Conductivity of Aqueous Solutions of Ionic Polysaccharides Containing Simple Salts

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ABSTRACT: Electrical conductivities were measured for aqueous solutions of sodium ι-carrageenan, sodium heparin, and sodium dextran sulfate in NaCl and Na_2SO_4 solution at 25 °C. Measurements were also made on diethylaminoethyldextran chloride, a polyelectrolyte of low charge density, in aqueous NaCl and $CaCl_2$. The polyelectrolyte concentration ranged from 0.000 050 to 0.010 N in 0.000 50, 0.001 0, 0.005 0, and 0.010 0 N simple salt so as to keep the polyelectrolyte–simple salt ratio between 0.1 and 10. Anomalous behavior was found for sodium dextran sulfate. The correlation between the experimental results and the Manning limiting law for electric transport is discussed. An empirical treatment of the data using a modified expression for the additivity of simple salt and polyelectrolyte conductivities was found to have a theoretical justification. For salt-containing polyelectrolyte solution, the theoretical equations for conductivity were developed for the case where the charge density of the polyelectrolyte is less than the critical charge density.

The Manning theory of polyelectrolyte solutions[1–6] has given impetus for further experimental and theoretical investigations. While the Manning model has achieved some success in explaining the equilibrium and mass transport properties at low concentrations, the limiting law for the conductance of rodlike polyelectrolytes shows poorer correlation with experimental findings.

Devore and Manning[7] extended the Manning model to interpret the electric transport properties for polyelectrolyte solutions containing simple salt. Their results were compared with a phenomenological theory of electrical transport[8] in which it was shown that the model is strictly valid in the limit of zero salt concentration and that the ionic equivalent conductances of simple salt to be used are not the limiting ones, but correspond to pure simple salt solution of the appropriate concentration. Both points have been stated by Devore and Manning.[7] The theory defines a quantity A_p by

$$\kappa - \kappa_s = 10^{-3} A_p N_p \tag{1}$$

where κ and κ_s are the specific conductivities of the solution and of the simple salt in the absence of polyelectrolyte, N_p is the equivalent concentration of polyelectrolyte, and A_p takes into account the interaction of the simple ions with the polyion and is theoretically calculated to be

$$A_p = \xi^{-1}\left[\left(t_1^{(s)} - \frac{1}{6}\right)\lambda_s + \lambda_p\right] \tag{2}$$

where ξ, a charge density parameter, is given by $e^2/\epsilon kTb$, where e is the proton charge, ϵ is the bulk solvent dielectric constant, k is the Boltzmann constant, T is the absolute temperature, and b is the average structural distance between charges on the polyelectrolyte; $t_1^{(s)}$ is the transference number of the counterion; λ_s is the equivalent conductance of the simple salt both at the given concentration and in the absence of polyelectrolyte; and λ_p, the equivalent conductance of the polyion, is given by

$$\lambda_p = (F/300)(\epsilon k\mathrm{T}/3\pi\eta e)|\ln Ka| \tag{3}$$

where F is the Faraday constant, η is the bulk solvent viscosity, and K takes on the value of the Debye screening constant for simple electrolytes in the absence of polyelectrolyte. Note that λ_p does not depend upon N_p nor upon ξ but is a function of the coion and counterion valence and of the simple salt concentration through K. As a result A_p depends upon the nature and concentration of both the coion and counterion but not upon N_p. Kowblansky and Ander[9] obtained values of A_p from linear regression plots of $(\kappa - \kappa_s)$ vs. N_p for sodium poly(styrene sulfonate) solutions containing several concentrations of NaCl and Na_2SO_4. As is predicted from the theory, the experimental A_p values were found to be independent of N_p. However, the theoretical A_p values should increase with decreasing simple electrolyte concentration and to decrease with increasing coion valence, but the experimental values were found to be independent of simple salt concentration and of coion valence. Also, the experimental values of A_p were found to be higher than the predicted ones, as were those reported for DNA in LiCl, NaCl, and KCl solutions.[6]

The concentration dependence of the equivalent conductance Λ of polyelectrolyte solutions containing simple salt was shown by Kowblansky and Ander[9] to be best described by an empirical modified additivity equation

$$\Lambda = 10^3[\kappa - \kappa_s(D_2/D_2^{\,0})]/N_p \tag{4}$$

where D_2 and $D_2^{\,0}$ are the coion self-diffusion coefficients in a salt-containing and in an infinitely dilute polyelectrolyte-free salt solution, respectively. Using $D_2/D_2^{\,0}$ as a quantitative measure of the effective interaction of uncondensed small ions in the presence of the polyelectrolyte, the effective specific conductance of the added simple salt would be $\kappa(D_2/D_2^{\,0})$. The modified additivity equation was shown to hold for sodium poly(styrene sulfonate) solutions containing NaCl and Na_2SO_4, lithium and ammonium poly(styrene sulfonates) containing their respective chlorides at 25 °C, sodium carrageenan in aqueous NaCl solutions at 0 °C.

