\left[\left(1 - \frac{2 \sum \bar{M}^{2+}}{\sum S} \right) (1 + \phi_{P_{M^{2+}}}) \right] \times (1 - \phi_{P_{M^+}}) \right]^2 (\bar{\gamma}_{M^+})^2 (\bar{m}_{MX_2}) (\gamma^0(MX_2))^3 = 1 \quad (4)$$

It was possible to determine the validity of the approach by comparing the value of the activity ratios so obtained with the sought-for value of unity. The theoretically based equation due to Manning² was used to provide an estimate of V_p .

The fact that Manning's free energy minimization based estimate of V_p provides a reasonable estimate of this parameter¹⁰ was believed to justify its use to reach the above goal. Even though Manning does not consider a Donnan potential mode it is difficult for this author to disregard this aspect of Manning's "condensation" model.

Experimental Section

The ion-exchange distribution method, first employed by Schubert,⁹ was used in the research program to facilitate the accurate assessment of $(\sum \bar{M}^{2+} / \sum S) / \bar{m}_{M^{2+}}$ in our examination of trace metal ion interaction with NaPSS.

All chemicals used in the experimental program were reagent grade. Deionized, triply distilled water was used in the preparation of all solutions. Sodium polystyrenesulfonate (NaPSS) of average

molecular weight 500 000 was supplied by the National Starch and Chemical Corporation, Bridgewater, NJ.

Stock solutions of the NaPSS, prepared for use as described in earlier research with this polyelectrolyte,^{7,8} were standardized by titrating the total H^+ ion form with standard 0.100 N NaOH. Their density was measured to permit conversion from molarity to molality units.

Sodium perchlorate, prepared by the controlled neutralization of perchloric acid with sodium carbonate prior to its crystallization, was dried to constant weight at 110 °C. Stock solutions of the desired molality were then prepared.

Analytical grade AG50W-X8 cation-exchange resin, 50–100 mesh, obtained in the hydrogen form from Bio-Rad Laboratories, Richmond, CA, was converted to the sodium form with NaOH. The resin, washed free of hydroxide ion, was then equilibrated isopiesticly with saturated ammonium chloride solution to control the resin water content.

The water content of the resin, following equilibration with 0.100 *m* and 0.300 *m* NaClO₄, was determined to be 0.9189 and 0.8984 per gram of dry resin by using the procedures described by Gregor, Held, and Bellin¹¹ and Scatchard and Anderson.¹² Salt invasion by the resin was not measured; it has been shown to be negligible even in 0.3 *m* solution.

The resin capacity (mequiv of Na⁺/g of dry resin) measured for each prepared batch of sodium-form resin was 4.68 ± 0.08 by using two procedures: weighed samples were converted to the hydrogen form prior to titrating the resin in the presence of NaCl with standard base in the first, and an isotope dilution technique using sodium-22 was employed in the second.

The radioisotopes calcium-45, cobalt-60, and zinc-65, which were employed as trace metal ions in the ion-exchange distribution studies, were purchased from either the ICN Chemical and Radioisotope Division or the New England Nuclear Corporation.

The distribution studies were carried out in solutions either 0.10 *m* or 0.30 *m* in NaClO₄; they contained NaPSS at concentrations ranging from 5.0×10^{-4} to approximately 2.0×10^{-2} *m* on a monomer basis. Approximately 2–4 μ Ci of the radioactive trace metal ion were added to the sample solution.

In a typical experiment two weighed aliquot portions of the sample solution were added to approximately 1.2-g samples of the solvated sodium-form resin previously weighed into polyethylene bottles. The samples were agitated at 25 ± 0.5 °C for a period of at least 24 h. The residual activity level of duplicate aliquot portions of the solution phase were measured for comparison with the activity level of the solution prior to contact with the resin.

In each distribution study, parallel experiments were carried out with the polyelectrolyte-free but otherwise equivalent solution. In addition, distribution measurements were performed over an extended concentration range of the bulk electrolyte in order to define the distribution pattern of the metal ion between the resin and solution phases. To assure the validity of the experimental program it was important to demonstrate that the distribution pattern agreed with theoretical predictions.

Radioactivity measurements were performed with a Packard Tri-Carb Spectrometer which was equipped with an Auto-Gamma Analyzer. Solutions containing the γ emitters, ⁶⁰Co and ⁶⁵Zn, were measured with the Auto-Gamma Analyzer which consisted of a well-type NaI(Tl) scintillation detector and a single-channel analyzer. The liquid scintillation detector was used to measure the β -emitting ⁴⁵Ca radionuclide; an emulsion counting technique using a toluene, Triton X-100 scintillant¹³ was employed.

In most cases at least 5×10^4 disintegrations were collected to assure high statistical precision in the measurements.

