Studies of Polyelectrolyte Solutions
I. Counterion Condensation by Poly(styrene sulfonate)

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ABSTRACT: Polyion-counterion interactions of poly(styrene sulfonate) have been studied in the mixed electrolyte systems $Pb^{2+}/H^{+}/NO_3^{-}$ and $Pb^{2+}/Na^{+}/NO_3^{-}$ at various ionic strengths, I, polyion concentrations, c_p, and temperatures, T, utilizing the dialysis equilibrium technique. The degrees of condensation, θ_1 and θ_2, obtained for the uni- and divalent counterions are compared with those predicted by the two-variable theory of Manning. It is found that the decrease (increase) in θ_2 (θ_1) observed with increasing ionic strength at fixed Pb^{2+}- and polyion concentration is very well predicted by this theory. The extent of Pb^{2+}-ion binding is largest for the Pb^{2+}/H^{+} counterion combination, and lowest for the Pb^{2+}/Na^{+} combination. In both cases the binding of one Pb^{2+}-ion releases close to two univalent counterions. A polyion concentration dependence of θ_1 and θ_2, on the other hand, could not be found at all. The reason may be, that the ionic strength of $0.01\,mol\,l^{-1}$ used is too low. At fixed I, c_p and c_{Pb}^{2+}, θ_1 and θ_2 decrease slightly as the temperature increases. According to the two-variable theory, θ_1 and θ_2 are independent of T. Agreement between theory and experiment can be achieved if b_{brut}, the brut (rough) average linear charge separation on the polyion, is an increasing function of the temperature.
KEY WORDS Polyelectrolyte / Counterion Condensation / Dialysis Equilibrium / Poly(styrene sulfonate) /

The binding of metal ions by polyelectrolytes exert various influences on their conformation. It has been shown[1] that, depending on the metal ion and its concentration, it is possible to either stabilize or destabilize the double-helical structure of DNA. The addition of Cu^{2+} or Cd^{2+}-ions, which can bind to the heterocyclic bases in addition to the phosphates, produces an effect on poly(A) and poly(C) at neutral pH that is similar to that raising the temperature, *i.e.*, the rotatory strength decreases and the near UV extinction coefficient increases. On the other hand, metal ions like Mg^{2+}, which coordinate almost exclusively with the phosphate, do not produce this effect.

Two main theories dominate the description of polyelectrolytes. They are the Poisson-Boltzmann theory[2] and Manning's counterion condensation theory.[3] The Poisson-Boltzmann theory provides a rigorous theoretical approach in which the levels of approximation can be well defined. Unfortunately, the Poisson–Boltzmann equation of a polyelectrolyte can only be solved exactly in limiting cases, and this approach has not been entirely tractable in describing experimental data. Manning's theory, on the other hand, provides a simple mathematical device by which a large body of experimental data[4-6] can be explained very well.

In the past, interactions between polyions and small ions have generally been studied in salt-free polyelectrolyte solutions or in poly-

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electrolyte solutions containing added salt with a single counterion.[7-9] Only very few data are available for polyelectrolyte solutions to which both uni-univalent and di-univalent salt have been added. This can in part be attributed by the fact that the measurements are time consuming and as well to a lack of theoretical treatments for such systems.

The purpose of this paper is to examine the applicability of the two-variable theory[10] to the binding of Pb^{2+}-ions to poly(styrene sulfonate) in the presence of HNO_3 or $NaNO_3$. The choice was made for poly(styrene sulfonate), PSS, as the polyion because of its degree of purification obtainable, and its great stability. Two different univalent counterions, H^+ and Na^+, are used to take into account specific ionic effects. The theoretical treatments so far are nonspecific, and the result of these measurements may be expected to be useful for the development of more refined theoretical calculations.