To further test the theoretical eq 1 and the empirical eq 4, we report the conductivity results obtained for sodium ι-carrageenan (NaCarr), sodium heparin (NaH), and sodium dextran sulfate (NaDS) in aqueous solutions of NaCl and Na_2SO_4 at 25 °C. ι-Carrageenan is a linear copolymer of β-D-galactose 4-sulfate and 3,6-anhydro-α-D-galactose 2-sulfate; the X-ray diffraction patterns indicate that the average distance between sulfate groups on the backbone is 0.43 nm.[10] Sodium heparin has a tetrasaccharide as its basic unit.[11] It is thought to be a helix of 1 → 4 linked α-D-glucosamine, β-D-glucuronate, and iduronate containing three types of pendant ionic groups, O-sulfate, N-sulfate, and carboxyl, with an average distance between ionic groups of 0.24 nm, as determined from X-ray fiber diffraction studies.[12] Sodium dextran sulfate, a sulfonated derivative of dextran, was found to have an average of 2.07 sulfate groups per glucosyl residue, giving an average distance between ionic groups of 0.25 nm. The samples of NaCarr, NaH, and NaDS used in this study were the same ones used in previous studies.[13,14]

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Table IV
A Comparison of the Predicted and Experimental Value of A_p for ι-Carrageenan in Aqueous Solutions of NaCl or Na_2SO_4 at 25 °C

		A_p, $cm^2\ ohm^{-1}\ equiv^{-1}$			
		NaCl		Na_2SO_4	
N_s	N_p	exptl	theor	exptl	theor
0.000 50	0.000 25-0.003 7	51.4 ± 0.2	55.3 (70.7)	46 ± 1	51.9 (66.8)
0.001 00	0.000 5-0.007 5	51.4 ± 0.2	50.1 (65.2)	45 ± 1	46.7 (61.4)
0.005 00	0.002 5-0.037	47.0 ± 0.4	38.0 (52.1)	49 ± 1	34.3 (48.0)
0.010 0	0.005-0.075	47.4 ± 0.2	32.6 (46.4)	48 ± 1	28.8 (42.0)

Table V
A Comparison of the Predicted and Experimental Values of A_p for Heparin in Aqueous Solutions of NaCl or Na_2SO_4 at 25 °C

		A_p, $cm^2\ ohm^{-1}\ equiv^{-1}$			
		NaCl		Na_2SO_4	
N_s	N_p	exptl	theor	exptl	theor
0.000 50	0.000 25-0.003 7	45.9 ± 0.7	32.8 (44.1)	45.9 ± 0.6	30.8 (42.1)
0.001 00	0.000 5-0.007 5	43.9 ± 0.7	29.7 (41.1)	42.8 ± 0.4	27.7 (39.0)
0.005 00	0.002 5-0.037	40.8 ± 0.3	22.5 (33.9)	39.1 ± 0.4	20.3 (31.6)
0.010 0	0.005-0.075	39.7 ± 0.3	19.3 (30.7)	37.9 ± 0.4	17.1 (28.2)

Conductivity measurements were also on aqueous solutions of diethylaminoethyldextran chloride (DEAEDCl) containing NaCl and $CaCl_2$. The parent dextran from which this polyelectrolyte was made was of average molecular weight 500000 and using the chemical analysis of the DEAEDCl sample gave 0.56 charges per sugar residue and 0.92 nm as the average distance between charges.

Experimental Section

Samples of sodium ι-carrageenan were donated by Marine Colloids Inc. and the sample of sodium heparin was the generous gift of Inolex Co. The equivalent weight of the ι-carrageenan salt was obtained by titration of the acid form with NaOH and was found to be 255.2 g/equiv. The equivalent weight of the heparin sample was found by similar methods to be 182.5 g/equiv, in good agreement with that obtained from the structure presented.[12] The purified DEAE dextran chloride sample was obtained from Pharmacia Fine Chemicals. The sample gave a chloride analysis of 8.36%, corresponding to a unit molecular weight of 424.1. The dextran sulfate sample obtained from Pharmacia Fine Chemicals contained a phosphate buffer which required each stock solution to be purified by repeated passage through an anion exchange resin and then titrated.

In making up the solutions each sample of polymer with the exception of dextran sulfate was dried in vacuo at 35 °C for a period of 24 h or until constant weight. The NaCl, Na_2SO_4, and $CaCl_2 \cdot 2H_2O$ salts used were ACS certified reagent grade obtained from Fischer Scientific Co. All solutions were made using double deionized distilled water.

Conductivity measurements were made in an oil filled bath at 25.00 ± 0.01 °C using a Pyrex conductivity cell of the modified Shedlovsky design. The electrodes had been platinized lightly with platinum black. A Beckman model RC-18A conductivity bridge which utilizes a precision ac Wheatstone bridge was employed using a frequence of 3000 Hz. The resistance of an aqueous solution of polyelectrolyte is not frequency dependent in the audio range and therefore no attempt was made to correct for frequency dependence. The cell constant was obtained from measurements of the conductivity of aqueous solutions of KCl. The resulting value of 1.1388 ± 0.0007 cm^{-1} was verified throughout the study. Measurements of the deionized distilled water yielded a conductivity value of the order of $10^{-6}\ \Omega^{-1}\ cm^{-1}$ which was considered negligible for all but the most dilute solutions. Specific conductivity measurements of the polymer solution were reproducible to within ±0.3%.

