Counterion Binding by Polyelectrolytes in Dilute Solutions

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ABSTRACT: Direct ultrafiltration techniques were used to determine the relative binding of cesium and sodium ions by poly(styrenesulfonate) and by poly(ethylenesulfonate) anions and the binding of bromide and chloride ions by poly[(vinylbenzyl)trimethylammonium] cation in dilute aqueous mixtures at 25 °C. Microcalorimetric measurements were made of the thermal effects accompanying the replacement of sodium counterions by cesium ions on each of the two polyanions and of the replacement of chloride counterions by bromide ions on the polycation. The magnitudes of the estimated standard-state thermodynamic property changes ($\Delta G°$, $\Delta H°$, $\Delta S°$) for counterion binding reactions with poly(styrenesulfonate) and with the polycation agreed well with the values determined earlier on lightly cross-linked polyelectrolyte gels containing the same polyions, respectively. The Gibbs energy decrease in the binding of Cs^+ ion by sodium poly(ethylenesulfonate) was slightly greater than with sodium poly(styrenesulfonate) but the enthalpy decrease was significantly larger. The binding of Br^- ion by the polycation was strong relative to Cl^- ion. The measured relative degrees of binding of cesium and sodium ions were in good agreement with the predictions of Dolar and Škerjanc, which are based on the cell model for rodlike polyions and an analytical solution of the Poisson–Boltzmann equation for two singly charged counterions of differing size.

A feature distinguishing aqueous polyelectrolyte mixtures from mixed simple electrolytes is the relatively much stronger interaction between the small counterions and the macroions in the former systems. This interaction manifests itself in numerous ways, as, for example, in the marked lowering of counterion activity coefficients and in changes in the conformations of the polyion in solution as reflected by viscosity, light scattering, and other measurements.[1] The closely related phenomenon of ionic selectivity shown in competitive counterion binding reactions involving polyelectrolytes is believed to arise in part because of strong and sometimes specific counterion macroion interactions.

Competitive ion binding reactions have received little systematic study other than in the investigations of Strauss and co-workers,[2,3] who in an important recent work[4] with a flexible, linear, high molecular weight polyelectrolyte, poly(vinylsulfonic acid) and its alkali metal and alkaline earth salts showed (a) that well-defined sequences existed in the relative degree of counterion binding, (b) that the tightness of the binding correlated well with the degree of binding, and (c) that apparent changes in the molecular dimensions of the polyion in solution ran parallel to the degree and tightness of binding. An interesting recent theoretical treatment by Dolar and Škerjanc[5] of relative ion binding by flexible polyelectrolytes in the absence of salt appears to give a basis for an understanding of (a). The applicability of this theory to measurements of the relative degree and tightness of counterion binding by us and by others will be discussed later in this paper.

Our research has continued studies on competitive ion binding with two high molecular weight linear polyanions and with one polycation, namely, poly(ethylenesulfonate), poly(styrenesulfonate), and poly[(vinylbenzyl)trimethylammonium], respectively. Measurements of the relative binding of Na^+ and Cs^+ ions and of Cl^- and Br^- ions, respectively, were facilitated by use of ultrafiltration separation techniques. The tightness of binding was assayed by calorimetric measurement of the enthalpy changes in the competitive binding reactions as a function of the counterion ratio. Our thermodynamic results have served to complement and possibly extend the results of Strauss[4] with poly(vinylsulfonates) which were obtained with equilibrium dialysis, dilatometric, and viscosity measurements. Comparisons of our findings and those of others with electrostatic theory predictions have served to test the theory and possibly thereby shed light on the mechanism of ion binding by flexible, strong polyelectrolytes.

