Interaction of Sodium and Potassium Ions with κ- and λ-Carrageenan in Aqueous Solutions with and without Added Salt

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ABSTRACT: The interactions of small ions with the sodium and potassium salts of κ- and λ-carrageenan were studied by measuring the counterion and coion activity coefficients in aqueous solutions of the polyelectrolytes with and without an added simple electrolyte. In solutions without added salt, the counterion activity coefficients for the λ forms were relatively constant with varying concentration, while for the κ forms they increased with dilution. The values for the sodium carrageenans were smaller than for the corresponding potassium salts, and were smaller for the λ form than for the κ form when the counterions were the same. These results indicated a greater amount of counterion binding for the λ-carrageenans, and that more sodium than potassium was bound. For solutions containing an added simple electrolyte, counterion activity coefficients were again lower for the λ-carrageenans. Counterion activity coefficients decreased with increasing polyelectrolyte concentration at constant simple salt concentration and decreased with decreasing salt concentration at constant polymer concentration. The additivity rule was best obeyed when the ratio of simple salt to polyelectrolyte concentration was high or low and the greatest deviation was evidenced when the salt and polyelectrolyte concentrations were approximately equal. Coion activity coefficients were slightly lower than those for the pure simple salt solutions and followed the same general trends as the counterion activity coefficients.

The interactions of small ions with polyelectrolytes has received much attention in recent years. Particular attention has been given to thermodynamic measurements.[2-10] The established concept of ion binding indicates that charged polyions are capable of binding simple ions, *i.e.*, a portion of the counterions in the solution is associated in some manner with the macroions.[4,5,11-15]

While the literature is replete with studies on small ion binding to polyions, relatively little attention has been given to the interaction of small ions with ionic polysaccharides. Investigations with salts of carboxymethylcellulose,[16,17] algin,[16,18] heparin,[7] and diethylaminodextran hydrochloride[6] have been reported. Dialysis equilibrium studies with salts of carrageenan have shown that there is no difference in the polyion interaction with Na^+ and K^+ ions.[19]

In our investigations of the solution properties of ionic polysaccharides, the interaction of Na^+ and K^+ ions with the Na and K salts of κ- and λ-carrageenan in aqueous media, with and without added simple electrolyte, have been studied by a potentiometric technique using cation-sensitive glass electrodes. Carrageenan is a hydrocolloid obtained from red marine algae. Two main components have been isolated: the one termed κ-carrageenan is precipitated from the supernatant by addition of alcohol.[20] κ-Carrageenan is predominantly a coploymer of D-galactose 4-sulfate residue joined by a β-1,4 linkage to a 3,6-anhydro-D-galactose residue, which, in turn, is joined by an α-1,3 link to another D-galactose 4-sulfate unit. κ-Carrageenan has been shown to be branched; evidence indicates that within each 25.2-Å period, a single side-chain residue of 3,6-anhydro-D-galactose is attached to the main chain through the 6-carbon of a sulfated D-galactose. λ-Carrageenan is a linear polymer and is predominantly composed of D-galactose 4-sulfate residues.[21]

The purpose of this paper was to compare experimentally the interactions of Na^+ and K^+ ions with κ- and λ-carrageenan with and without varying concentrations of simple electrolytes. Since ionic polysaccharides are stiffer than vinyl-type polyelectrolytes and most others, they should be a better approximation for rodlike models than other types of polyelectrolytes. In a subsequent publication in this journal, the experimental results presented here will be applied to a theoretical rodlike model proposed recently.

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Experimental Section

Materials. Sodium and potassium salts of κ- and λ-carrageenan were prepared by and donated by Marine Colloids, Inc., Rockland, Maine. The carrageenan samples were derived from the red sea plant *Chondrus Crispus.* Flame photometry measurements indicated no contaminating cations, except for a trace of Ca^{2+}, *i.e.*, less than 0.5%. Equivalent weights of the polymer were obtained gravimetrically by ignition of a weighed sample to the corresponding sodium or potassium sulfate. The water content of the polymer samples were obtained by drying to constant weight in a vacuum oven at 40°. Each analytical procedure was repeated at least once.

Dried, reagent grade inorganic chemicals were used to prepare all solutions. Deionized, distilled water was employed. All solutions were used within 3 days of preparation.

Apparatus. Single ion activities were determined in a manner similar to that described by Ise, *et al.*[22] Activities of sodium ion were determined with a Corning NAS 11-18 No. 476210 sodium-selective glass electrode. Potassium ion activities were determined with a Corning potassium-selective glass electrode, which was a gift of the Corning Glass Works, Medford, Mass. A saturated calomel electrode was used as the reference electrode.

Chloride ion activities were measured by using a Beckman No. 39048 silver–silver chloride electrode, coated with AgCl and tested according to the specifications of the manufacturer. A saturated calomel electrode was used as the reference electrode.