Results and Discussion

A representative presentation of the equilibrium distribution behavior of a trace metal ion between resin and polyelectrolyte-free NaClO₄ solution as the electrolyte concentration is varied is given

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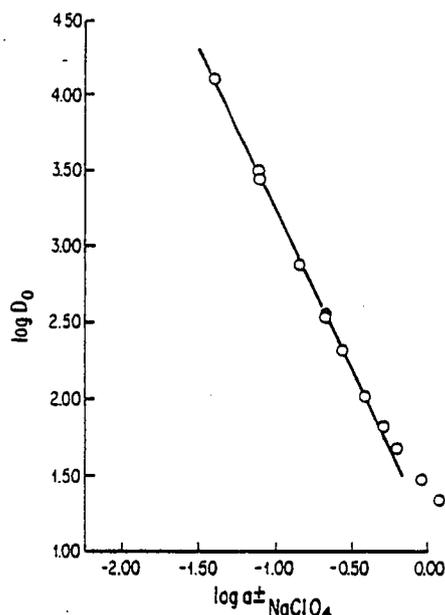


Figure 1. Distribution, D_0 , of ^{60}Co between PSS resin and NaClO_4 solution.

in Figure 1. In this figure the logarithm of D^0 (counts/s/g of dry resin/counts/s/g of soln) is plotted vs. the logarithm of the mean molal activity of NaClO_4 . Such examination of the distribution data provides a stringent assessment of the salt concentration range in which the ion-exchange distribution method can be employed to measure quantitatively the extent of sequestering of trace metal ion by the polyelectrolyte under investigation in our systems. As long as (1) curvature is absent in the resultant line and (2) the straight line has a slope of -2.00 for the trace divalent ions the fundamental assumption that is the basis of the method can be assumed to be obeyed. As soon as deviation from the straight line occurs this basic assessment of the situation, i.e., the constancy of the macrocounterion composition of the resin phase, is no longer valid due to significant imbibement of the resin by NaClO_4 . Such deviation from ideal behavior is noticeable in Figure 1, curvature from the straight line observed (slope = -2.10) occurring when the concentration level of the NaClO_4 reaches 0.60 m . In the other trace activity (^{65}Zn , ^{45}Ca) NaClO_4 systems examined straight lines were also obtained (a slope of -2.08 for $^{60}\text{Co}(\text{II})$ and -2.04 for $^{65}\text{Zn}(\text{II})$) beyond the limited ($\leq 0.3\text{ M}$) NaClO_4 concentration range examined. In every case D_0 is well-behaved in the concentration range of our experimental program and use of the ion-exchange distribution method to examine the removal of trace metal ion from the solution phase by polyelectrolyte as described in the Experimental Section of this manuscript is shown to be most appropriate.

The distribution data obtained for the trace metal ion- $\text{NaPSS}-\text{NaClO}_4$ systems are summarized in column 2 of Table I. Estimates of the apportionment of the trace element between NaPSS and the NaClO_4 solution from these data are listed in the last column of this table.

The $(D_0 - D)/D$ parameters resolved from the distribution data to define the ratio $({}^u\text{M}^{2+})/({}^u\text{M}^{2+})$ are listed in Table I and have been employed in eq 1b to test whether the Donnan model provides a meaningful description of the system under investigation. Resolution, with this equation, of numbers close to unity would provide substantial support for the validity of the premises put forward in development of this equation.

To facilitate the computations a value of 879 mL/mol was assigned to V_p ; this estimate of V_p was obtained with the following theoretically based equation of Manning.²

$$V_p = 4.11(\xi - 1)(b)^3 \quad (5)$$

In this equation V_p has the units of cm^3/mol when b , the struc-

TABLE I: Apportionment of Trace Metal Ion (${}^u\text{M}^{2+}$) between NaPSS and NaClO_4 Solution As Deduced from Ion-Exchange Distribution Measurements

NaPSS, m	D	$D_0 - D$	$(D_0 - D)/D^a$
System: $^{60}\text{Co}^{2+}$, $\text{NaPSS}, 0.300\text{ m}$ NaClO_4			
0.00094	180.1	3.5	0.0194
0.00130	178.4	5.2	0.0291
0.0025	175.9	7.7	0.0438
0.0052	171.5	16.1	0.0961
0.0080	161.0	22.0	0.137
0.0105	155.7	27.9	0.179
System: $^{60}\text{Co}^{2+}$, $\text{NaPSS}, 0.100\text{ m}$ NaClO_4			
0.00084	1344.6	136.3	0.113
0.0017	1146.8	197.8	0.172
0.0026	1122.3	222.3	0.198
0.0054	866.0	478.6	0.553
0.0092	615.0	729.6	1.186
0.0123	498.4	846.2	1.698
System: $^{65}\text{Zn}^{2+}$, $\text{NaPSS}, 0.300\text{ m}$ NaClO_4			
0.00059	177.7	1.5	0.00851
0.000923	175.0	2.7	0.0154
0.0013	173.6	4.1	0.0236
0.0025	170.8	6.9	0.0404
0.0050	163.5	14.2	0.0869
0.0079	156.0	21.7	0.1391
0.0100	150.2	27.5	0.183
System: $^{45}\text{Ca}^{2+}$, $\text{NaPSS}, 0.300\text{ m}$ NaClO_4			
0.0052	322.2	37.8	0.117
0.0070	315.5	44.5	0.141
0.0099	290.0	70.0	0.241
0.0293	219.2	140.8	0.642
0.0513	167.2	192.8	1.153