Experimental Section

Two of the three water-soluble polyelectrolytes employed were received as special commercial products by courtesy of Dow Chemical Co., Midland, Mich. Aqueous solutions of these preparations of sodium poly(styrenesulfonate), NaPSS, and poly[(vinylbenzyl)trimethylammonium chloride], $BzMe_3NCl$, were exhaustively dialyzed against distilled water to remove salts, unreacted monomers, and degradation products. Cells (Bio-Rad beaker dialyzer, Model b/HFD-1) fitted with hollow cellulose fiber bundles (25-μm wall, nominal molecular weight cutoff of 5000 and 20^3 cm^2 total area) were found especially effective for this purpose. The polyelectrolyte dialysate was concentrated by ultrafiltration to give a retentate from which a pure, colorless, amorphous solid was isolated by freeze-drying. Subsequent drying at 60 °C in a vacuum over liquid nitrogen gave moisture-free compounds which were used to prepare aqueous stock solutions by weight with ultrapure (Millipore Q-2) water. The solutions were stored at ca. 40 °F in securely capped Teflon (FEP) bottles. Our sample of pure solid sodium poly(ethylenesulfonate), NaPES, was generously given to us by Professor U. P. Strauss, Rutgers University. Details on its synthesis and properties have been described.[4] Its viscosity-average molecular weight was ca. 1×10^5.

The NaPSS and $PVBzMe_3NCl$ preparations were characterized by measurement of their equivalent weights, 206.5 and 228.8, respectively, and by measurements of the ultraviolet absorption spectra of their dilute aqueous solutions.[6] Viscosity-average molecular weights of 40 000 ± 2000 for NaPSS and ca. 1.4×10^5 for $PVBzMe_3NCl$ were provided by Dow. A wide molar mass distribution undoubtedly existed in all of the purified polyelectrolytes used in this research.

Counterion Binding Measurements. Relative counterion binding by the polyions of NaPSS, NaPES, and $PVBzMe_3NCl$ was determined by measurements in aqueous solution of the distribution of ions between the polyelectrolyte and dilute mixtures of simple electrolytes containing the desired pair of cations (or anions) and a common anion (or cation). A quantitative separation of the equilibrium-mixed electrolyte from the polyelectrolyte was a necessary prerequisite to analysis. An ultrafiltration technique was employed using magnetically stirred cells of 3- and 80-mL volume which were fitted with asymmetric membrane ultrafilters[7a] with nominal molecular weight cutoffs of either 1000 or 25 000, respectively. The assembled cells were tested for leaks with 30 psi of nitrogen gas, and the membranes were preconditioned by forcing 2–3 cell volumes of ultrapure water through them. Aqueous polyelectrolyte plus salt mixture prepared by mixing predetermined weights of stock polyelectrolyte solution of accurately known concentration with stock alkali halide[8] solution of known concentration was placed in the cell. A "direct" rather than a "constant-volume" filtration procedure[7b] was employed: a given polyelectrolyte–salt mixture was filtered 5 times

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at 30 psi to separate the "free" counterions from the counterions associated with the polyelectrolyte. Pure water was mixed with the retentate after each filtration, in which volume reductions of 60–90% were effected.[9]

The concentrations of Na^+ and Cs^+ ions in the filtrate and retentate solutions from the experiments with NaPSS and NaPES solutions were determined after dilution to 10^{-3}–10^{-4} M with a Perkin-Elmer Model 305B atomic absorption spectrophotometer. The presence of organic mass from the polyelectrolyte did not appear to affect the accuracy of the analyses. An internal standard procedure with potassium as a reference ion present in large excess (1500 μg/mL) was employed to suppress atomic ionization. The test samples were compared with blank solutions containing only K^+ ion at 1500 μg/mL. The intensities of the sodium or cesium emission spectra were calibrated with NaCl and CsCl solutions of accurately known concentration. Linear absorbance–concentration plots were obtained with the calibration and unknown solutions.

The filtrate and retentate solutions from the experiments with poly[(vinylbenzyl)trimethylammonium chloride] and Cl^- and Br^- ion were analyzed by a thermometric titration procedure[10] in which a sensitive isoperibol microcalorimeter was employed.[11] Approximately 20 g of filtrate or retentate solution containing 0.05–0.3 mmol of Cl^- or Br^- ion was placed in the 50-mL microcalorimeter Dewar cell, a 10-fold excess of 1 M NH_4OH plus 1 M NH_4NO_3 was added, and the mixture was titrated with 0.1505 M silver nitrate. The titration was stopped after the Br^- ion end point was reached, a 20-fold excess of chilled 1.6 M HNO_3 was added to the Dewar cell, and the titration was continued to the chloride ion end point. The total millimoles of Br^- and Cl^- ion in the filtrate or retentate solutions from the ultrafiltration cell were computed from the $AgNO_3$ titrant volumes at the thermometric end points and the weight of filtrate or retentate placed in the calorimeter cell. An accuracy of ±0.1% for this procedure was established by thermometric titration of known aqueous mixtures of reagent grade alkali chloride and bromide salts.