Results and Disucssions

For NaCarr, NaH, and NaDS conductance data were obtained for aqueous solutions of the polymer in solutions containing NaCl or Na_2SO_4. Measurements were made at simple salt concentrations of 0.000 50, 0.001 0, 0.005 0, and 0.010 N. The polymer concentration was adjusted from 0.000 050 to 0.010 N in such a way as to keep the concentration variable X, defined by $X = N_p/N_s$, where N_p and N_s are the polymer and simple salt equivalent concentration, respectively, in the range of 0.1 to 10. Data were also obtained for salt-free solutions of polymer over this concentration range. The data obtained for the specific conductance of the solutions studied can be found in Tables I, II, and III in the supplementary material.[15] The linearity of κ with N_p is observed for all salt concentrations. In addition to increasing with increasing polymer concentration, κ was found to increase with increasing salt concentration as expected. Note from eq 3 that λ_p does not depend upon N_p nor upon ξ but is a function of the coion and counterion valence and of the simple salt concentration. As a result A_p depends upon the nature and concentration of both the coion and counterion but not upon N_p, in agreement with experiment.

Experimental values of A_p were calculated by taking linear regression plots of κ vs. N_p for NaCarr, NaH, and NaDS solutions for each of the different salt concentrations. Theoretical values of A_p were calculated from eq 2 and 3 using $\xi = 1.66$ for NaCarr, $\xi = 3.0$ for NaH, $a = 9$ Å for both polymers, $\xi = 2.9$ and $a = 8$ Å for NaDS. The other electrochemical constants were obtained from Robinson and Stokes.[16] The bulk viscosity of water was used in the calculations because the theory is expected to be valid in the limit of infinite dilution. A comparison of the theoretical and experimental values of A_p is presented in Tables IV, V, and VI. As can be seen the theoretical values of A_p are predicted to decrease with increasing simple electrolyte concentration and also to decrease with increasing coion valence. Both of these trends are observed to some extent in the heparin data; however, the magnitude of the dependence is greatly exaggerated in the theoretical values. For example, in the case of NaCl and heparin an increase in salt concentration from 0.000 50 to 0.010 N causes an observable decrease in A_p of 6.2 $cm^2\ ohm^{-1}\ equiv^{-1}$, whereas the predicted decrease is 13.5. The agreement is even worse with the Na_2SO_4 salt. Furthermore, the theoretical values consistently underestimate the experimental values. For ι-carrageenan the average magnitude of the theoretical A_p is in rough agreement with

Table VI
A Comparison of the Predicted and Experimental Values of A_p for Dextran Sulfate in Aqueous Solutions of NaCl or Na_2SO_4 at 25 °C

		A_p, cm^2 ohm^{-1} equiv^{-1}			
		NaCl		Na_2SO_4	
N_s	N_p	exptl	theor	exptl	theor
0.000 50	0.000 050-0.003 4	23.3 ± 0.6	35.4	23.8 ± 0.5	33.3
0.001 00	0.000 10-0.007 5	24.0 ± 0.4	32.2	23.6 ± 0.4	30.1
0.005 00	0.000 50-0.037	26.4 ± 0.5	24.7	25.6 ± 0.3	22.3
0.010 0	0.001 0-0.075	28.1 ± 0.7	21.4	26.5 ± 0.3	18.8

Table VIII
A Comparison of the Predicted and Experimental Values of A_p for DEAE Dextran in Aqueous Solutions of NaCl or $CaCl_2$ at 25 °C

		A_p, cm^2 ohm^{-1} equiv^{-1}			
		NaCl		Na_2SO_4	
N_s	N_p	exptl	theor	exptl	theor
0.000 50	0.000 050-0.004 0	67.8 ± 1.4	132	68.5 ± 1.5	125.0
0.001 0	0.000 10-0.007 8	63.6 ± 0.7	118.3	63.8 ± 0.8	115.6
0.005 0	0.000 50-0.039	57.0 ± 0.4	100.8	56.7 ± 0.2	92.8
0.010 0	0.001 0-0.078	53.0 ± 0.6	91.0	50.9 ± 0.4	82.5

the experimental values. However, with the carrageenan the actual dependence of A_p on salt concentration is hardly noticeable, whereas the theoretical values again predict a large decrease of A_p with increasing N_s. Similar results were obtained[9,17] for NaPSS–NaCl solutions at 25 °C and by Ross, Scruggs, and Manning[6] for DNA in LiCl, NaCl, and KCl solutions at 0 °C. Most important is that the experimental A_p values appear to be independent of the nature of the coion whereas the theoretical values indicate a coion dependency.