$$^a (D_0 - D)/D = {}^u\text{M}^{2+}/\text{g of soln}/{}^u\text{M}^{2+}/\text{g of soln.}$$

turally based distance between charged sites, is expressed in angstrom units.

The ratio of $(\bar{\gamma}_{\text{Na}^+})^2/(\bar{\gamma}_{\text{M}^{2+}})$ in 0.30 m NaClO_4 was calculated as described earlier by using the published mean molal activity coefficients for NaClO_4 and $\text{M}(\text{ClO}_4)_2$ at this ionic strength. When an ionic strength of 0.10 was employed in the experimental program the single ion activity coefficients available from Kieland's computations of this parameter⁶ were employed directly.

A ${}^u\text{K}_{\text{Ac}}$ parameter has been defined as the product of the molality-based ion-exchange selectivity coefficient measured for the exchange of macro-level concentrations of H^+ ion with M^{2+} ion, present at tracer level concentrations, ${}^u\text{M}^{2+}$, and the mean molal activity coefficient ratio of HX and MX_2 , $(\gamma_{\pm}^0(\text{HX}))^4/(\gamma_{\pm}^0(\text{MX}_2))^2$, in the solution phase.⁷ On this basis ${}^u\text{K}_{\text{Ac}}$ is equal to the activity ratio, $(\gamma_{\text{H}^+})^2/(\gamma_{\text{M}^{2+}})$, of hydrogen and trace divalent metal ion in the resin phase and the activity coefficient ratio $\bar{\gamma}_{\text{M}^{2+}}/(\bar{\gamma}_{\text{Na}^+})^2$ in our polyelectrolyte-salt systems could be deduced from plots of ${}^u\text{K}_{\text{Ac}}$ vs. resin-phase molality obtained in an earlier investigation of ion-exchange selectivity.⁷ Assignment of the reciprocal of this term from extrapolation of the resultant line to the polymer domain concentration value of 0.91 ($\text{M}^+(1 - \phi_{\text{P,Na}})/V_p = 1(0.8)/0.879 = 0.91$) as shown in Figure 2 could be made to yield $\bar{\gamma}_{\text{M}^{2+}}/(\bar{\gamma}_{\text{Na}^+})^2$ directly since $\bar{\gamma}_{\text{Na}^+}/\bar{\gamma}_{\text{H}^+} \approx 1$ at the polymer domain molality. This can be seen from the plot of ${}^u\text{K}_{\text{Ac}}$ ^{13,14} that is included in Figure 2.

There are in Figure 2 two plots of ${}^u\text{K}_{\text{Ac}}$ for the $^{65}\text{Zn}-\text{HClO}_4$ -resin (HPSS) system, one set of numbers having been derived from selectivity studies in 0.016 m HClO_4 while the other set was obtained from measurements in 0.168 m HClO_4 . Because some error has to be introduced into the assessment of ${}^u\text{K}_{\text{Ac}}$ by assigning the mean molal activity coefficient of the pure divalent metal perchlorate at the ionic strength of the system to the trace metal ion, the deduced value of ${}^u\text{K}_{\text{Ac}}$ must be less affected by

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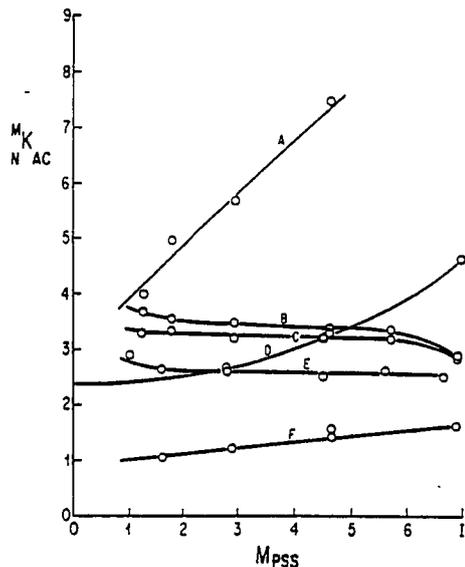