The estimated total uncertainties in the ionic analyses of the filtrate and retentate solutions were estimated as ±2% for Na^+ and Cs^+ ions and ±0.5% for Cl^- and Br^- ions. Tests were made to check on the reliability of the ultrafiltration technique itself. Control experiments without added polyelectrolyte indicated neither absorption nor rejection of the alkali metal or halide ions by the membrane. Material balances of the amounts of ions in the filtrate and retentate were computed for every experiment. These balances indicated that polyelectrolyte losses of 10–20% occurred from the retentate. It was shown that approximately half or more of this loss resulted from concentration polarization at the membrane surface, at which polyelectrolyte was trapped in a gelatinous layer. This gel remained in contact with retentate solution in the ultrafiltration cell at all times and its ionic composition was the same as the polyelectrolyte in solution. A small correction was necessary, however, for the leakage of polyelectrolyte into the filtrate. This loss was attributed to the passage through the membrane of low molecular weight polyions, which were detected at very low concentration by ultraviolet absorption measurements. Recent studies[12] suggest that the interaction of flexible polyelectrolytes with ultrafiltration membranes is a very complex phenomenon involving conformational changes with ionic strength and shear rate effects in transmembrane flow.

Enthalpy Changes in Competitive Ion Binding Reactions. The thermal changes accompanying the mixing of dilute aqueous polyelectrolyte with simple salt solution to give a counterion exchange reaction were measured with an isothermal microcalorimeter[13] possessing a sensitivity of ±0.1 mcal. The counterion exchange reaction with NaPSS (or NaPES) was

$$\mathrm{NaPSS} + \mathrm{Cs}^+ = \mathrm{CsPSS} + \mathrm{Na}^+ \qquad \text{(Ia)}$$

while that with $PVBzMe_3NCl$ was

$$\mathrm{PVBzMe_3NCl} + \mathrm{Br}^- = \mathrm{PVBzMe_3NBr} + \mathrm{Cl}^- \qquad \text{(Ib)}$$

The experimental procedure described in our earlier calorimetric studies[14] on the mixing of polyelectrolytes with salt solutions was followed. Corrections to the observed thermal effects in the competitive counterion exchange reaction were made for baseline shifts caused (a) by changes in the viscosity of the polyelectrolyte, which altered the heat transfer characteristics of the thermistor sensor, and (b) by the increase in the volume of liquid in the calorimeter on adding salt. Although the magnitude of these corrections was relatively large (i.e., 6–7 mcal), the reproducibility and hence the uncertainty in it was shown in a large number of test experiments to be only ±0.2 mcal. Small corrections (0.1–0.4 mcal) also were applied for the difference between the temperature of the titrant and the calorimeter cell solution and for a constant (ca. 0.4 mcal) heat absorption by the titrant solution as it passed through the stainless steel cover plate that closed the calorimeter cell. The overall precision of the thermal measurements was estimated as ±0.5 mcal.

Several corrections to the observed heat of reaction, ΔQ_R, are necessary before values for the enthalpy changes for the competitive ion binding reactions may be estimated. The observed heat associated with the mixing of polyelectrolyte with simple salt solution having no common ion may be related to the sum of separate effects, each arising from one of three simultaneous physical chemical processes that take place. Thus

$$\Delta Q_R = \Delta Q_{Ex} + \Delta Q_S + \Delta Q_M \qquad (1)$$

where ΔQ_{Ex} is the heat evolved (or absorbed) in the competitive exchange of the counterions on the polyion, ΔQ_S is the heat evolved because of the change in the composition of the simple salt solution resulting from the counterion exchange, and ΔQ_M is the heat associated with the change in the ion atmosphere surrounding the polyelectrolyte when salt is added to the solution in the calorimeter.