Recently, Manning recalculated the electrical mobility of the polyion by considering the polyion to be a hydrodynamic particle of a linear array of points with the Debye–Hückel screening factor in the hydrodynamic interaction between fixed charges.[18] The resulting equation is similar to eq 3 except that the distance of closest approach a is replaced by b, the axial distance between charges on the chain. Tables IV and V contain the resulting A_p values in parentheses for NaCarr and NaH, respectively. (These calculations were not repeated for NaDS because of the anomolous conductance behavior of its solutions.) The theoretical values in the parentheses of Table IV indicate better agreement with the experimental A_p values than with the other theoretical values for the two higher simple salt concentrations and poorer agreement for the two lower salt concentrations. It was of interest to perform this new calculation for sodium poly(styrene sulfonate) in NaCl solutions because the experimental A_p values were reported to be almost independent of the simple salt concentration. Here again, the newer A_p calculations were found to be in better agreement with the experimental A_p values at the higher salt concentrations and poorer at the lower salt concentrations, where screening between the fixed charges is lower. The newer A_p values in the parentheses of Table V for NaH show better agreement with the experimental values than do the previously calculated theoretical values for every NaCl and Na_2SO_4 concentration. It may be that the more fundamental parameter b should be used in place of the more vague parameter a. More data on different polyelectrolyte systems are needed for a further analysis.

From Table VI it is surprisingly noted that NaDS behaves differently when compared to the other polyelectrolytes because the experimental A_p values increase with increasing N_s for NaCl and Na_2SO_4 solutions. The specific effect of dextran sulfate on the conductivity was first noted by Kwak et al.[19] where it was reported that the equivalent conductivity of alkali-metal dextran sulfates in salt-free aqueous solution decreased with decreasing N_p, a trend opposite that found for most other polyelectrolytes. It is gratifying to us to note that our Λ values for salt-free NaDS solution are in close agreement to the reported values.

Conductivity results were also obtained for the polycation DEAECl in NaCl and $CaCl_2$ solutions and are given in Tables VII[15] and VIII. While NaCarr, NaH, and NaDS all have values of $\xi > 1$, for DEAE $\xi = 0.78$ and $a = 8.0$ Å. It should be noted that the experimental A_p values in Table VIII decrease with increasing N_s, as is found for most polyelectrolytes, and that the value of A_p is independent of the nature of the coion. To compare the A_p values for the DEAE solutions with those predicted from Manning's theory, the appropriate equation must be derived for $\xi < 1$ since Manning's derivation is only for $\xi > 1$. According to the model, for $\xi < \xi_{\mathrm{critical}}$ all small ions are uncondensed and interact with the polyion to the same extent so that $D_1/D_1^0 = D_2/D_2^0$, where subscripts 1 and 2 represent the counterion and coion, respectively, and the self-diffusion ratios are of the small ions in the presence of polyelectrolyte to the small ions in the absence of polyelectrolyte at infinite dilution. Thus, Manning's equation for the specific conductance of the solution becomes

$$10^3\kappa = (D_2/D_2^0)[N_p(\lambda_1^0 + \lambda_p) + N_s(\lambda_1^0 + \lambda_2^0)] \quad (5)$$

using Manning's approximation[2]

$$D_2/D_2^0 = 1 - \tfrac{1}{6}\xi X \quad (6)$$

and dropping second-order terms in X gives

$$10^3\kappa = N_p(\lambda_1^0 + \lambda_p) + N_s(\lambda_1^0 + \lambda_2^0) - \tfrac{1}{6}\xi N_p(\lambda_1^0 + \lambda_2^0) \quad (7)$$

which simplifies using standard electrochemical notation to

$$10^3(\kappa - \kappa_s) = N_p[(t_1^0 - \tfrac{1}{6}\xi)\lambda_s^0 + \lambda_p] \quad (8)$$

giving

$$A_p = (t_1^0 - \tfrac{1}{6}\xi)\lambda_s^0 + \lambda_p \qquad \xi < 1 \quad (9)$$

which is valid for univalent counterions and $\xi < 1$. Upon comparing eq 9 and 2, it should be noted that A_p is less for $\xi > 1$ as compared to $\xi < 1$. Note from Table VIII that the theoretical values of A_p greatly overestimate the

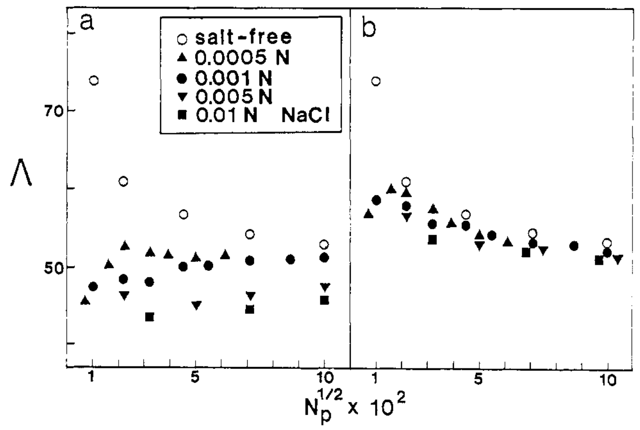

Figure 1. A comparison of Λ values for aqueous solutions of sodium ι-carrageenan in the presence and absence of NaCl at 25 °C (a) calculated from eq 10 and (b) calculated from eq 12.