Figure 2. Plots of $M_{H^+} K_{Ac}$ vs. resin-phase molality.^{7,13-15} A: $^{45}Ca^{2+} K_{Ac} = (\bar{\gamma}_H)^2/\bar{\gamma}_{Ca^{2+}}; 0.168\ m\ HClO_4$. B: $^{65}Zn^{2+} K_{Ac} = (\bar{\gamma}_H)^2/(\bar{\gamma}_{Co^{2+}}); 0.168\ m\ HClO_4$. C: $^{65}Zn^{2+} K_{Ac} = (\bar{\gamma}_H)^2/(\bar{\gamma}_{Co^{2+}}); 0.168\ m\ HClO_4$. D: $^{65}Zn^{2+} K_{Ac} = (\bar{\gamma}_H)^2/(\bar{\gamma}_{Ca^{2+}}); I = 0.1$. E: $^{65}Zn^{2+} K_{Ac} = (\bar{\gamma}_H)^2/(\bar{\gamma}_{Zn^{2+}}); 0.016\ m\ HClO_4$. F: $^{65}Zn^{2+} K_{Ac} = (\bar{\gamma}_H)^2/(\bar{\gamma}_{Na^+}); I = 0.1$.

neglect of ion-ion interaction at the lower ionic strength. We have as a consequence used the ^{65}Zn selectivity data obtained in 0.0160 $m\ HClO_4$ to assign a value of 2.8 to both $(\bar{\gamma}_{Co^{2+}}/(\bar{\gamma}_{Na^+})^2)$ and $(\bar{\gamma}_{Zn^{2+}}/(\bar{\gamma}_{Na^+})^2)$ for use in eq 1a. Selectivity data at this lower ionic strength are unavailable for the ^{45}Ca - $NaClO_4$ -resin (HPSS) system and we have used the value of 3.8 extrapolated from the ^{65}Zn K_{Ac} vs. m_{HPSS} plot presented for the higher ionic strength system to test the Donnan model applicability in this instance.

The results of the above treatment of the ion-distribution data compiled to test the Donnan model are summarized in Table II which follows. It can be observed that even when polyelectrolyte concentration is varied more than tenfold and salt concentration a factor of 3 there is no real deviation from the Donnan-predicted behavior. Deviation from the expected value of unity is about 20%. In those experiments where $D_0 - D$ is small, error of this order of magnitude was possible.

To test the Donnan model further the data obtained by Mattai and Kwak with the $LiCl$ - $MgCl_2$ -dextran sulfate and the $CsCl$ - $MgCl_2$ -dextran sulfate systems have been interpolated from the Scatchard curves presented in Figures 1, 5, and 6 of their publication for use in eq 1a. The parameter $\sum \bar{M}^{2+}/\sum S(\bar{m}_{M^{2+}})$ of eq 1a was obtained directly from their plots of K_2 vs. θ_2 ($\sum \bar{M}^{2+}/\sum S(\bar{m}_{M^{2+}})$ vs. $\sum \bar{M}^{2+}/\sum S$ in our notation). The quantity $(\sum \bar{M}^{2+}/\sum S)$ was then assessed as shown: $\sum \bar{M}^{2+}/\sum S = (1 - 2(\sum \bar{M}^{2+}/\sum S)(1 + \phi_{P_{M^{2+}}})) / (1 - \phi_{P_{M^{2+}}})$. A careful stoichiometric balance of counterions led to the precise estimate of $\bar{m}_{M^{2+}}$. Kielland's table of single ion activity coefficient projections⁶ was used to evaluate $(\bar{\gamma}_{M^{2+}})^2/(\bar{\gamma}_{M^{2+}})$. Equation 5 from Manning² was employed to evaluate a V_p of 1300 mL/mol of polyelectrolyte. A charge density parameter, ξ , of 2.8 and a mean interchange distance of 2.6 Å for the fully extended polyelectrolyte chain was used in this equation. These parameters were employed earlier by Mattai and Kwak¹ in their application of the two-variable theory of Manning for the examination of their data. Finally the values of $(\bar{\gamma}_{M^{2+}})^2/(\bar{\gamma}_{M^{2+}})$ were deduced by using Figure 2. By reference to the literature¹⁴ it is determined that $M_{Li^+}^{\#} K_{Ac}$ is about equal to $^{45}Ca^{2+} K_{Ac}$ accessible from Figure 2 so that $\bar{\gamma}_{Mg^{2+}}/(\bar{\gamma}_{Li^+})^2$ was taken to be about equal to $1/2.8$ or 0.36. From Figure 2 we also were able to determine that at a resin molality of 0.6, the concentration presumed to prevail in the dextran sulfate polymer domain ($m_p = \sum S(1 - \phi_{P_{M^{2+}}})/\sum S V_p = 0.8/1.3 = 0.62\ M$), $\bar{\gamma}_{Li^+}/\bar{\gamma}_{Ca^{2+}} \approx 2.4$ so that $\bar{\gamma}_{Mg^{2+}}/(\bar{\gamma}_{Ca^{2+}})^2 = \bar{\gamma}_{Mg^{2+}}(\bar{\gamma}_{Li^+})^2/(\bar{\gamma}_{Li^+})^2(\bar{\gamma}_{Ca^{2+}})^2 \approx (0.36)(2.4)^2 = 2.1$.