The thermal correction for the change in composition of the simple salt solution may be given to a good approximation by the difference between the changes in the molar enthalpies of dilution, $\Delta\phi_L$, for each salt times the number of moles of each salt involved, respectively. For example, in the cesium–sodium competitive counterion binding reaction

$$\Delta Q_S = n_{\mathrm{CsCl}}\Delta\phi_L(\mathrm{CsCl}) - n_{\mathrm{NaCl}}\Delta\phi_L(\mathrm{NaCl}) \qquad (2)$$

Corrections for the enthalpy of mixing of the dilute simple salt solutions employed in this work can be shown to be negligibly small. The values of ϕ_L required for the computations indicated in eq 2 were interpolated from large-scale plots of data[15] for the concentration dependence of the enthalpies of dilution of NaCl, CsCl, and NaBr at 25 °C. The appropriate magnitudes of n_{CsCl} and n_{NaCl} (and n_{NaBr} and n_{NaCl}) were obtained from the volumes and concentrations of the CsCl (or NaBr) solutions added to the calorimeter; requisite values for n_{NaCl} were computed (vide infra) from the extent of the exchange reaction.

Estimates of ΔQ_M were obtained with an equation that may be derived[14] from the infinite line charge theory of polyelectrolyte solutions.[16] Thus

$$\Delta Q_M\ (\mathrm{mcal}) = -(n_pRT/2\xi)[1 + (\mathrm{d}\ln D/\mathrm{d}\ln T)_P]\ln[(m_p{}^f + 2\xi m_s{}^f)/m_p{}^i] \qquad (3)$$

where ξ is the linear charge density parameter[16] (2.828 for vinyl polymers at 25 °C), n_p is the number of milliequivalents of polymer involved in the mixing reaction, $m_p{}^i$ and $m_p{}^f$ are the initial and final polyelectrolyte concentrations in reaction I, and $m_s{}^f$ is the final total salt concentration. On substitution of the appropriate numerical values for ξ, R, and T and taking $(\mathrm{d}\ln D/\mathrm{d}\ln T)_P = -1.357$,[17] eq 3 becomes

$$\Delta Q_M\ (\mathrm{mcal}) = 86.1n_p\log[(m_p{}^f + 5.656m_s{}^f)/m_p{}^i] \qquad (4)$$

Note that ΔQ_M is always positive (endothermic) and increases with the final salt concentration in the salt–polyelectrolyte mixture. In the experiments with the polyanions ΔQ_M varied from 1.1 to 7.5 mcal and with the polycation from 2.1 to 7.3 mcal. Values for ΔQ_S were always negative (exothermic) and usually significantly smaller than ΔQ_M, with typical variations from −0.6 to −3.0 mcal. The gross reaction heat, ΔQ_R, was always negative (exothermic) and varied from −3 to −25 mcal for the binding of the preferred counterion (i.e., Cs^+ or Br^-). The reverse reaction for the binding of the lesser preferred ion (i.e., Na^+ or Cl^-) was observed to be endothermic without exception.

The enthalpy of partial counterion exchange, ΔH_{Ex}, for the competitive binding reaction may be expressed in terms of calories per equivalent of exchange reaction using estimated ΔQ_{Ex} values (eq 1) and estimated values for the mequivalents of exchange reaction, Δr. Thus, $\Delta H_{Ex} = \Delta Q_{Ex}/\Delta r$. Accurate values of Δr, which

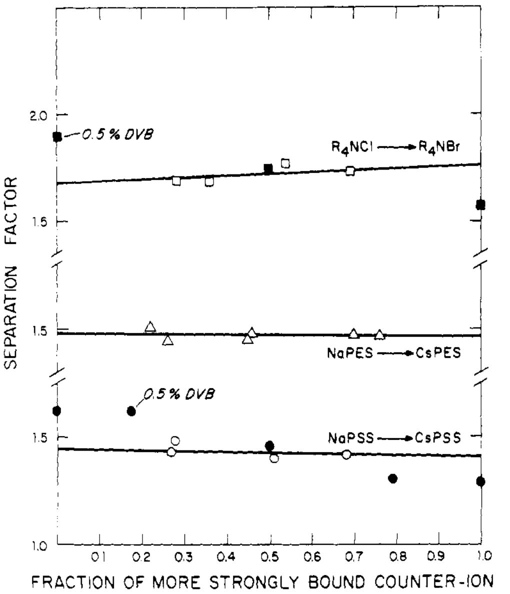

Figure 1. Competitive counterion binding by linear polyelectrolytes in solution at 25 °C. PSS = poly(styrenesulfonate); PES = poly(ethylenesulfonate); R_4N = poly[(vinylbenzyl)trimethylammonium].