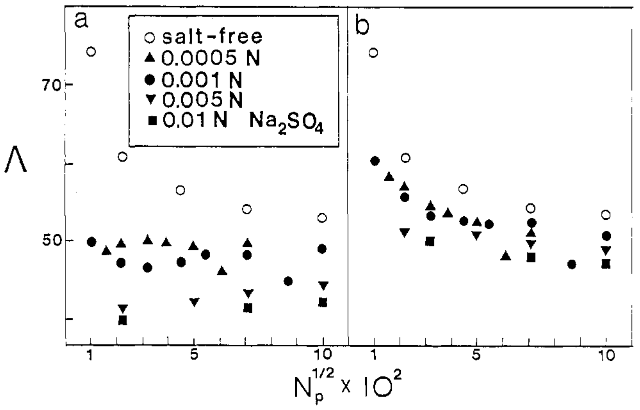

Figure 2. A comparison of Λ values for aqueous solutions of sodium ι-carrageenan in the presence and absence of Na_2SO_4 at 25 °C (a) calculated from eq 10 and (b) calculated from eq 12.

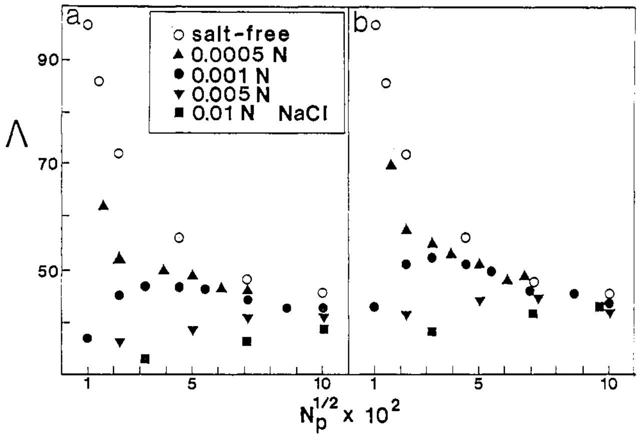

Figure 3. A comparison of Λ values for aqueous solutions of sodium heparin in the presence and absence of NaCl at 25 °C (a) calculated from eq 10 and (b) calculated from eq 12.

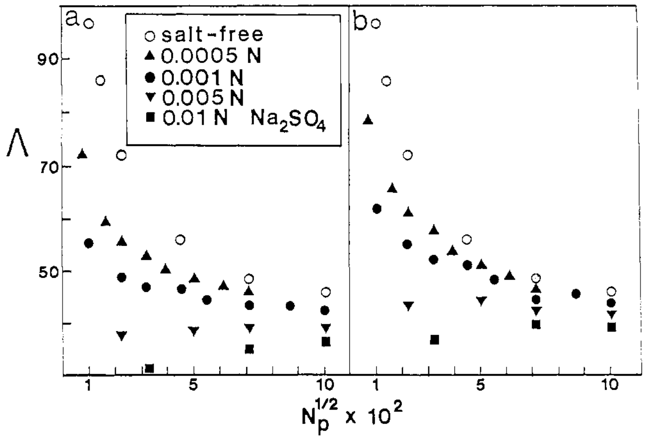

Figure 4. A comparison of Λ values for aqueous solutions of sodium heparin in the presence and absence of Na_2SO_4 at 25 °C (a) calculated from eq 10 and (b) calculated from eq 12.

electrostatic interactions between the small ions and the polyion and that a dependence on the nature of the coion is predicted but was not experimentally found. While a reasonable value of $a = 8.0$ Å was used in the calculations, the theoretical value of λ_p is not strongly dependent on the value of a.

Because of the discrepancy between Manning's predictions concerning the conductance of polyelectrolyte solutions containing simple salt and the experimentally observed values, an empirical approach to the problem seems in order. Traditionally this approach takes the form of an assumed additivity of the specific conductance of the polymer and of the salt, which gives the equivalent conductance of the polyelectrolyte in a salt solution,