The values resolved for the activity quotient defined by eq 1a

TABLE II: Test of Donnan Model Using Ion-Exchange Distribution Data

NaPSS(m_p)	$(D_0 - D)/D$	$\sum \bar{Na}^+ / g\ H_2O$ $(m_p(1 - \phi_p))$	$[(\bar{a}_{M^{2+}})(\bar{a}_{Na^+})^2] /$ $[(\bar{a}_{Na^+})^2(\bar{a}_{M^{2+}})]$
System: $^{60}Co^{2+}$, NaPSS, 0.30 $m\ NaClO_4$; $V_p = 0.879\ mL/0.0010$ mol; $\bar{\gamma}_{^{60}Co^{2+}}/(\bar{\gamma}_{Na^+})^2 = 2.8$; $(\gamma_{\pm}^0(NaClO_4))^4/(\gamma_{\pm}^0(Co(ClO_4)_2))^3 = 1.318$			
0.00094	0.0194	0.000752	1.202
0.00130	0.0291	0.00104	1.302
0.00250	0.0438	0.00200	1.019
0.0052	0.0961	0.00416	1.075
0.0080	0.137	0.00640	0.996
0.0105	0.179	0.00840	0.991
System: $^{60}Co^{2+}$, NaPSS, 0.10 $m\ NaClO_4$; $V_p = 0.879\ mL/0.0010$ mol; $\bar{\gamma}_{^{60}Co^{2+}}/(\bar{\gamma}_{Na^+})^2 = 2.8$; $(\gamma_{Na^+})^2/(\gamma_{Co^{2+}}) = 1.229$			
0.00084	0.143	0.000672	0.991
0.0017	0.172	0.00136	0.743
0.0026	0.198	0.00208	0.561
0.0054	0.553	0.00432	0.754
0.0092	1.186	0.00736	0.950
0.0123	1.698	0.00984	1.017
System: $^{65}Zn^{2+}$, NaPSS, 0.30 $m\ NaClO_4$; $V_p = 0.879\ mL/0.0010$ mol; $\bar{\gamma}_{^{65}Zn^{2+}}/(\bar{\gamma}_{Na^+})^2 = 2.8$; $(\gamma_{\pm}^0(NaClO_4))^4/(\gamma_{\pm}^0(Zn(ClO_4)_2))^3 = 1.318$			
0.00059	0.00851	0.000472	0.839
0.00093	0.0154	0.000744	0.963
0.0013	0.0236	0.00104	1.056
0.0025	0.0404	0.0020	0.941
0.0050	0.0869	0.0040	1.011
0.0079	0.139	0.00632	1.024
0.010	0.183	0.0080	1.064
System: $^{45}Ca^{2+}$, NaPSS, 0.30 $m\ NaClO_4$; $V_p = 0.879\ mL/0.0010$ mol; $\bar{\gamma}_{^{45}Ca^{2+}}/(\bar{\gamma}_{Na^+})^2 = 3.8$; $(\gamma_{\pm}^0(NaClO_4))^4/(\gamma_{\pm}^0(Ca(ClO_4)_2))^3 = 1.307$			
0.0052	0.117	0.00416	1.023
0.0070	0.141	0.00560	0.916
0.0099	0.241	0.0079	1.107
0.0213	0.642	0.0234	0.996
0.0513	1.153	0.0410	1.022

using these assignments of the various parameters are listed in the last column of Table III. The terms pertinent to their computation are listed in the first three columns of this table; other pertinent parameters are presented in the table subheadings describing each system under analysis.

Examination of the values obtained for the activity quotients based on the Donnan model shows that they are less than unity in most instances. For the $MgCl_2$ - $LiCl$ -dextran sulfate system the value of the activity quotient resolved is fairly constant at each ionic strength studied over the complete range of univalent metal ion replacement by divalent metal ion in the polyelectrolyte domain. In this system the activity quotient increases in value with increase in ionic strength very closely approaching the theoretically predicted value of unity at $I = 0.02$ and 0.04, the highest ionic strengths examined. This result could very well be a reflection of the fact that V_p is a function of water activity increasing somewhat with decreasing ionic strength; such a response to a change in water activity is in fact a quite reasonable expectation.

