activation energy leading to unit E is 0.96 kcal/mol lower than that corresponding to the formation of units B + C and D.

The important parameters responsible for the structure of poly(1) are the polarity of the solvent plus the polymerization temperature.

The influence of the reaction medium on cationic isomerizations was discussed elsewhere.[25] The tendency for rearrangement to a more stable cation is lower in better solvating solvents. On the other hand, there are examples in which rearrangement is greater in less nucleophilic solvents, and still others in which nucleophilic solvation of the more exposed hydrogen seems to aid its migration.[26] At the present time we are unable to account for these opposite trends in hydrogen and carbon participation in rearrangements.[27] Perhaps this lack of fundamental knowledge of the chemistry of carbenium ions may explain why we are unable to find experimental conditions under which poly(1) containing a unique type of structural unit is formed.

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Interaction of Univalent and Divalent Cations with Carrageenans in Aqueous Solution

G. Pass,* G. O. Phillips, and D. J. Wedlock

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, United Kingdom. *Received June 25, 1976*

ABSTRACT: The activity coefficients of sodium, potassium, and calcium counterions have been determined for κ-, ι- and λ-carrageenans. Electromotive force measurements were made at 25 °C in aqueous solutions containing sodium, potassium, and calcium carrageenans, with and without added simple electrolyte. In the absence of added salt the activity coefficients increased with increasing dilution, and at a given concentration the observed order is $\gamma_{Na} > \gamma_K > \gamma_{Ca}$. The experimental ratio γ_{Na}/γ_{Ca} is in agreement with values predicted from Manning's theory. The activity coefficients of the sodium and potassium counterions increase with increasing concentration of added simple electrolyte. The behavior of the sodium counterion agrees more closely than the potassium counterion with the theoretical predictions. The activity coefficients of the counterions were found to depend upon the degree of substitution, and hence on the charge of the polyanion, in agreement with the theory.

The interaction between cations and polyanions has been extensively studied with particular reference to the relative order of cation binding strength and the effect of the anionic substituents in the macromolecule. The condensation of the cations on to the polyanion and the electrostatic interaction of the uncondensed cations with the polyanion have been considered theoretically in terms of the influence of the charge density of the polyanion.[1,2] The theoretical treatment has been applied to the interaction of counterions with a variety of polyanions including polyanionic polysaccharides.[3-11] Although in general satisfactory agreement with the theory is reported, the relative order of activity coefficients $Na^+ < K^+$ found for κ- and λ-carrageenans[5] is the opposite of reported values for sulfated polyanions.[6,7]

We have now investigated the interactions of sodium, potassium, and calcium counterions with κ-, ι-, and λ-carra-

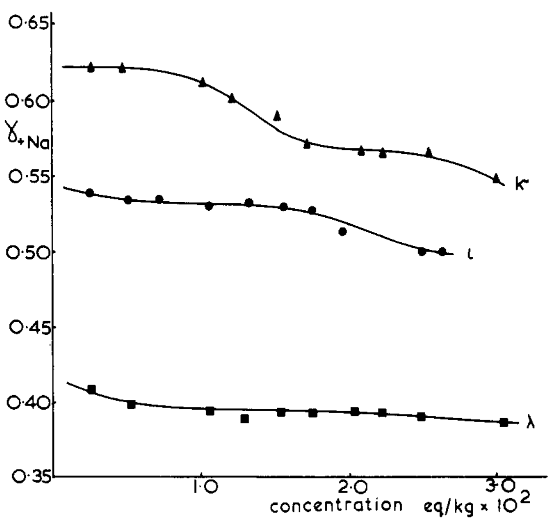

Figure 1. Activity coefficient of sodium counterion vs. concentration for κ-, ι-, and λ-carrageenan.

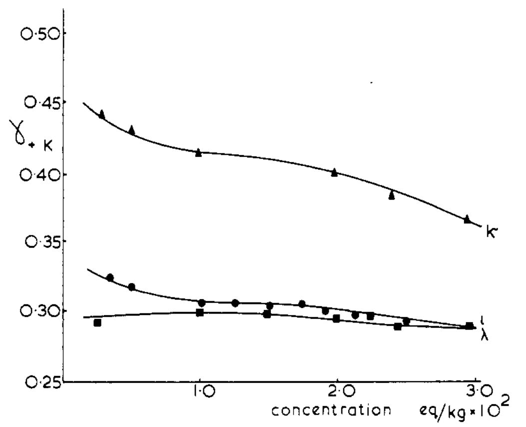

Figure 2. Activity coefficient of potassium counterion vs. concentration for κ-, ι-, and λ-carrageenan.