$$\Lambda = 10^3(\kappa - \kappa_s)/N_p \qquad (10)$$

where $\kappa_s = 0$ in the absence of salt. The major problem with the assumption of additivity is that it becomes approximately true only at extremely low concentrations. For a finite concentration it is always observed that κ, i.e., for the polyelectrolyte in a salt-free solution, is greater than $(\kappa - \kappa_s)$ for the salt-containing polyelectrolyte solution for a given concentration of polymer.[20,21] Furthermore, since Λ for both these cases represents the equivalent concentration of the polyelectrolyte they should be approximately equal for a given polymer solution; however, this is not observed. This can be seen from Figures 1, 2, 3, and 4, where for each figure the left-hand side, labeled side a, plots are shown of the equivalent conductance of both the salt-free and salt-containing solutions derived from the assumption of simple additivity. In the salt-free case the equivalent conductance increases with decreasing polymer concentration, whereas in the salt-containing case it stays more nearly constant. The salt-free equivalent conductance is noticeably higher than the salt, with this split becoming very well pronounced at the lower polymer concentrations. All of these observations were previously reported by Kowblansky and Ander,[9] where it was suggested that the law of additivity is not strictly obeyed and suggests that this law be modified. An empirical modified additivity equation by using Manning's theoretical prediction concerning the diffusion coefficient of unbound ions was used. The theory predicts that all the unbound ions interact with the polyion through Debye–Hückel interactions to the same extent as do the coions. It has been found through measurements of diffusion coefficients that the interactions of the coions are independent of the coion valence and that, therefore, the ratio of the diffusion coefficients for unbound ions is given by[2]

$$D_2/D_2^0 = 1 - \tfrac{1}{3}A \qquad (11)$$

where A is a theoretical interaction term. Using the Nernst–Einstein equation which states that the equivalent conductance and diffusion coefficients are linearly related, it becomes reasonable to assume that the specific conductance of the salt, all of whose ions are uncondensed, is lowered to the value $(D_2/D_2^0)\kappa_s$. This leads to a modified additivity rule which yields the following equation for the equivalent conductance

$$\Lambda = 10^3[\kappa - \kappa_s(D_2/D_2^0)]/N_p \qquad (12)$$

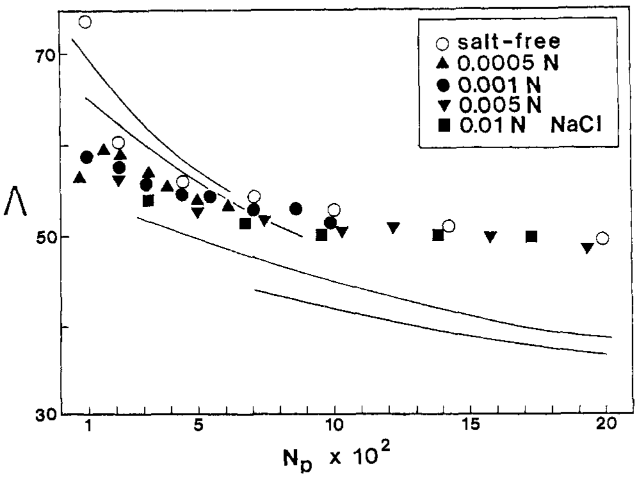

Figure 5. A comparison of Λ values calculated from the empirical modified additivity equation 12 with the theoretical lines calculated from equation 13 in order of increasing salt concentration from top to bottom for sodium ι-carrageenan in NaCl solutions.

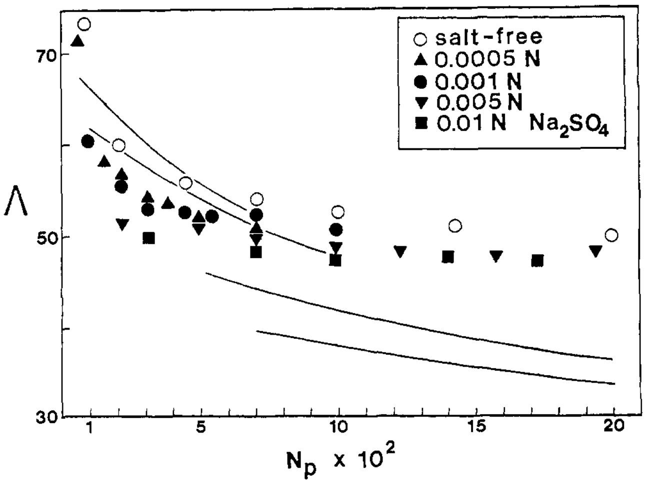

Figure 6. A comparison of Λ values calculated from the empirical modified additivity eq 12 with the theoretical lines calculated from eq 13 in order of increasing salt concentration from top to bottom for sodium ι-carrageenan in Na_2SO_4 solutions.

Values of Λ were calculated using eq 12 and the b side of Figures 1, 2, 3, and 4. With the correction employed, better agreement is obtained between Λ of the salt-free and Λ of the salt-containing solutions. This is particularly evident in the case of the NaCarr–NaCl solutions, where the corrected values are nearly superimposable upon the salt free until N_p becomes less than 0.000 10 N. For most of the data the corrected values of Λ are still somewhat lower than the salt-free values. Part of the reason for this is the use of the theoretical value of D_2/D_2^0 instead of the experimental value in calculating Λ. It has been observed that an increase in the ionic strength causes a decrease in the diffusion coefficient and correcting for this would result in an increase in the values of the modified Λ. Results similar to these have been observed for solutions of $NH_4PSS–NH_4Cl$, NaPSS–NaCl, and LiPSS–LiCl.[9]