However, with the $CsCl$ - $MgCl_2$ -dextran sulfate system there is no such effect of ionic strength noticeable. Instead the value of the activity quotient is sensitive to the relative degree of replacement of the univalent Cs^+ ion by Mg^{2+} ion, decreasing approximately a factor of 1.5-2 over the range of metal ion exchange encountered. This result could be a consequence of neglect of ion-ion interaction on the value of $\bar{\gamma}_{M^{2+}}/(\bar{\gamma}_{M^{2+}})^2$ which for convenience was considered to remain unchanged. It may very well be that such perturbations, while small for the highly solvated ions in the Mg^{2+} - Li system, is sizeable in the Mg^{2+} - Cs^+ system where the degree of ion solvation is so different. The sparingly solvated Cs^+ ion may be responsible as well for the higher insensitivity of V_p to ionic strength in this system.

Finally it must be remembered that assignment of $(\bar{\gamma}_{Mg^{2+}})^2/(\bar{\gamma}_{M^{2+}})^2$

TABLE III: Test of Donnan Model Using Data from Mattai and Kwak

System: MgCl ₂ , LiCl, Dextran Sulfate; C _p = 0.0010; V _p = 1.3 mL; $\bar{\gamma}_{Mg^{2+}}/(\bar{\gamma}_{Li^+})^2 = 0.36$							
$\frac{\sum \bar{M}_{Mg^{2+}}}{\sum S(\bar{M}_{Mg^{2+}})}$	$(\bar{m}_{Li^+})^2$	$\frac{(\sum \bar{Li}^+)}{(\sum S)^2}$	$\frac{[(\bar{a}_{Mg^{2+}})(\bar{a}_{Li^+})^2]}{[(\bar{a}_{Li^+})^2(\bar{a}_{Mg^{2+}})]}$	$\frac{\sum \bar{M}_{Mg^{2+}}}{\sum S(\bar{M}_{Mg^{2+}})}$	$(\bar{m}_{Li^+})^2$	$\frac{(\sum \bar{Li}^+)}{(\sum S)^2}$	$\frac{[(\bar{a}_{Mg^{2+}})(\bar{a}_{Li^+})^2]}{[(\bar{a}_{Li^+})^2(\bar{a}_{Mg^{2+}})]}$
<i>I</i> = 0.005; $(\bar{\gamma}_{Li^+})^2/(\bar{\gamma}_{Mg^{2+}}) = 1.143$							
1.796 × 10 ⁴	2.352 × 10 ⁻⁵	3.348 × 10 ⁻¹	0.675	6.552 × 10 ³	9.730 × 10 ⁻⁵	4.489 × 10 ⁻¹	0.793
1.155 × 10 ⁴	2.271 × 10 ⁻⁵	2.234 × 10 ⁻¹	0.628	5.596 × 10 ³	9.655 × 10 ⁻⁵	3.613 × 10 ⁻¹	0.833
6.859 × 10 ³	2.176 × 10 ⁻⁵	1.521 × 10 ⁻¹	0.526	4.025 × 10 ³	9.448 × 10 ⁻⁵	2.669 × 10 ⁻¹	0.795
4.50 × 10 ³	2.066 × 10 ⁻⁵	1.021 × 10 ⁻¹	0.487	3.00 × 10 ³	9.216 × 10 ⁻⁵	2.007 × 10 ⁻¹	0.769
3.105 × 10 ³	1.938 × 10 ⁻⁵	7.023 × 10 ⁻²	0.459	1.751 × 10 ³	8.553 × 10 ⁻⁵	1.233 × 10 ⁻¹	0.678
1.534 × 10 ³	1.557 × 10 ⁻⁵	2.979 × 10 ⁻²	0.429	1.282 × 10 ³	8.096 × 10 ⁻⁵	7.398 × 10 ⁻²	0.783
<i>I</i> = 0.0075; $(\bar{\gamma}_{Li^+})^2/(\bar{\gamma}_{Mg^{2+}}) = 1.159$							
9.585 × 10 ³	5.463 × 10 ⁻⁵	4.281 × 10 ⁻¹	0.663	1.986 × 10 ³	3.94 × 10 ⁻⁴	4.967 × 10 ⁻¹	0.898