Table I
Equivalent Weights of Sodium Carrageenans

Carrageenan (Na salt)	κ	ι	λ
Equivalent mass	294	254	209

geenan by an emf method. The results have been examined in terms of the line charge model and in terms of the relative order of counterion binding.

Experimental Section

Three purified carrageenan fractions with different degrees of substitution were used, κ,[12] ι,[13] and λ.[14] Potassium salts were supplied by Copenhagen Pectin Factory S.A., Copenhagen, and Marine Colloids Inc., Rockland, Maine. Sodium salts were obtained by passing a 0.4% w/v aqueous solution of a carrageenan fraction through an ion-exchange column (Amberlite IR 120) using at least a fivefold excess of resin to ensure complete conversion. The solution was concentrated in a rotary evaporator at 35 °C and freeze dried. Equivalent weights of the polymers were obtained gravimetrically by ignition of a weighed sample to the corresponding sodium or potassium sulfate by evaporating from sulfuric acid (concentrated), until all signs of charring had disappeared. Any pyrosulfate formed was converted to sulfate by heating with excess ammonium carbonate. Determinations were carried out in triplicate and agreed within 2%, mean values being used. Calcium salts of κ- and λ-carrageenan were prepared by a similar procedure, but equivalent weights were determined by EDTA titration of a solution of the calcium salts using Calcon Indicator. The end point is not affected by the polyion in solution. Moisture contents were determined by drying overnight at 105 °C and by drying at 40 °C under vacuum. The two procedures gave identical results.

Activities of the counterions were measured using a saturated calomel reference electrode with (a) a sodium responsive glass electrode (E.I.L. type), (b) a potassium responsive glass electrode (E.I.L. type), (c) a calcium responsive liquid ion exchange membrane type static electrode (Orion Inc. 92-20 Ca^{2+} electrode). The electrodes were calibrated with solutions of known concentration of the chloride salts. Values of a_+, the cation activities, in the calibrating solutions were calculated from the activity coefficients calculated on a KDF 9 English Electric Computer using the extended Debye–Huckel equation for aqueous solutions at 25 °C with the ion size parameters of Kielland.[15] The response of the electrodes was in good agreement with the Nernst equation. An E.I.L. Model 7050 millivoltmeter was used to measure the potential to ±0.1 mV for the calcium electrode and ±0.2 mV for the monovalent ion electrodes. Electrode response times of 15 min were allowed for both glass electrodes, followed by immediate checks on calibration using standard solutions of the chloride salt. Five-minute response times were allowed for the liquid membrane electrode, followed by calibration checks with calcium chloride standards. Diffusion from the orifice of the reference electrode was shown not to effect the results. Activity coefficients were determined for the cations, from the measured activity together with the concentration of cations calculated from the weight of polyelectrolyte in solution and its known equivalent weight. Where appropriate the concentra-

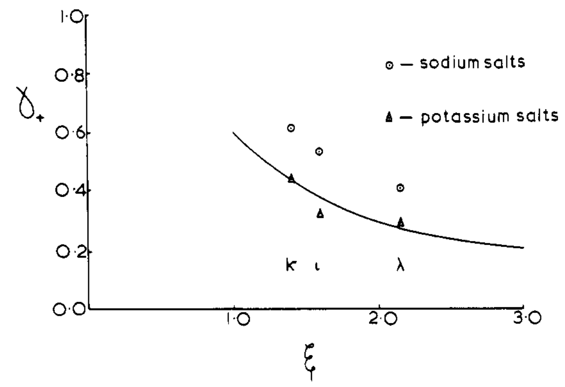

Figure 3. Activity coefficients of counterions in most dilute solution against linear charge parameter.