THEORY

Manning's condensation theory[3] of polyelectrolyte solutions is based on the two-state model which represents the solution as composed by a polyelectrolyte domain, in which counterions are condensed (bound) forming the ion atmosphere, and by uncondensed mobile ions diffused in the zone outside the polyion domain. The polyelectrolyte is considered to consist of a linearly charged cylinder whose charge density is characterized by the dimensionless parameter ξ, defined as

$$\xi = e^2/4\pi\varepsilon_0\varepsilon kTb \qquad (1)$$

ε is the bulk dielectric constant of the solvent, b is the average spacing between the charges on the polyion, and e is the electronic charge. In a system, where only counterions of the valence Z are present, the counterions will be bound by (condensed on) the polyion if the parameter ξ exceeds the critical value $\xi_c =$

$(Z \times Z_p)^{-1}$. Z_p is the valence of the charged groups on the polyion. In this case, the neutralized charge fraction of the polyelectrolyte, f_Z, is given by

$$f_Z = Z \times \theta_Z = 1 - (ZZ_p\xi)^{-1} \qquad (2)$$

θ_Z, the degree of condensation of the metal ion with valence Z, is defined as the molar ratio of bound metal ions per equivalent polyelectrolyte charge. Equation 2 holds only for the limit of infinite dilution and for systems containing added salt in excess, i.e., for solutions where the polyion to coion concentration ratio, X, is smaller than 1. If these conditions are sufficiently well fulfilled, eq 2 is remarkably successful.[3]

For systems, where both uni- and divalent counterions are present, the predictions from Manning's theory are more complicated. Depending on the value of the divalent ion to polyion concentration ratio, c_2/c_p, three regions can be distinguished. If Z_p is set 1, and if the concentration of the univalent counterions, c_1, is in excess to c_2 and c_p, it holds

(a) $$c_2/c_p < 1/2(1 - \xi_{brut}^{-1}) \qquad (3)$$
$$\theta_1 = (1 - \xi_{brut}^{-1}) - \theta_2 ; \quad \theta_2 = c_2/c_p$$

All divalent counterions will be bound, and sufficient many univalent counterions will be bound until $\xi_{net} = 1$, where ξ_{brut} and ξ_{net} denote the values of ξ before and after the counterions are bound by the polyelectrolyte.

(b) $$1/2(1 - \xi_{brut}^{-1}) \leq c_2/c_p \leq 1/2(1 - (1/2\xi_{brut}))$$
$$\theta_1 = 0; \quad \theta_2 = c_2/c_p \qquad (4)$$

The divalent counterions are bound, and all univalent counterions are free. ξ_{net} achieves a value between 0.5 and 1.

(c) $$c_2/c_p > 1/2(1 - (1/2\xi_{brut})) \qquad (5)$$
$$\theta_1 = 0; \quad \theta_2 = 1/2(1 - (1/2\xi_{brut}))$$

Divalent counterions will be bound until $\xi_{net} = 1/2$; and all univalent ions are free.

Equations 3 to 5 are the results of Manning's simple condensation theory.[3] The predictions

of this theory are experimentally quite well fulfilled in electrolyte–polyion mixtures of very low ionic strength.[11] A more general meaning, on the other hand, has Manning's two-variable theory.[10] The mean difference to the simple condensation theory is that in the two-variable theory the entropy of the condensed ions is not supposed to be zero. The entropy is rather equal to the entropy of an ion free to move in a volume V_p around the polyion. In the two-variable theory, the degree of condensation of the univalent ions (θ_1) and that of the divalent ions (θ_2) are calculated from the following expressions:

$$\ln[A(\theta_1/c_1)]$$
$$= -2\xi_{\text{brut}}(1 - \theta_1 - 2\theta_2)\ln[1 - \exp(-\kappa b)] \tag{6}$$

$$\ln K_2 = 2\ln(\theta_1/c_1) - \ln(1/A) \tag{7}$$

$$c_2 = \theta_2(c_p + K_2^{-1}) \tag{8}$$

$$A = c_1/[(1 - \xi_{\text{brut}}^{-1})(\kappa b)^2] \tag{9}$$

$$\kappa^2 = (2e^2/\varepsilon_0\varepsilon kT)(3c_2 + c_1)(N_A \times 10^3) \tag{10}$$

κ is the Debye–Hückel parameter for an electrolyte mixture containing both a 1:1 salt of concentration c_1 and a 2:1 salt of concentration c_2. K_2 presents a quantity which is proportional to the equilibrium constant for the transfer of a divalent counterion from the bulk solution to the region V_p around the polyion, where $V_p = 2718.28/A$.

Equations 6 to 10 can be solved as follows. For a given value of θ_2, eq 6 is solved by iteration for θ_1, and subsequently K_2 is obtained from eq 7. A and κ^2 are given by the experimentation. Equation 8 yields the value for c_2 at which θ_2 is reached. The dependence of κ^2 on c_2 can be neglected because $c_1 \gg c_2$, thus the ionic strength will be simply equal c_1.