typically varied between 0.02 and 0.04 mequiv, were computed from (a) the separation factor, α, in Figure 1, (b) information on the initial composition of the solution in the calorimeter before an incremental addition of salt solution, and (c) the milliequivalents of salt added. Usually a complete calorimeter experiment consisted of five or six heat measurements, each following the addition of an accurately known volume of salt solution (of predetermined concentration) from a microsyringe maintained at the same temperature as the reaction cell. A simple computer program was devised to compute the final solution composition after each addition and, hence, the value of Δr. The uncertainty in the computed Δr was very much less (± 0.2–0.5%) than the uncertainty in α, which was estimated as $\pm 5\%$. Hence, if ΔQ_R is known to ± 0.5 mcal and $\Delta r = 0.02$ mequiv, the uncertainty in ΔH_{Ex} is ± 25 cal equiv^{-1}. The least-squares fits to the ΔH_{Ex} data (Figure 3) gave standard deviations for the actual minus the predicted points of 29, 49, and 32 cal equiv^{-1} for the poly(styrenesulfonate), poly(ethylenesulfonate), and poly[(vinylbenzyl)trimethylammonium] ion solutions, respectively.

Results and Discussion

The relative degrees of ion binding were expressed in terms of a separation factor, α, based on the equilibria in eq I. The quantity α is defined as the ratio of the measured concentrations of the two cations (or two anions) present in the retentate from the ultrafiltration experiment to the ratio of their concentrations in the filtrate

$$\alpha = ([M^{\pm}]/[N^{\pm}])_r/([M^{\pm}]/[N^{\pm}])_f$$

The computed α values were plotted (Figure 1) as a function of the mole fraction of the preferred counterion on the polyion. Values of $\alpha > 1$ signify selectivity for the ion $M^{\pm}$. Several features in Figure 1 may be noted: (a) The slope of α vs. the mole fraction of the preferred counterion is very small and probably zero for binding to the polyanions; (b) the selective binding of Cs^+ ion to PES^- appears to be slightly greater than to PSS^-; and (c) both polyions preferentially bind the less hydrated and presumably smaller counterion. Values of α for the selective binding of the same counterions by lightly cross-linked (0.5% divinylbenzene) polyelectrolyte gels based on poly(styrenesulfonate) and poly[(vinylbenzyl)trimethylammonium] ions are also shown in Figure 1. Agreement with the average values of α taken over the complete range in binding was found, and, because a quite different phase separation technique was employed, it is suggested that the results with the polyelectrolyte solutions are reliable. Our measurements with poly(ethylenesulfonate) ion are compared in Figure 2 with values of α calculated from data published by Hen and Strauss.[4] A value of $\alpha_{0.5} = 1.33$ for the reaction NaPES → KPES derived from these data[18] is consistent with $\alpha_{0.5} = 1.47$ for NaPES → CsPES from our work.

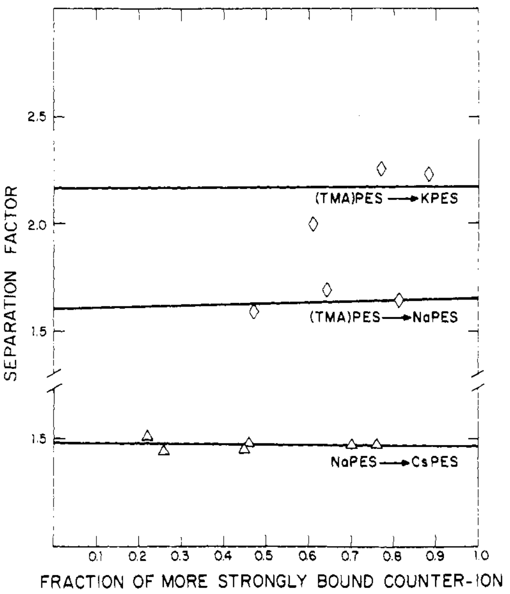

Figure 2. Competitive counterion binding by poly(ethylenesulfonate) in solution at 25 °C. TMA = tetramethylammonium. Two uppermost curves constructed from data of Hen and Strauss.[4]