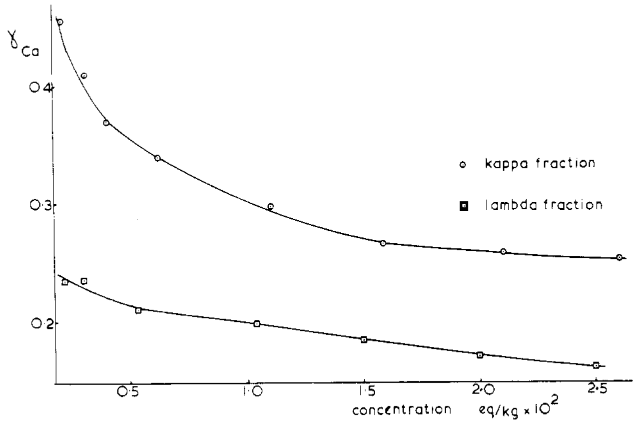

Figure 4. Activity coefficients of calcium counterions vs. concentration for calcium salts of κ- and λ-carrageenan.

Table II
Degree of Substitution (DS), Average Distance between Charges (*b*), and Linear Charge Parameter (ξ) for κ-, ι-, and λ-Carrageenans

	κ	ι	λ
DS	0.87	1	1.35
b, nm	0.510	0.445	0.330
ξ	1.40	1.60	2.16

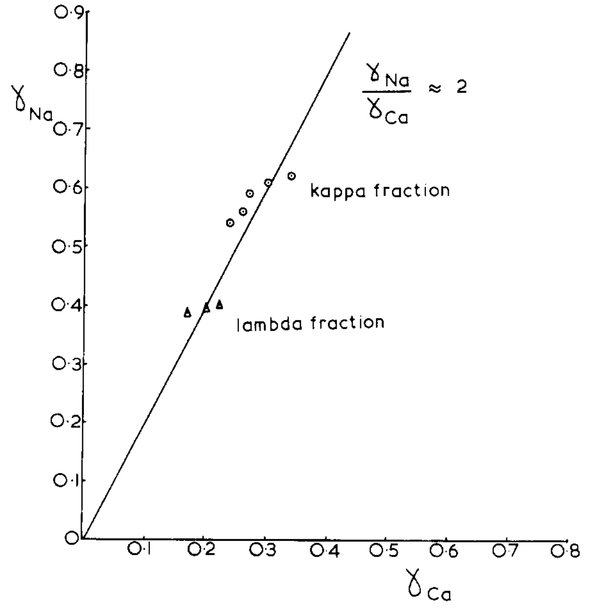

Figure 5. Activity coefficients of sodium counterions vs. activity coefficients of calcium counterions at identical concentrations for κ- and λ-fractions.

tion of simple electrolyte was added to the concentration of polyelectrolyte. Activity coefficients are given by the usual relationship.

$$\gamma_+ = a_+/m_+$$

Results

The results obtained for the activity coefficients, γ_+, of the univalent ions in pure polyelectrolyte solutions show that whereas the sodium salts of κ- and λ-carrageenan are comparable with the results previously reported,[5] the results for the potassium salts are different. One effect of this is to reverse the relative order of activity coefficients, so that now $\gamma_{Na^+} > \gamma_{K^+}$. Although this represents a difference from the earlier work on carrageenans,[5] it does accord with results found for other sulfated polysaccharides.[6,7] Thus the activity coefficients, γ_+, of the monovalent ions in pure polyelectrolyte solution have magnitudes greater for the sodium ion than the potassium ion, when comparing like fractions, Figures 1 and 2. The activity coefficient is observed to increase with dilution for the κ fraction but is relatively constant with concentration for the ι and λ fractions, in both univalent ion forms. The experimental values measured for the activity coefficient in the most dilute solution of each carrageenan fraction are plotted in Figure 3 against the appropriate linear charge parameter, ξ, calculated from

$$\xi = e^2/\epsilon kTb \qquad (1)$$

with e = protonic charge, ϵ = the dielectric constant of pure water, k = Boltzmann's constant, T = the absolute temperature, and b = average distance between charges. The value of b was obtained from measurement of molecular models using the degree of substitution data and a mean value of 0.445 nm for the length of a sugar unit in a carrageenan molecule in its most extended form. The values of ξ obtained were 1.40 (κ), 1.60 (ι), and 2.16 (λ). Only the value for the κ fraction varied greatly from that for the idealized repeating unit (one sulfate per disaccharide residue). κ-Carrageenan is known to have a certain proportion of 2- and 2,6-sulfated galactose which would cause a higher degree of substitution.