EXPERIMENTAL

Materials
Sodium poly(styrene sulfonate) (NaPSS) was

purchased from Pressure Chemical Co., Pittsburg (U.S.A.). The degree of sulfonation, estimated by elemental analysis, was 84%. Purification and conversion to the H^+ form by dialysis was done as described by Kwak.[12] The average molar mass, M_w, of HPSS was estimated by static light scattering in 0.01 M HNO_3 at $T = 25°C$. M_w was 3.54×10^5 g mol^{-1}. HNO_3 was a product of Merck, Darmstadt (FRG). Vacuum dried reagent grade $NaNO_3$ and $Pb(NO_3)_2$ (both Merck) were used without further purification.

Dialysis Equilibrium
Solutions of HPSS which had previously been brought to the desired polyion molarities c_p, expressed in moles of sulfonate groups per liter, were placed into visking cellulose casing bags. The bags were tumbled in the desired "outside" solution. Final equilibration was attained by tumbling for 48 hours at constant temperature. The outside solutions were prepared to contain the cations H^+ and Pb^{2+} or the cations Na^+ and Pb^{2+}. The anion was always nitrate. HNO_3 and $Pb(NO_3)_2$ stock solutions and $NaNO_3$ and $Pb(NO_3)_2$ stock solutions, respectively, were mixed and diluted by weight to obtain different series of HNO_3/$Pb(NO_3)_2$ and $NaNO_3$/$Pb(NO_3)_2$ mixtures with matching total ionic strength. The water used was deionized and afterward doubly distilled. The concentrations of the Na^+ and Pb^{2+}-ions in the final inside and outside solutions were determined with a Perkin-Elmer atomic absorption spectrophotometer. We therefore diluted the solutions to 10^{-3} to 10^{-4} M. The presence of PSS and H^+ did not affect the accuracy of the results. Analysis for the NO_3^--ion was carried out by the Devarda method.[13] The hydrogen ion concentration was determined by potentiometric titration.

Data Handling
The degrees of condensation, θ_1 and θ_2, are calculated from the condition of Donnan equilibrium. It holds

$$\frac{^{\circ}a_-}{^ia_-}=\left(\frac{^{\circ}a_2}{^ia_2}\right)^{0.5}=\frac{^{\circ}a_1}{^ia_1} \qquad (11)$$

where $^{\circ}a_{1(2)}$ and $^ia_{1(2)}$ are the activities outside and inside the dialysis bag of the univalent (divalent) counterions. $^{\circ}a_-$ and $^ia_-$ are the corresponding activities of the univalent coion. The activities are given by

$$a=\gamma\times c \qquad (12)$$

where γ and c are the activity coefficient and the total ion concentration. Values of $^{\circ}c_1$, $^ic_1$, $^{\circ}c_2$, $^ic_2$, $^{\circ}c_-$, and $^ic_-$ were obtained by atomic absorption and potentiometric titration, respectively. In all cases, the neutrality condition was fulfilled. The activity coefficients of the outside solutions (which contain no polyelectrolyte), $^{\circ}\gamma_1$, $^{\circ}\gamma_2$, and $^{\circ}\gamma_-$, were calculated by means of the Debye-Hückel equation and the ion size parameter of Kielland.[14] It should be noted that since ratios of activity coefficients are used in the final result (eq 15), the results are not noticeably affected by the uncertainity in activity coefficients introduced by the choice of the calculation method. $^{\circ}a_1$, $^{\circ}a_2$, and $^{\circ}a_-$ were subsequently obtained from eq 12. The value of $^{\circ}a_-$, which is the activity of the coion in the outside solution, was proofed by a NO_3^--electrode. The agreement between the calculated and the measured value of $^{\circ}a_-$ was in all cases quite well. The NO_3^--electrode was also used to estimate $^ia_-$, the activity of the coion (NO_3^-) in the inside solution. Hence, the ratio $^{\circ}a_-/^ia_-$ is known, and eq 11 was used to calculate the remaining activities $^ia_1$ and $^ia_2$. It should be noted that the data can also be proofed by pH-measurements since $^{\circ}a_{H^+}/^ia_{H^+} = ^{\circ}a_{OH^-}/^ia_{OH^-} = ^{\circ}a_-/^ia_-$. However, the pH difference is very small by the presence of an excess of $NaNO_3$. Subsequently, the activity coefficients $^i\gamma_1$ and $^i\gamma_2$ were calculated from eq 12.