The sample solutions contained the polyelectrolyte having the cation reversible to the electrode, or, polyelectrolyte plus added simple salt with the cation in common with that of the polyelectrolyte. The electrodes were preconditioned for at least 2 weeks in a 0.1 *m* solution of NaCl or KCl, until a constant emf was recorded. Before and after each emf determination on a sample solution, the cation and silver–silver chloride electrodes were calibrated by using the appropriate 0.1 *m* salt solution. Calibration curves for the pure NaCl or KCl solutions were also obtained using the above cells, by varying the concentration of the simple electrolyte.

All emf measurements were made with a Corning Model 12 pH meter, utilizing the millivolt scale. The input impedance of 10^{13} eliminated the possibility of polarization of the glass electrodes. All measurements were made in a constant-temperature oil bath at 25.00 ± 0.03°. Medium-size polyethylene beakers were used as cell vessels. The electrodes were supported in a rubber stopper tightly fitting into the top of a large beaker, into which the cell vessel was placed. A potential reading constant over a 10–15-min period was regarded as a reliable emf. Usually, it took about 5 min to obtain a stable potential for solutions with added salt, and 15 min for solutions of pure polyelectrolyte. As determined from at least duplicate measurements, the reproducibility of the data with solutions containing added salt was± 0.1 mV, corresponding to a maximum uncertainty of ±0.002 activity coefficient units. For solutions of pure polyelectrolyte, reproducibility of ±0.2 mV for Na^+ ion and ±0.4 mV for K^+ ion was obtained, corresponding to maximum uncertainties in activity coefficients of ±0.004 and ±0.008 units, respectively. The response of the electrodes was in excellent agreement with the theoretical Nernstian response of a 59.1 mV change per tenfold change in activity. Deviations greater than 0.5 mV were seldom obtained, indicating that the electrodes were reversible to the counterions.

In order to show that diffusion from the orifice of the calomel electrode did not affect the results of the activity measurements, a series of control experiments was carried out with pure NaCl and KCl solutions. Over the desired concentration range of electrolyte, the emf measurement was constant within 0.2 mV over a 24-hr period. If diffusion of KCl had occurred to any significant degree, it would have resulted in a change in the emf leading to subsequent errors in the calculation of activities and activity coefficients. Measurements were also carried out to determine if there were any pressure effects due to the tightly fitting stopper over the cell compartment. The same value of the emf was obtained when the measurements were made with a stoppered or an unstoppered system. The absence of measurable pressure effects was thus indicated.

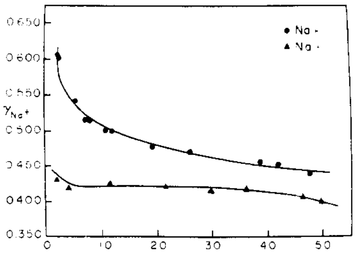

Figure 1. Counterion activity coefficients as a function of Na κ- and Na λ-carrageenan concentration in aqueous solutions.

Results and Discussion

Single Ion Activity Coefficients in Pure Polyelectrolyte Solutions. Figures 1 and 2 give the results of the measurements of the counterion activity coefficients for the pure polyelectrolyte systems, that is, in the absence of simple salt. Concentrations are expressed as equivalents per kilogram of solvent, or, analogously, in monomolal units, that is, the molality of repeating monomer units. This convention will be used throughout this discussion.

Turning attention to the sodium carrageenans, it is noted that the activity coefficients γ_{Na^+} for κ-carrageenan are higher than those for the λ form, the range being approximately 0.440–0.600 for κ-carrageenan, and 0.395–0.430 for λ-carrageenan over the concentration range of approximately 2×10^{-3} to 5×10^{-2} monomolal. Values of γ_{Na^+} for κ-carrageenan increase markedly at low polymer concentrations, while for λ-carrageenan, this increase is very slight, and the values are relatively constant throughout most of the concentration range. Inspection of the data for the potassium carrageenans reveals similar trends: γ_{K^+} for the κ-carrageenan is higher than for the λ form, and there is a constancy of γ_{K^+} throughout the concentration range for λ-carrageenan. On comparing the differences be-

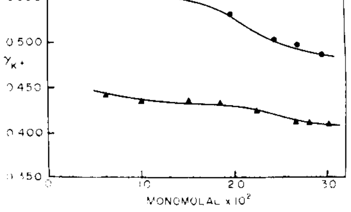

Figure 2. Counterion activity coefficients as a function of K κ-and K λ-carrageenan concentration in aqueous solutions.

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[22] T. Okubo, Y. Nishizaki, and N. Ise, *J. Phys. Chem.*, **69**, 3690 (1965).

tween the potassium and sodium salts, it can be seen that γ_{K^+} values are higher than γ_{Na^+} for both κ-carrageenan and the λ-carrageenan.