The theoretical limiting value of the activity coefficient is given by the solid line when applying Manning's treatment as given by eq 2 for univalent cations,

$$\gamma_+ = e^{1/2}/|z|\xi \qquad (2)$$

where $|z|$ is the magnitude of the charge on the counterion. Figure 3 shows that better agreement with the theoretical value is obtained for the potassium salts. Sodium salts give values in excess of the theoretical value according to eq 2.

It is seen in Figure 4 that calcium κ-carrageenan shows an increase in the value of the calcium ion activity coefficient with dilution, while calcium λ-carrageenan shows relative constancy of the activity coefficient with concentration. This is similar to the univalent ion cases.

For the univalent ions sodium and potassium, the values of γ_+ are not independent of ion size. Thus a comparison of activity coefficients of divalent and univalent ions may only be valid for ions of similar size. Therefore the calcium ion is

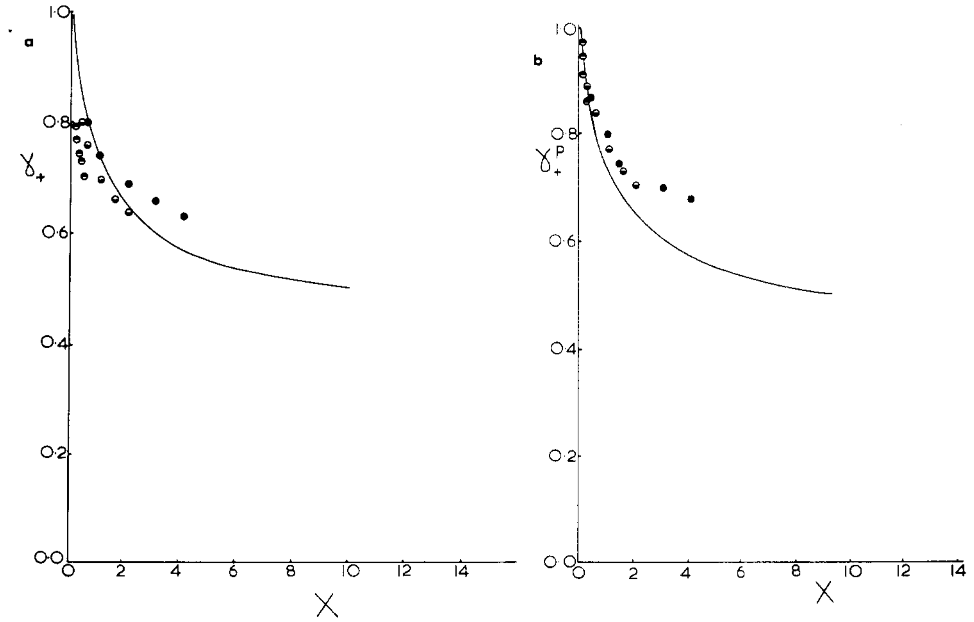

Figure 6. (a) Activity coefficient of common cation in κ-carrageenan/simple electrolyte mixture, uncorrected for small ion–small ion interactions. Comparison with theoretical curve according to eq 3. NaCl: (●) 5×10^{-3} m: (◒) 1×10^{-2} m; (◓) 5×10^{-2} m. (b) Activity coefficient of common cation in κ-carrageenan/simple electrolyte mixture, with values corrected for small ion–small ion interactions. Same symbols as for (a).