$^ia_1$ and $^ia_2$ are identically to the activities $^ia_{1f}$ and $^ia_{2f}$ of the free (uncondensed) ions.

Consequently, it holds:

$$^i\gamma_1\,^ic_1 = {}^i\gamma_1^0\,^ic_{1f} \quad \text{and} \quad {}^i\gamma_2\,^ic_2 = {}^i\gamma_2^0\,^ic_{2f}, \qquad (13)$$

where $^i\gamma_1^0$ and $^i\gamma_2^0$ are the activity coefficients of the uni- and the divalent ions in a solution of the same ionic strength as in the dialysis bag but without polyelectrolyte present. Values of $^i\gamma_1^0$ and $^i\gamma_2^0$ were given by the Debye-Hückel equation.[14] $^ic_{1f}$ and $^ic_{2f}$ are the concentrations of the free ions in the inside solution. By taking into account that $^ic_1 = {}^ic_{1b} + {}^ic_{1f}$ and that $^ic_2 = {}^ic_{2b} + {}^ic_{2f}$, the combination of these equations with eq 13 yields

$$^ic_{1b} = {}^ic_1(1-\gamma_1^c) \quad \text{and} \quad {}^ic_{2b} = {}^ic_2(1-\gamma_2^c) \qquad (14)$$

where $\gamma_1^c = {}^i\gamma_1/^i\gamma_1^0$ and $\gamma_2^c = {}^i\gamma_2/^i\gamma_2^0$. $^ic_{1b}$ and $^ic_{2b}$ denote the concentrations of the bound (condensed) ions. Finally, the degrees of condensation of the ions 1 and 2, θ_1 and θ_2, were calculated by

$$\theta_1 = {}^ic_{1b}/c_p = ({}^ic_1/c_p)(1-\gamma_1^c)$$

and $\qquad \theta_2 = {}^ic_{2b}/c_p = ({}^ic_2/c_p)(1-\gamma_2^c)$. $\qquad (15)$

In the following, $^ic_1$ and $^ic_2$ are denoted shortly by c_1 and c_2.

RESULTS AND DISCUSSION

The experimental results for the systems poly(styrene sulfonate)/Pb(NO$_3$)$_2$/HNO$_3$, which we will call the PSS/Pb/H system, and PSS/Pb/Na are presented in Figures 1—9. θ_1 versus c_2/c_p and θ_2 versus c_2/c_p data, obtained for two different ionic strengths, are given in Figures 1 and 2, θ_1 and θ_2 are calculated via eq 11 to 15. The temperature is $T=25°C$, and the polyion concentration, c_p, is 0.001 M expressed in sulfonate groups per liter. The ionic strengths of 0.01 and 0.02 mol l^{-1} are, within an experimental error of 5%, equal to c_1, the concentration of the univalent counterion in the inside solution. At each I the ratio c_2/c_p covers the range between 0.00 and 1.20. The theoretical curves are calculated from the simple condensation theory (eq 3—5, discontinuous straight lines) and from the two
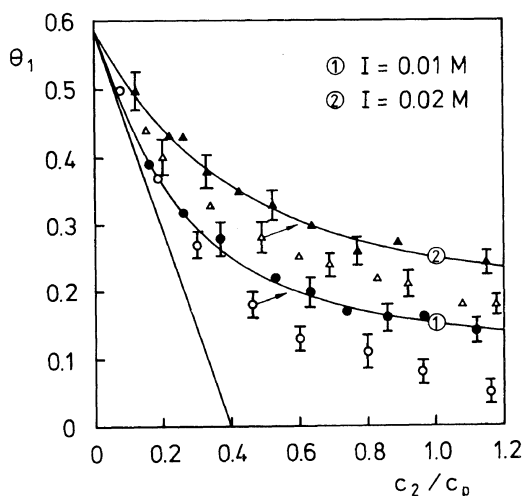
Figure 1. θ_1 *versus* c_2/c_p. $c_p = 0.001\ \mathrm{mol\,l^{-1}}$. θ_1, degree of condensation of univalent counterions; c_2, molar concentration of divalent ions; c_p, polyion concentration expressed in moles of sulfonate groups per liter. PSS/Pb/H, (○) $I = 0.01\ \mathrm{M}$, (△) $I = 0.02\ \mathrm{M}$; PSS/Pb/Na, (●) $I = 0.01\ \mathrm{M}$, (▲) $I = 0.02\ \mathrm{M}$. Straight line, simple condensation model; upper curves, two-variable theory. Arrows indicate the theoretical curves calculated for the ionic strength of a given series of data.
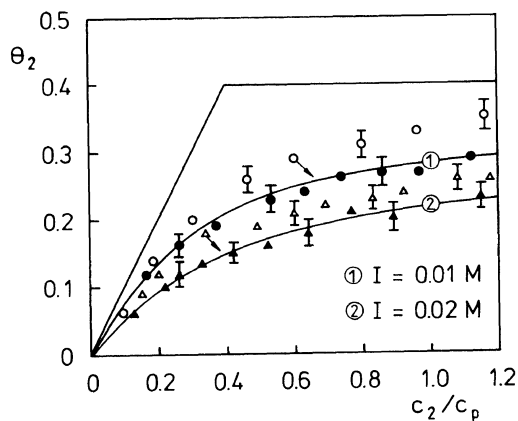