Values of the standard Gibbs energy change in the competitive counterion binding reaction, $\Delta G°$, may be estimated from the separation factors if the standard states for the polyelectrolytes are chosen as their respective pure, homoionic salt forms (NaPSS, CsPSS, etc.) in dilute aqueous solution and if it is assumed that the activity coefficients for the counterions in the dilute electrolyte solution are effectively all the same:[19] To a good approximation

$$\Delta G° = -2.3RT \int_0^1 \log \alpha \, dN_{M\pm} \tag{5}$$

where $N_{M\pm}$ is the mole fraction of the selectively bound counterion associated with the polyelectrolyte.

A plot of the dependence of the enthalpies of partial binding on the mole fraction of the preferred counterion is given in Figure 3 for the same three polyelectrolyte systems as in Figure 1. The enthalpies are plotted as horizontal chords representing the average value of the change in ΔH_{Ex} over the indicated composition range. The solid curve in Figure 3 therefore is the differential enthalpy of binding, $d\Delta H_{\text{Ex}}/dN_{M\pm} = (\Delta H_{\text{Ex}})_{\text{av}}$. The standard enthalpy of binding, $\Delta H°$, may be estimated from the relation

$$\Delta H° = \int_0^1 (\Delta H_{\text{Ex}})_{\text{av}} \, dN_{M\pm} \tag{6}$$

again taking the respective homoionic salt forms of the polyelectrolytes in dilute solution as standard states.[20]

Several interesting features may be noted in Figure 3: (a) Heat is always evolved (i.e., the energy is lowered) in the binding of the preferred (i.e., smaller) ion; (b) the tighter the binding (i.e., directly related to $\Delta H°$), the greater the relative degree of binding (as represented by $\Delta G°$); and (c) the tightness of binding of Cs^+ relative to Na^+ ion is significantly greater for PES^- than for PSS^- polyion.

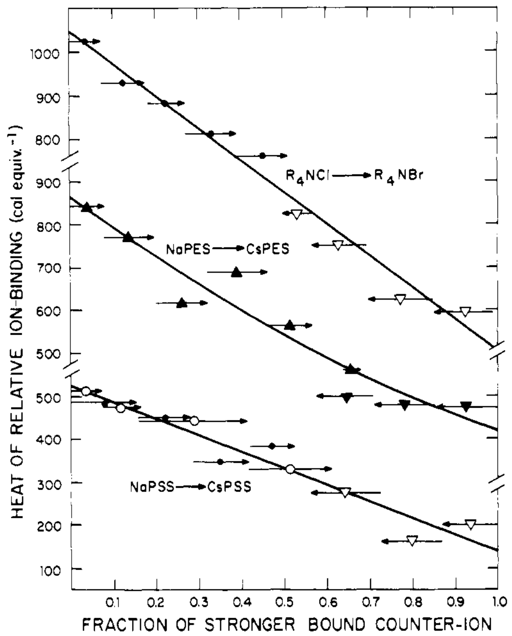

Figure 3. Enthalpy changes at 25 °C in competitive ion binding reactions with linear polyelectrolytes.

Table I
Thermodynamic Property Changes in Ion Binding Reactions[a]

binding reaction	$\Delta G°$	$\Delta H°$	$T\Delta S°$	$\Delta S°$
NaPSS → CsPSS	−0.21	−0.33	−0.12	−0.4
NaPES → CsPES	−0.23	−0.54	−0.31	−1.0
CsCMC → NaCMC	−0.07[b]	+0.47[b]	+0.54[b]	+1.8[b]
$PVBzMe_3NCl$ → $PVBzMe_3NBr$	−0.32	−0.88	−0.55	−1.9

[a] $\Delta G°$, $\Delta H°$, and $T\Delta S°$ in kcal/equiv; $\Delta S°$ in cal/(K equiv). [b] Computed from data in ref 21.