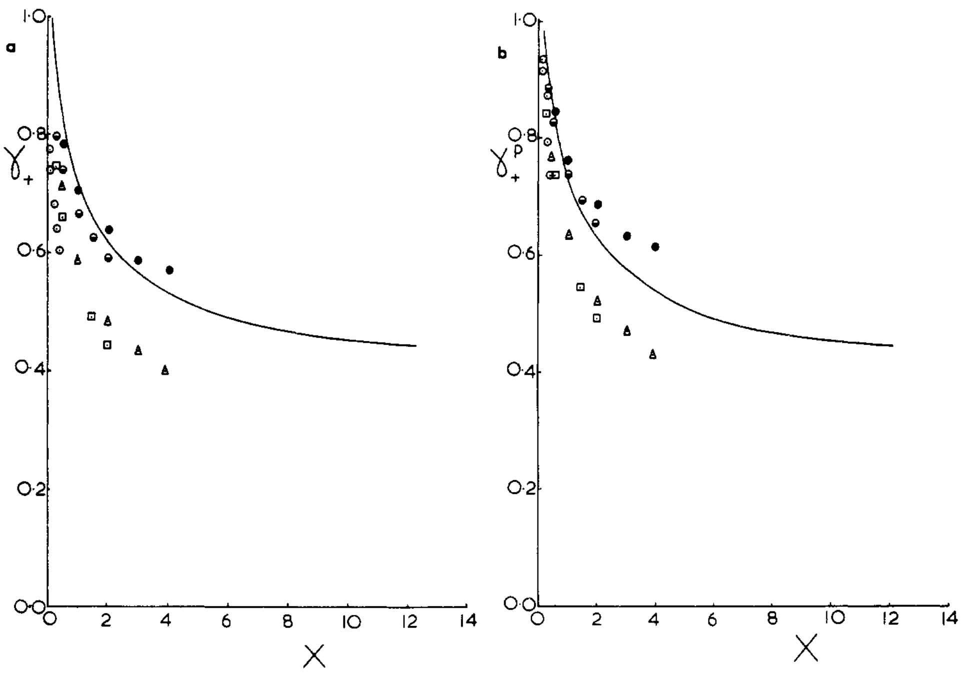

Figure 7. (a) Activity coefficient of common cation in ι-carrageenan/simple electrolyte mixture, uncorrected for small ion–small ion interactions. Comparison with theoretical curve according to eq 3. NaCl: (●) 5 × 10^{-3} m; (◒) 1 × 10^{-2} m. KCl: (△) 5 × 10^{-3} m; (⊡) 1 × 10^{-2} m; (⊙) 5 × 10^{-2} m. (b) Activity coefficient of common cation in ι-carrageenan/simple electrolyte mixture, corrected for small ion interactions. Same symbols as for (a).

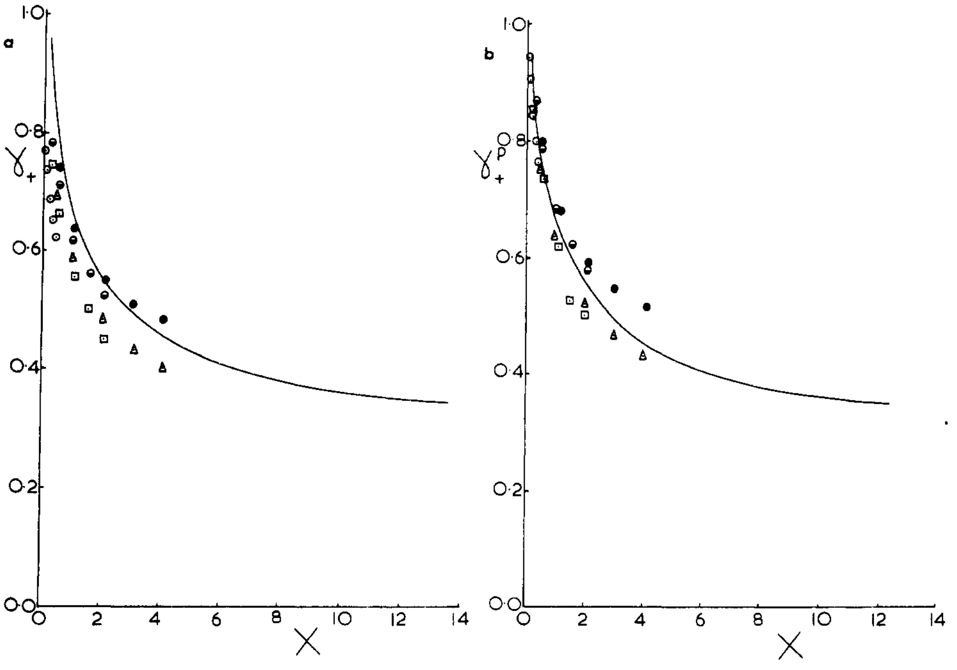

Figure 8. (a) Activity coefficient of common cation in λ-carrageenan/simple electrolyte mixture, uncorrected for small ion–small ion interactions. Comparison with theoretical curve according to eq 3. NaCl: (●) 5 × 10^{-3} m; (◒) 1 × 10^{-2} m. KCl: (△) 5 × 10^{-3} m; (⊡) 1 × 10^{-2} m; (⊙) 5 × 10^{-2} m. (b) Activity coefficient of common cation in λ-carrageenan/simple electrolyte mixture, corrected for small ion–small ion interactions. Same symbols as for (b).

compared with the sodium ion which is of similar though not identical hydrated ion size.[15] The activity coefficient of the sodium salt is plotted against the activity coefficient of the calcium salt at the same equivalent concentration over a range of concentrations for both λ and κ fractions, as is shown in Figure 5. This shows that the sodium ion has an activity coefficient almost twice that of the calcium ion at a particular concentration in a particular fraction, in good agreement with eq 2.