Figure 2. θ_2 *versus* c_2/c_p. $c_p = 0.001\ \mathrm{mol\,l^{-1}}$. Symbols as in Figure 1.

variable theory (eq 6—10). The most important feature of the data is the strong dependence of θ_1 and θ_2 on c_2/c_p and I. Clearly, at fixed values of c_p and I, θ_2 increases as the ratio c_2/c_p increases, and simultaneously θ_1 decreases. H^+ or Na^+-ions are released and

Pb^{2+}-ions are bound by a sulfonate group. At fixed values of c_p and c_2/c_p, θ_2 increases as I decreases, and at low ionic strength it tends to approach the value, predicted by the simple condensation theory. θ_1 shows the opposite behavior. An explanation for these observations can be given as the condensation process is viewed to be governed by the entropy gain accompanying the release of about $2H^+$ or $2Na^+$-ions when one Pb^{2+}-ion is bound. The entropy gain is caused by the fact that the concentration of the various ions in the condensed state (in the volume V_p) is much higher than in the bulk of the solution. Thus at constant c_p, the higher the bulk ionic strength the lower the entropy gain when the univalent ions are released from V_p to the bulk of the solution, leading in turn to lower θ_2 and larger θ_1 values.

These results are valid for both divalent/univalent counterion combinations, studied here. However, the $\theta_1(\theta_2)$ values of the system PSS/Pb/H at a given c_2/c_p and I are lower (larger) than the corresponding values of the system PSS/Pb/Na. The reason may be that a H^+-ion possesses a larger hydrated radius than a Na^+-ion. With respect to the electrostatic attraction of a sulfonate group it may be expected that a Pb^{2+}-ion can remove a H^+-ion more easily than a Na^+-ion, and hence it holds $\theta_2(Pb^{2+}/H^+) > \theta_2(Pb^{2+}/Na^+)$. Interestingly, in the case where a PSS solution contains a single counterion the binding affinity of H^+ to PSS is not different from that of Na^+ as stated by Span.[11] Manning's two variable theory does not consider such specific effects at all, and the theoretical curves drawn in the Figures are identical for both ion pairs studied here. However, the differences between the ion pairs are small and the dependence of θ_1 and θ_2 upon I is remarkably well described by eq 6—10.