8.718 × 10 ³	5.423 × 10 ⁻⁵	3.393 × 10 ⁻¹	0.756	1.552 × 10 ³	3.862 × 10 ⁻⁴	3.502 × 10 ⁻¹	0.976
6.697 × 10 ³	5.307 × 10 ⁻⁵	2.894 × 10 ⁻¹	0.667	1.083 × 10 ³	3.759 × 10 ⁻⁴	2.664 × 10 ⁻¹	0.872
4.82 × 10 ³	5.155 × 10 ⁻⁵	2.055 × 10 ⁻¹	0.656	7.94 × 10 ²	3.625 × 10 ⁻⁴	2.007 × 10 ⁻¹	0.818
3.069 × 10 ³	4.918 × 10 ⁻⁵	1.347 × 10 ⁻¹	0.608	5.415 × 10 ²	3.364 × 10 ⁻⁴	1.246 × 10 ⁻¹	0.833
1.859 × 10 ³	4.500 × 10 ⁻⁵	7.113 × 10 ⁻²	0.638	4.332 × 10 ²	3.3112 × 10 ⁻⁴	7.590 × 10 ⁻²	1.014
9.75 × 10 ²	3.688 × 10 ⁻⁵	3.386 × 10 ⁻²	0.576				
6.14 × 10 ²	2.714 × 10 ⁻⁵	1.332 × 10 ⁻²	0.678				
<i>I</i> = 0.020; $(\bar{\gamma}_{Li^+})^2/(\bar{\gamma}_{Mg^{2+}}) = 1.219$							
<i>I</i> = 0.040; $(\bar{\gamma}_{Li^+})^2/(\bar{\gamma}_{Mg^{2+}}) = 1.312$							
				4.513 × 10 ²	1.534 × 10 ⁻³	3.73 × 10 ⁻¹	1.139
System: MgCl ₂ , CsCl, Dextran Sulfate; C _p = 0.001; V _p = 1.300 mL; $(\bar{\gamma}_{Mg^{2+}})/(\bar{\gamma}_{Cs^+})^2 = 2.1$							
$\frac{\sum \bar{M}_g}{\sum S(\bar{M}_{Mg^{2+}})}$	$(\bar{m}_{Cs^+})^2$	$\frac{(\sum \bar{Cs}^+)}{(\sum S)^2}$	$\frac{[(\bar{a}_{Mg^{2+}})(\bar{a}_{Cs^+})^2]}{[(\bar{a}_{Cs^+})^2(\bar{a}_{Mg^{2+}})]}$	$\frac{\sum \bar{M}_g}{\sum S(\bar{M}_{Mg^{2+}})}$	$(\bar{m}_{Cs^+})^2$	$\frac{(\sum \bar{Cs}^+)}{(\sum S)^2}$	$\frac{[(\bar{a}_{Mg^{2+}})(\bar{a}_{Cs^+})^2]}{[(\bar{a}_{Cs^+})^2(\bar{a}_{Mg^{2+}})]}$
<i>I</i> = 0.005; $(\bar{\gamma}_{Cs^+})^2/(\bar{\gamma}_{Mg^{2+}}) = 1.131$							
5.538 × 10 ³	2.403 × 10 ⁻⁵	4.175 × 10 ⁻¹	0.986	1.72 × 10 ³	9.841 × 10 ⁻⁵	5.61 × 10 ⁻¹	0.963
4.54 × 10 ³	1.337 × 10 ⁻⁵	3.89 × 10 ⁻¹	0.840	1.075 × 10 ³	9.444 × 10 ⁻⁵	4.481 × 10 ⁻¹	0.724
3.00 × 10 ³	2.215 × 10 ⁻⁵	2.93 × 10 ⁻¹	0.700	8.065 × 10 ²	9.011 × 10 ⁻⁵	3.731 × 10 ⁻¹	0.621
2.14 × 10 ³	2.060 × 10 ⁻⁵	2.13 × 10 ⁻¹	0.638	6.129 × 10 ²	8.203 × 10 ⁻⁵	2.687 × 10 ⁻¹	0.594
1.29 × 10 ³	1.648 × 10 ⁻⁵	1.271 × 10 ⁻¹	0.516	4.194 × 10 ²	6.331 × 10 ⁻⁵	1.290 × 10 ⁻¹	0.656
9.68 × 10 ²	1.388 × 10 ⁻⁵	6.564 × 10 ⁻²	0.633				
7.10 × 10 ²	9.989 × 10 ⁻⁶	3.258 × 10 ⁻²	0.673				
<i>I</i> = 0.020; $(\bar{\gamma}_{Cs^+})^2/(\bar{\gamma}_{Mg^{2+}}) = 1.178$							
				2.90 × 10 ²	3.844 × 10 ⁻⁴	6.050 × 10 ⁻¹	0.593
				2.47 × 10 ²	3.706 × 10 ⁻⁴	4.90 × 10 ⁻¹	0.600
				2.15 × 10 ²	3.424 × 10 ⁻⁴	3.894 × 10 ⁻¹	0.609
				1.667 × 10 ²	2.941 × 10 ⁻⁴	2.862 × 10 ⁻¹	0.551
3.108 × 10 ³	5.364 × 10 ⁻⁵	5.439 × 10 ⁻¹	0.972				
1.892 × 10 ³	5.268 × 10 ⁻⁵	3.531 × 10 ⁻¹	0.894				
1.151 × 10 ³	4.840 × 10 ⁻⁵	2.863 × 10 ⁻¹	0.616				
8.28 × 10 ²	4.382 × 10 ⁻⁵	2.159 × 10 ⁻¹	0.532				
5.59 × 10 ²	3.468 × 10 ⁻⁵	1.258 × 10 ⁻¹	0.488				