A summary of the thermodynamic property changes for the competitive binding reactions examined in this research is given in Table I together with values for the cesium–sodium ion reaction with (carboxymethyl)cellulose (CMC) calculated from the results of Rinaudo and Milas.[21] In those systems (Table I) where selective binding of the smaller ion in solution occurred there was also an energy lowering which was partially compensated by an entropy decrease. Because of thermodynamic compensation effects the magnitude of $\Delta G°$ frequently is not particularly revealing.[22] Thus, in the cesium–sodium counterion exchange reaction with poly(ethylenesulfonate) $\Delta G°$ differs only slightly from that with poly(styrenesulfonate), but $\Delta H°$ and $\Delta S°$ are significantly more negative. Interestingly, with CMC the larger sodium ion is preferentially bound; this is clearly a consequence of the substantial entropy increase in the competitive binding reaction on this polyelectrolyte.

As was mentioned earlier a purely electrostatic theory of the degree of counterion binding has been developed by Dolar and Škerjanc[5] based on the cell model of Lifson and Katchalsky[23] for dilute polyelectrolyte solutions and on an analytical solution of the Poisson–Boltzmann equation for two singly charged counterions of different size. Calculations with the theory show that the degree of binding (i.e., fraction of bound counterion) is greater for the smaller ion in solution and that the fraction of bound smaller ion decreases as its mole fraction on the polyion increases. The equations in the theory also predict that the degree of counterion binding increases with decreasing polyion diameter (assuming rodlike conformation) and increases with the linear charge density, ξ, of the polyion. Quite reasonable magnitudes may be estimated for the separation factor for counterions B and C (B < C), α(B/C), defined by

$$\alpha(\mathrm{B/C}) = (b_\mathrm{B}/b_\mathrm{C})/(f_\mathrm{B}/f_\mathrm{C}) = (b_\mathrm{B}/b_\mathrm{C})/[(1 - b_\mathrm{B})/(1 - b_\mathrm{C})] \quad (7)$$

where b_B and b_C are the fractions of bound B and C and f_B and f_C are the fractions of "free" counterion, respectively. Thus, for $r_\mathrm{B} = 1$ Å and $r_\mathrm{C} = 4$ Å the value of α(B/C) decreases from 2.15 to 1.60 when the mole fraction of B, X_B, on the polyelectrolyte increases from $X_\mathrm{B} = 0$ to $X_\mathrm{B} = 1.0$.

Two limitations in the comparison of the Dolar–Škerjanc electrostatic theory calculations with experiment must be noted: (a) The theory applies only to salt-free polyelectrolyte solutions; (b) a primitive model was employed in the estimation of the free energy of counterion binding. The only basis for selectivity in the model is the difference in the distance of closest approach of the respective counterions to the surface of a uniformly charged, cylindrical polyion of finite diameter. The local counterion concentration will be high in such a model, however, and hence short-range interactions among the counterions can never become negligible. Accordingly, the following comments about Table I may be made:

(1) The observed preferred binding of Cs^+ over Na^+ ion with poly(styrenesulfonate) and poly(ethylenesulfonate) solutions, and the magnitudes of the measured Cs^+–Na^+ ion separation factors appear to be in agreement with the Dolar–Škerjanc theory. The lowering of the electrostatic energy of the system appears to be the predominant factor in the competitive counterion binding reactions of the alkali metal cations with these polyelectrolytes.

(2) The larger binding of cesium relative to sodium ion observed with poly(ethylenesulfonate) and, particularly, the larger enthalpy decrease measured in the competitive binding reaction compared with poly(styrenesulfonate) are in agreement with the theory, which predicts a larger selectivity for the polyion of smaller diameter.