Figure 3 shows a plot of θ_e *versus* c_2/c_p, where θ_e is the fraction of sulfonate groups per PSS^--ion which are not neutralized by counterions, *i.e.*, $\theta_e = 1 - \theta_1 - 2\theta_2$. It is seen that θ_e decreases with increasing c_2/c_p as predicted
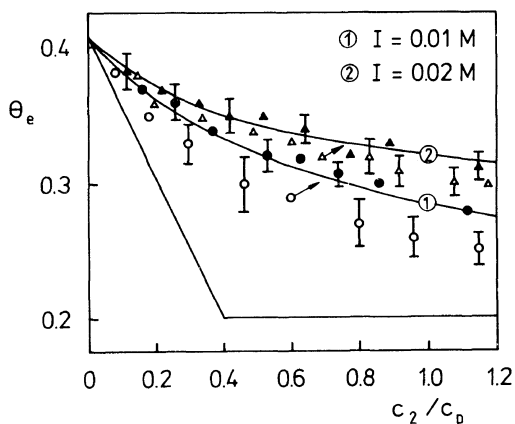
Figure 3. θ_e *versus* c_2/c_p. $c_p = 0.001$ mol 1^{-1}. Symbols as in Figure 1.
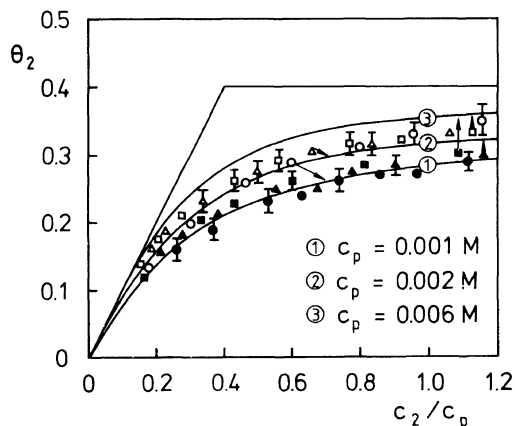
Figure 5. θ_2 *versus* c_2/c_p. $I = 0.01$ M. Symbols as in Figure 4.
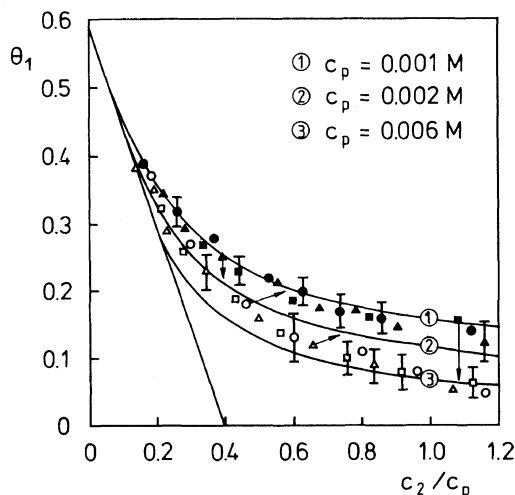
Figure 4. θ_1 *versus* c_2/c_p. $I = 0.01$ M. PSS/Pb/H: ($\bigcirc$) $c_p = 0.001$ M; ($\triangle$) $c_p = 0.002$ M; ($\square$) $c_p = 0.006$ M. PSS/Pb/Na: ($\bullet$) $c_p = 0.001$ M; ($\blacktriangle$) $c_p = 0.002$ M; ($\blacksquare$) $c_p = 0.006$ M. Lower curve, simple condensation model; upper curve, two-variable theory.

Figure 6. θ_e *versus* c_2/c_p. $I = 0.01$ M. Symbols as in Figure 4.

by condensation theory. The agreement is best for the system PSS/Pb/Na and worst for the system PSS/Pb/H. At constant c_2/c_p the total PSS$^-$-ion charge (which is proportional to θ_e) increases as I is increased. As a consequence the radius of gyration of the polyion increases as will be shown in the following paper.

Figures 4 to 6 illustrate the c_p dependence of θ_1, θ_2, and θ_e. I is 0.01 mol 1^{-1}, and T is 25°C.
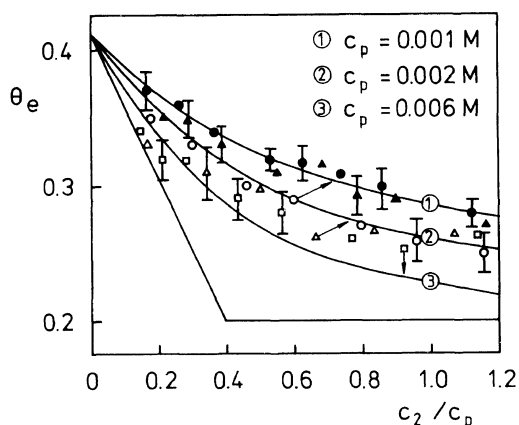
The c_p values used are 0.001, 0.002 and 0.006 mol 1^{-1}. We see that θ_1, θ_2, and θ_e are independent upon c_p, within the experimental error. This behavior holds for both PSS systems, studied here. According to the theory, if c_2/c_p is fixed, θ_2 increases slightly as c_p increases, and simultaneously θ_1 and θ_e decrease. At the moment, we have no explanation for this discrepancy. It seems that the entropy gain accompanying the release of two univalent ions by one Pb^{2+}-ion is nearly the same for all c_p's at low ionic strength. Thus, it may be interesting to repeat these measure-
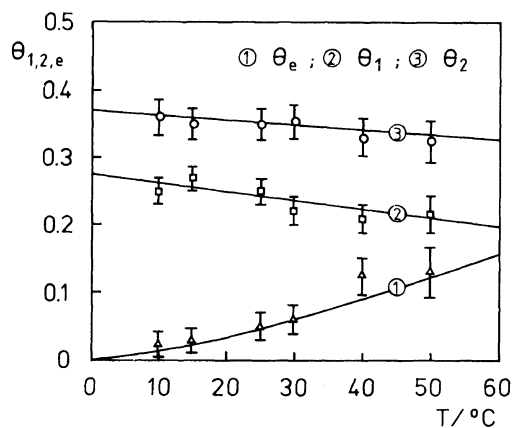
Figure 7. θ_1, θ_2, and θ_e versus T for the system PSS/Pb/H. $c_2/c_p \in [1.16 - 1.22]$. $I = 0.01$ M. ($\triangle$) θ_e; ($\square$) θ_1, ($\bigcirc$) θ_2.