It is clear, therefore, that the rule of modified additivity offers improvement over the assumption of simple additivity but does not fully account for the observation conductivities, especially for X less than three. Combining the equations for κ_1, κ_2, and κ_p derived independently by Devore and Manning[7] and by Schmitt, Varoqui, and Meullenet[8] for univalent counterions and making use of the relationship between D_1/D_1^0 and D_2/D_2^0 gives

$$10^3[\kappa - \kappa_s(D_2/D_2^0)]N_p = f(D_2/D_2^0)(\lambda_1^0 + \lambda_p) \quad (13)$$

where $f = \xi^{-1}$ if $\xi \geq 1$ and $f = 1$ if $\xi < 1$. The right-hand side of eq 13 is identical in form to the salt-free equation derived by Manning. An important difference to note is that λ_p depends upon both N_p and N_s. However, as X becomes large, N_p becomes dominant and one would expect λ_p to tend toward its salt-free value. According to the Manning theory, the concentration dependence of λ_p is principally through K, the Debye–Hückel screening parameter, where K is proportional to $[(1 + |z_2|N_s + fN_p]^{1/2}$. Thus, when $fN_p >> (1 + |z_2|)N_s$ salt-free behavior might be expected. For most of the polyelectrolytes reported, this condition is where X is approximately four. Also, if the relaxation effect were taken into account in the calculation of λ_p, it would be expected to further decrease the dependence of λ_p on N_s. The other term with a dependence on N_s is D_2/D_2^0, which tends toward its constant salt-free value quickly with increasing X.

Values of $f(D_2/D_2^0)(\lambda_1^0 + \lambda_p)$ were calculated for each polyelectrolyte and the salt solution studied for $0.1 \leq X \leq 10$ with λ_p given by eq 3 except that the screening constant K now takes into account both N_s and N_p. The theoretical lines are shown in Figures 5 through 12, with the top line for 0.000 50 N salt, the second line for 0.0010 N, the third line for 0.0050 N and the fourth line for 0.010 N. These theoretical curves are functions of both N_p and N_s. It appears that dependence on salt concentration is

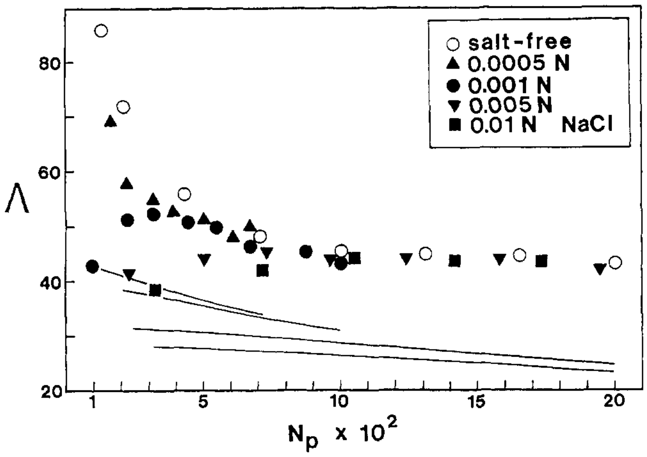

Figure 7. A comparison of Λ values calculated from the empirical modified additivity eq 12 with the theoretical lines calculated from eq 13 in order of increasing salt concentration from top to bottom for sodium heparin in NaCl solutions.

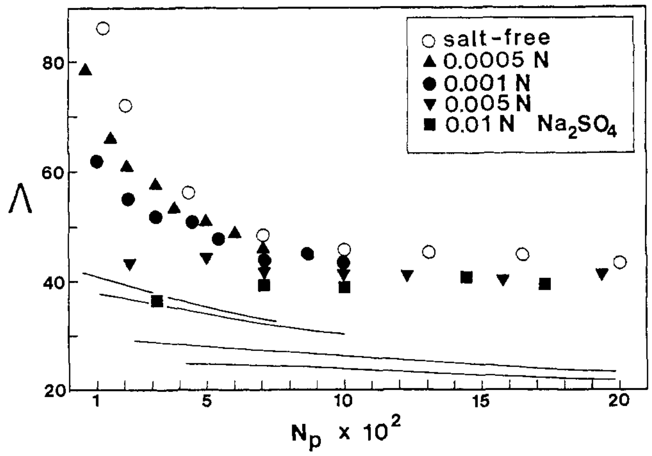

Figure 8. A comparison of Λ values calculated from the empirical modified additivity eq 12 with the theoretical lines calculated from eq 13 in order of increasing salt concentration from top to bottom for sodium heparin in Na_2SO_4 solutions.