5.05 × 10 ²	2.927 × 10 ⁻⁵	7.301 × 10 ⁻²	0.640				
System: MgCl ₂ , CsCl, Dextran Sulfate; C _p = 0.002; V _p = 2.600 mL; $(\bar{\gamma}_{Mg^{2+}})/(\bar{\gamma}_{Cs^+})^2 = 2.1$							
$\frac{\sum \bar{M}_g}{\sum S(\bar{M}_{Mg^{2+}})}$	$(\bar{m}_{Cs^+})^2$	$\frac{(\sum \bar{Cs}^+)}{(\sum S)^2}$	$\frac{[(\bar{a}_{Mg^{2+}})(\bar{a}_{Cs^+})^2]}{[(\bar{a}_{Cs^+})^2(\bar{a}_{Mg^{2+}})]}$	$\frac{\sum \bar{M}_g}{\sum S(\bar{M}_{Mg^{2+}})}$	$(\bar{m}_{Cs^+})^2$	$\frac{(\sum \bar{Cs}^+)}{(\sum S)^2}$	$\frac{[(\bar{a}_{Mg^{2+}})(\bar{a}_{Cs^+})^2]}{[(\bar{a}_{Cs^+})^2(\bar{a}_{Mg^{2+}})]}$
<i>I</i> = 0.0050; $(\bar{\gamma}_{Cs^+})^2/(\bar{\gamma}_{Mg^{2+}}) = 1.138$							
4.806 × 10 ³	2.319 × 10 ⁻⁵	5.70 × 10 ⁻¹	0.607	1.107 × 10 ³	9.372 × 10 ⁻⁵	4.237 × 10 ⁻¹	0.781
4.398 × 10 ³	2.222 × 10 ⁻⁵	3.752 × 10 ⁻¹	0.808	7.85 × 10 ²	8.834 × 10 ⁻⁵	3.824 × 10 ⁻¹	0.579
3.538 × 10 ³	2.137 × 10 ⁻⁵	3.207 × 10 ⁻¹	0.732	6.129 × 10 ²	8.422 × 10 ⁻⁵	2.963 × 10 ⁻¹	0.568
2.892 × 10 ³	2.043 × 10 ⁻⁵	2.722 × 10 ⁻¹	0.675	4.95 × 10 ²	7.078 × 10 ⁻⁵	2.058 × 10 ⁻¹	0.543
2.355 × 10 ³	1.906 × 10 ⁻⁵	2.109 × 10 ⁻¹	0.660	3.548 × 10 ²	5.497 × 10 ⁻⁵	1.330 × 10 ⁻¹	0.468
1.667 × 10 ³	1.682 × 10 ⁻⁵	1.471 × 10 ⁻¹	0.592	3.065 × 10 ²	4.443 × 10 ⁻⁵	9.139 × 10 ⁻²	0.475
1.108 × 10 ³	1.356 × 10 ⁻⁵	9.437 × 10 ⁻²	0.494				
<i>I</i> = 0.0075; $(\bar{\gamma}_{Cs^+})^2/(\bar{\gamma}_{Mg^{2+}}) = 1.150$							
2.57 × 10 ³	5.358 × 10 ⁻⁵	4.896 × 10 ⁻¹	0.882				
2.048 × 10 ³	5.203 × 10 ⁻⁵	4.281 × 10 ⁻¹	0.781				
1.355 × 10 ³	4.858 × 10 ⁻⁵	3.348 × 10 ⁻¹	0.618				
1.043 × 10 ³	4.493 × 10 ⁻⁵	2.626 × 10 ⁻¹	0.560				
7.489 × 10 ²	3.959 × 10 ⁻⁵	1.891 × 10 ⁻¹	0.492				
5.054 × 10 ²	2.954 × 10 ⁻⁵	1.170 × 10 ⁻¹	0.401				
4.30 × 10 ²	2.276 × 10 ⁻⁵	7.022 × 10 ⁻²	0.438				
3.548 × 10 ²	1.567 × 10 ⁻⁵	4.157 × 10 ⁻²	0.420				

in the dextran sulfate containing mixtures was based on the assumption that its properties exactly paralleled those of the polyrenesulfonate used to quantify this parameter.

In spite of these uncertainties that are inadvertently introduced in the analytical procedures employed to examine the validity of the Donnan-based model developed by one of us (J.A.M.) the agreement between prediction and computation is we believe quite striking. It is our conclusion that the Donnan model employed

to interpret ion interactions in polyelectrolyte-salt mixtures is correct and merits in-depth examination.

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