(3) When a larger counterion (Na^+) is preferred over a smaller counterion (Cs^+) in solution, the competitive binding reaction is "entropy driven" (cf. (carboxymethyl)cellulose, CMC, in Table I). Electrostatic factors are not determining, and the electrostatic theory does not apply. The gross observed entropy increase may be interpreted in terms of counterion site binding accompanied by significant changes in ion solvation. However, it must be recognized that the $\Delta S°$ for the competitive counterion binding reaction is the sum of possibly several positive and negative entropy contributions. For example, a negative entropy contribution would be expected because of losses in ion translational degrees of freedom on site binding.

(4) The relatively strong preference of bromide over chloride ion in the competitive anion binding reaction with the poly[(vinylbenzyl)trimethylammonium] cation appears to be greater than can be explained by the difference in the respective hydrated halide ion sizes or by the increased radius of the polycation chain, assuming electrostatic forces are dominant. The possibility of counterion binding mechanisms in addition to electrostatic binding must be considered.[24,25]

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(9) In an alternative procedure a predetermined weight of dry solid polyelectrolyte was dissolved in pure water and added to the cell. This solution was ultrafiltered by washing with water to remove low molecular weight polymer until the filtrate showed negligible absorption in the ultraviolet. A known weight of alkali halide solution was added and the polyelectrolyte–salt mixture was stirred to give a homogeneous solution which then was ultrafiltered.
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End Effects in Polyelectrolytes by the Mayer Cluster Integral Approach

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ABSTRACT: We apply the Mayer cluster expansion theory to the interaction of point ions with a polyion, modeling the polyion as a line charge of length $2L$ with suitable polyion–mobile ion distances of closest approach. By summing over all simple ring clusters we obtain limiting law expressions for contributions to the excess free energy and various colligative properties of the solution due to mobile ion–polyion interactions. These expressions include explicit end-effect corrections to the expressions derived by Manning for the case of an infinitely long polyion. We show that for a polyion of *fixed* dimensions, even though its length may be very large, cluster terms of higher order than the simple ring terms do not diverge in the limit of infinite dilution but instead disappear more rapidly than the ring terms. This indicates the absence of counterion condensation in this limit and validates the simple ring term expressions as limiting law expressions.

I. Introduction

In 1969 Manning[1,2] presented a theory of polyelectrolyte solutions based on the Mayer[3] cluster theory of ionic solutions. The Manning theory models the polyion as a uniformly charged line of infinite length interacting with a solution of mobile ions (taken as point charges), with assumption of a suitable distance of closest approach of mobile ions to the polyion. Interactions between polyions are neglected, and "uncondensed" (see below) mobile ions are treated in the Debye–Hückel approximation; that is, only simple "ring term" contributions to the free energy for "uncondensed" mobile ions are considered.

A fundamental quantity in the Manning theory is a (dimensionless) polyion charge-density parameter, ξ, defined by

$$\xi = \frac{e\sigma}{DkT} = \frac{e^2}{bDkT}$$

where e is the magnitude of the electronic charge, D the pure bulk solvent dielectric constant, k Boltzmann's constant, T the absolute temperature, and σ the polyion's charge density, equal to e/b with b the equivalent axial charge spacing distance on the polyion. For a polyion in a solution of univalent ions, if ξ is initially greater than 1, the condensation hypothesis requires that (in the limit of infinite dilution) sufficiently many counterions "condense" on the polyion to reduce ξ effectively to 1; if ξ is less than 1 initially, no counterion condensation occurs.

The theoretical justification given by Manning[1,2] for hypothesizing condensation involves the divergence of certain free energy terms in the limit of infinite dilution. Specifically, Manning showed that the leading ("ring") term in the Mayer cluster expansion corresponded to that obtained in the Debye–Hückel approximation; this term diverged logarithmically with increasing dilution of the system. Manning then analyzed the next higher order terms in the cluster expansion and showed that for $\xi \geq 1$, certain of these terms diverged even more rapidly than the ring term. Manning interpreted this result as implying counterion condensation.

In more recent work, Manning[4-7] and Iwasa[8,9] have treated polyion–counterion interactions by minimizing the free energy of the polyelectrolyte solution with respect to transfer of counterions from a bulk ("free") phase to a polyion-bound ("condensed") phase; the results obtained agree with the original condensation hypothesis. In a

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