Figure 8. Scatchard plots, K_2 ($1\,\text{mol}^{-1}$) versus θ_2 for the systems PSS/Pb/H and PSS/Pb/Na. $c_p = 0.001$ M. Symbols and theoretical curves as Figure 2.

Table I. Theoretical and experimental values of K_2^o

I $\text{mol}\,\text{l}^{-1}$	K_2^o (theor)[a]	K_2^o (PSS/Pb/Na)	K_2^o (PSS/Pb/H)
0.01	6166.2	6224.5	6315.0
0.02	1565.2	1493.8	2548.2

[a] $c_p = 0.001\,\text{mol}\,\text{l}^{-1}$; $\zeta_{\text{brut}} = 2.40$; $T = 25°\text{C}$.

ments with PSS-solutions of much higher ionic strength, where the predictions of the theory are more successful as can be seen from other binding experiments.[12]

For the system PSS/Pb/H the temperature dependence of θ_1, θ_2, and θ_e at constant c_p, c_2/c_p, and I is illustrated in Figure 7. c_p is $0.001\,\text{mol}\,\text{l}^{-1}$, and I is $0.01\,\text{mol}\,\text{l}^{-1}$. Figure 7 shows that θ_1 and θ_2 decrease with increasing temperature while θ_e increases. Hence, the fraction of condensed ions is lowered as T is increased. The decrease is stronger for θ_1 than for θ_2 which indicates that a H^+-ion may be more easily replaced from the bound state (the volume V_p) than a Pb^{2+}-ion. According to the condensation theory there is no dependence of T on θ_1, θ_2 or θ_e. This is due to the fact that the dielectric constant, ε, of water decreases nearly as fast as T increases, and thus $\partial(\varepsilon \cdot T)/\partial T \approx 0$. Agreement between theory and experiment can only be achieved if b_{brut}, the brut average linear charge separation on the polyion, is allowed to increase as the temperature is increased. A proof of this idea is difficult because a polyion system is needed that contains no counterions. A subsequent paper will deal this problem in some detail.

Figure 2 does not clearly show the variation of θ_2 with ionic strength in the region of low c_2/c_p ratios. An alternative and more sensitive
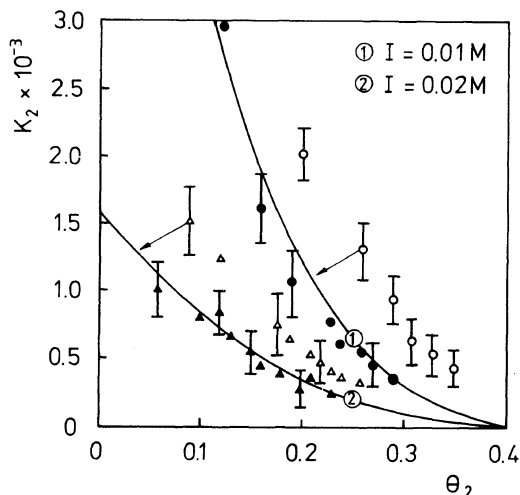
way of representing the data is in the form of a Scatchard plot which is a plot of K_2 versus θ_2. We recall that K_2 is a quantity proportional to the equilibrium constant for the transfer of a divalent ion from a free state to a region V_p around the polyion in which the counterions are mobile but territorially bound.[15] The Scatchard plots drawn in Figure 8 clearly show the downward convexity or anticooperative behavior at each ionic strength. This means that when a Pb^{2+}-ion is bound by a PSS^--sulfonate group the affinity for further binding of Pb^{2+}-ions is decreased for the remaining free PSS^--groups. This effect is more noticeable at lower I and at low θ_2.