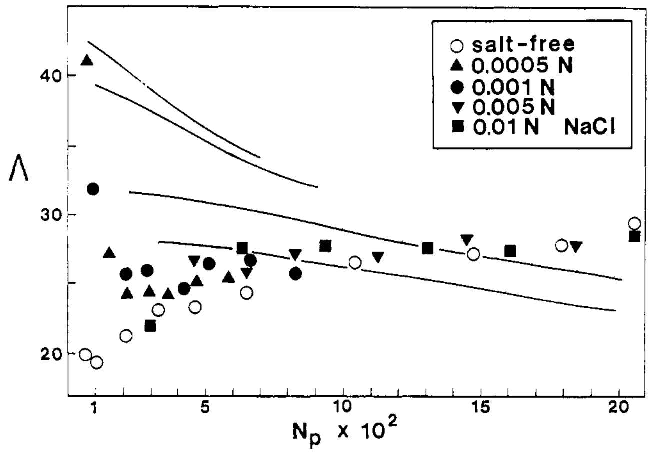

Figure 9. A comparison of Λ values calculated from the empirical modified additivity eq 12 with the theoretical lines calculated from eq 13 in order of increasing salt concentration from top to bottom for sodium dextran sulfate in NaCl solutions.

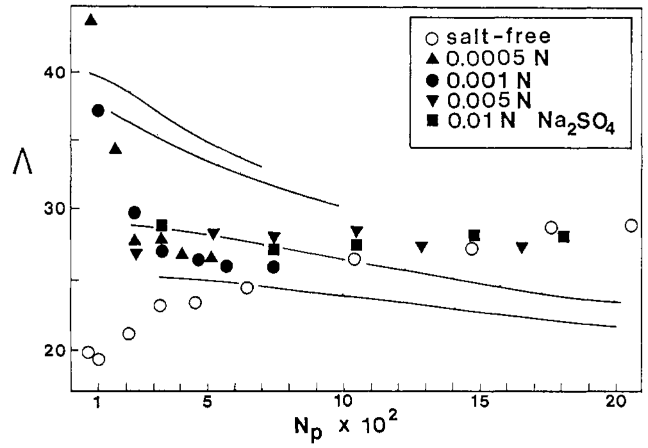

Figure 10. A comparison of Λ values calculated from the empirical modified additivity eq 12 with the theoretical lines calculated from eq 13 in order of increasing salt concentration from top to bottom for sodium dextran sulfate in Na_2SO_4 solutions.

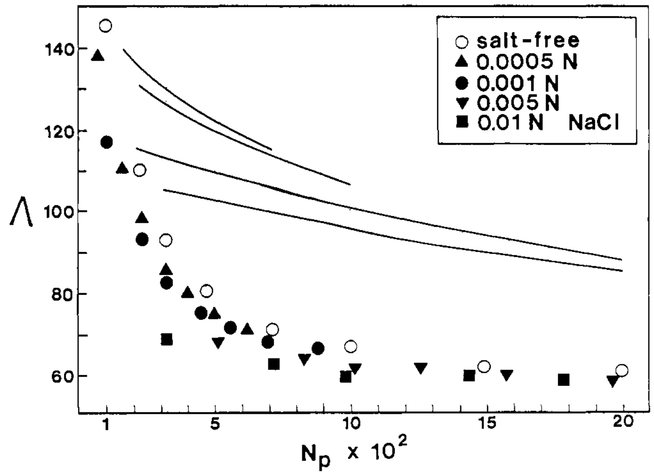

Figure 11. A comparison of Λ values calculated from the empirical modified additivity eq 12 with the theoretical lines calculated from eq 13 in order of increasing salt concentration from top to bottom for DEAE chloride in NaCl solutions.

exaggerated, probably due to the neglect of the relaxation effect. The quantitative agreement is poor, except for NaCarr. The theoretical curves are too low for NaH and too high for DEAE and the anomalous behavior for NaDex has been noted previously. Since λ_1^0 is a constant, f has been shown to be in accord with several different experimental results, and D_2/D_2^0 is in fairly good agreement with experimental findings, it is reasonable to assume that the greatest error resides in the calculation of λ_p. Even if the relaxation effect was considered in the calculation of λ_p, it appears doubtful that it would fully account for the discrepancies observed.

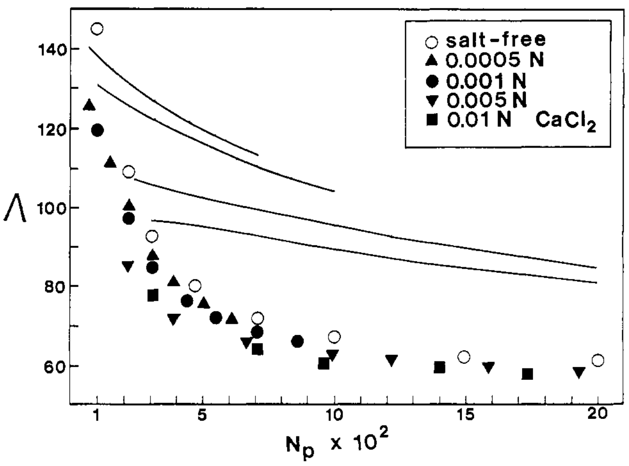

Figure 12. A comparison of Λ values calculated from the empirical modified additivity eq 12 with the theoretical lines calculated from eq 13 in order of increasing salt concentration from top to bottom for DEAE chloride in Na_2SO_4 solutions.

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Supplementary Material Available: Tables I, II, III, and VII containing the specific conductivities of all the solutions reported (4 pages). Ordering information is given on any current masthead page.

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