Manning gives an expression for single counterion activity coefficients of univalent ions in a polyelectrolyte plus added salt system for $\xi > 1$,

$$\gamma_+ = (\xi^{-1}X + 1)(X + 1)\exp\frac{-\frac{1}{2}\xi^{-1}X}{(\xi^{-1}X + 2)}$$

where $X = n_e/n_s$, the ratio of the number of equivalents of polyelectrolyte to the number of equivalents of simple electrolyte in unit volume of solution. Figures 6a–8a show that solutions most dilute in added salt (5 × 10^{-3} M) demonstrate the best correspondence between theory and practice. The correspondence becomes less satisfactory as the concentration of simple salt increases. This may be attributed to neglect of mutual interaction between ions of the simple electrolyte,[2] so that the activity of these ions is overestimated. An empirical correction of mean activity coefficients has been proposed[16] in which the mean activity coefficient of the ions in the pure simple electrolyte solution is taken as a measure of their mutual interaction in the presence of polyelectrolyte. If a similar correction is applied to the single ion activity coefficients this may be written in the form

$$\ln \gamma_+ = \ln \gamma_+{}^{\mathrm{p}} + \ln \gamma_+{}^{\mathrm{c}}$$

where γ_+ is the single ion activity coefficient of the cation determined experimentally, $\gamma_+{}^{\mathrm{p}}$ is the single ion activity coefficient calculated according to Manning, and $\gamma_+{}^{\mathrm{c}}$ is the single ion activity coefficient of the cation in the absence of polyelectrolyte. At low concentrations $\gamma_+{}^{\mathrm{c}} \rightarrow 1$ and $\gamma_+ = \gamma_+{}^{\mathrm{p}}$ in agreement with Figures 6a–8a. The corrected activity coefficients are plotted in Figures 6b–8b and show good agreement with the values calculated from Manning's theory. The value of the empirical correction is that it allows calculation of single ion activity coefficients over a wider range of concentration. The activity coefficient of the sodium salt plus added sodium chloride remains higher than the potassium salt plus added potassium chloride for the ι and λ fractions. Measurements were not carried out on κ-carrageenan plus potassium chloride because of the tendency of κ-carrageenan to gel in the presence of excess potassium ions.

Discussion

We observe in pure polyelectrolyte solution lower activity coefficients, which we can reasonably ascribe to a greater degree of ion binding, for the potassium salts compared to the sodium salts of the three carrageenan fractions. This is in accord with the hypothesis[17] that the interaction of the sulfate ester group with the cation is less than the interactions of the water of hydration with the cation. Consequently it is energetically unfavorable for the sulfate ester group to displace water from around a sodium or potassium cation. The results obtained using ultrasonic relaxation techniques to study the binding process of sulfated polyelectrolytes,[18] and from an examination of the ion exchange properties of sulfated cellulosic polyanions,[19] leads to the general conclusion that condensation occurs between hydrated ions, the smallest hydrated ion being bound most strongly. Potassium has a smaller hydrated ion size than sodium and hence is bound more strongly. Conversely carboxylate and phosphate groups interact more strongly than water with the cation and therefore displace hydration water from the cation. Hence the smallest crystallographic ion binds most strongly. Sodium has a smaller crystallographic radius than potassium and hence is bound more strongly. This explains the often observed change in affinity sequence on changing from a sulfate polyanion to a carboxylate or phosphate polyanion. Both Satake[6] and Noguchi[7] have observed this affinity sequence for potassium and sodium binding to dextran sulfates.

We conclude that agreement between experimental values of γ_+ and values of γ_+ calculated according to Manning's equations can be obtained in dilute solution. In the presence of added salt the range of agreement may be improved by an empirical correction for interaction between the mobile ions. The values of single ion activity coefficients also show a dependence on hydrated ion size in accord with reported sequences of cation binding to sulfated polyanions.

Acknowledgment. We gratefully acknowledge the financial support provided by Dari-Tech Company, Atlanta, Ga.

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