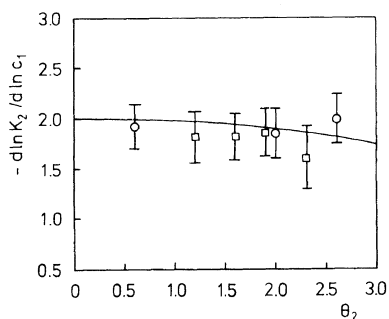Table I presents the corresponding experimental and theoretical intrinsic binding

Figure 9. Plot of $-[d(\ln K_2)/d(\ln c_1)]$ *versus* θ_2. ($\bigcirc$) PSS/Pb/H; ($\square$) PSS/Pb/Na. $c_p = 0.001$ M. Solid line, two-variable theory.

constants. K_2^0, at zero divalent counterion concentration for different I. The experimental values are obtained by extrapolating the Scatchard plots to $\theta_2 = 0$, while the theoretical values are calculated by using eq 7. For the system PSS/Pb/Na the values are close to the theoretically predicted values. The K_2^0 values of the system PSS/Pb/H are, on the other hand, systematically higher than the theoretical one. However, the differences are slight in comparison to other polyions.[16] The variation of K_2 with ionic strength and with θ_2 may be also expressed in a plot of $-d(\ln K_2)/d(\ln c_1)$ *versus* θ_2 as is done in Figure 9. We recall that c_1 is the molarity of the univalent salt. The two-variable theory (solid line) predicts a value of $-d(\ln K_2)/d(\ln c_1) = 2$ at zero θ_2, and only a moderate decrease with increasing θ_2. Both predictions are in good agreement with the experimental results. The theory of Record, Anderson and Lohman,[17] on the other hand, predicts that for a divalent ligand $-d(\ln K_2)/d(\ln c_1) = 2(1 - 1/2\xi_{brut})$. Here, ξ_{brut} is 2.40; thus Record's equation predicts that $-d(\ln K_2)/d(\ln c_1) = 1.58$. This value slightly underestimates the observed one, a result that is also found in a number of other binding experiments.[11,16]

CONCLUSIONS

The binding studies on the systems PSS/

Pb/H and PSS/Pb/Na show that the two-variable theory of Manning gives quite an accurate quantitative description of the degree of divalent and univalent metal ion binding. In particular, the dependence of the counterion condensation degrees, θ_1 and θ_2, on the divalent metal ion concentration and on the ionic strength is well described by the theory. Additionally, the binding constants, K_2, are in reasonable agreement with the calculated ones. This is remarkable because the theoretical curves do not contain any adjustable parameters. They are solely determined by the structural parameter, ξ_{brut}, the ionic strength, and the polyion concentration.

Nevertheless, there are some facts which are not predicted by the two-variable theory. Our data show that there is no influence of c_p on θ_2 and θ_1 at low I while the theory predicts a slight increase (decrease) of $\theta_2(\theta_1)$ as c_p is increased. Additionally, the theoretically calculated values of θ_1 and θ_2 do not depend on the temperature while the experimental ones decrease slightly as T is increased. We have also shown that there are some differences according to the different combinations of divalent and univalent counterions. At fixed I, c_p, and T the degree of Pb^{2+}-ion binding, θ_2, decreases as the hydrated radius of the univalent counterion becomes smaller. Consequently, refinements of the theoretical treatment are necessary. First improvements can be already found in the literature.[18] It should be noted that if the quantity V_p is used as an adjustable parameter, all experimental curves can be fitted very well within reasonable V_p values. This was done by other authors.[19,23] Na-NMR results,[20] on the other hand, seem to indicate that the divalent ions are not located closer to a polyion than the univalent ions. Thus we think, it is more reasonable to define only a single region, V_p, around the polyion for condensed counterions even in mixed counterion systems. The differences between the systems PSS/Pb/H and PSS/Pb/Na are then due to differences in the specific binding affinity

of a sulfonate group for the various metal ions. Finally, it should be noted that the data reported for poly(styrene sulfonate) here may be quite different from those of carboxylate or phosphate fixed charged groups. Consequently, it is desirable to extend the measurements to different types of polyions and to other combinations of uni- and divalent counterions.

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