For solutions of polyelectrolytes without added salts, the degree of ion binding f has been operationally defined by[5]

$$f = (1 - \gamma_+) \qquad (1)$$

where γ_+ is the counterion activity coefficient. The data then are interpreted to mean that the degree of binding is greater when sodium is the counterion; that is, the degree of binding is greater for counterions with a smaller crystallographic radius. It is to be concluded then that the hydration layer of the counterion is being penetrated by the charged groups on the carrageenan anion. This is a trend which has already been noted for the binding of cations by phosphate groups of long-chain polyphosphates,[23] the strength of the binding, falling in the order $Li^+ > Na^+ > K^+$. A similar trend has been deduced from potentiometric titrations of polyacrylic[24] and poly(methacrylic acids)[25] with various hydroxides. Also, salts of poly(L-cysteate) indicate this trend.[26] However, it should be noted that the binding of alkali metal ions to poly(vinyl sulfonate) and poly(styrene sulfonate) appears to follow the reverse sequence.[12]

The difference in the results obtained for κ-carrageenan and λ-carrageenan can be explained on the basis of their structures.[27] The distances between charged groups on the κ chains are greater than on the λ chains, and their are fewer sulfated units on the κ-carrageenan molecule than on the λ-carrageenan molecule. This gives λ-carrageenan a charge density which is significantly higher than that for κ-carrageenan. The counterions come under the influence of the negative charge on the polymer chain to a greater extent with the λ form, and consequently the counterion activities are lower. As is illustrated in Figures 1 and 2, the greater rise in γ_{Na^+} and γ_{K^+} with the ϵ-carrageenan upon dilution as compared to λ-carrageenan is also due to the fact that the branched κ chains are stiffer than the linear λ chains;[27] they achieve a greater fraction of full extension with dilution and the concentration of negative charges on the chain become more diffuse.[27] One would predict that for the λ-carrageenans, further dilution would produce a rise in the counterion activity coefficients analogous to the behavior of the κ-carrageenans. (It was not possible to work with pure polyelectrolyte solutions of concentration less than 0.5×10^{-2} monomolal.) A decreased charge density on the surface of the polyion may be due to a more extended form of the polyion.[1] It has been suggested[28] that a conformational change caused by the dissociation of ionizable groups induces strong interactions between the pendant charged groups and water molecules. This may be responsible for a lower effective charge density on the polyion as its concentration is decreasing.

Single Ion Activity Coefficients for Polyelectrolyte Solutions with Added Simple Electrolyte. Values of the counterion activities a_+ and activity coefficients γ_+ are given in Table I for polyelectrolyte solutions containing an added simple salt having a cation in common with the polyelectrolyte. It is evident from Table I that counterion activity coefficients decrease with increasing polymer concentration at constant simple salt concentration, and decrease with a decrease in the salt concentration at a constant polymer concentration. This is fairly common polyelectrolyte behavior[13] that has been usually explained by considering the effect of shielding of the charges on the polyion by the ions of the simple salt. The higher values of γ_{Na^+} for the 0.09090 *m* added salt system is due to enhanced shielding, either of the ionic atmosphere surrounding the polyions, or of the charges on the polyions, caused by the high concentration of ions from the salt. This shielding effect greatly outweighs the effect of the increased ionic strength, which would be expected to lower the γ_{Na^+} values. When the concentration of salt is as high as 0.09090 *m*, the concentration of counterions originating from the added salt is much greater than those from the polymer. The shielding is so extensive that γ_{Na^+} values obtained for 0.09090 *m* salts in the presence of polyelectrolytes are only slightly below those for pure salt solutions of the given sodium ion concentration. As the concentration of salt is reduced the ionic strength decreases, but an increasing number of neighboring charged groups on the polyions become effective in strengthening the binding of cations by the polyion. Obviously, the decrease in the shielding is predominant over the effect of a lower ionic strength, and γ_{Na^+} values are extremely low. Shielding is most noticeable when the concentration of salt is much larger than that of the polyelectrolyte. Therefore, at a constant salt concentration, as the concentration of polyelectrolyte is decreased, there is a tremendous rise in the counterion activity coefficient values, and the curves gradually converge at very low polymer concentration.

The γ_{Na^+} values for the λ-carrageenan are lower than for the κ form, as they were for solutions without added salt. Differences in γ_{Na^+} for the two forms increase as the concentration of salt is decreased. The same is also true for the potassium carrageenans: γ_{K^+} for λ-carrageenan is lower than for κ-carrageenan. Because K^+ cause the gelation of κ-carrageenan, it was not possible to study solutions containing added salt at a concentration higher than 0.00800 *m*.

The additivity of cationic activities observed for polyelectrolyte–salt solutions has been investigated experimentally[5,10,18,29,30] and theoretically.[31,32] It can be expressed as

$$a_+^{\text{obsd}} = a_+^{\text{p}} + a_+^{\text{s}} \qquad (2)$$

where a_+^{p} is the counterion activity of cations from the polyelectrolyte in pure polyelectrolyte solution, and

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TABLE I

COUNTERION ACTIVITIES AND ACTIVITY COEFFICIENTS AS A FUNCTION OF POLYELECTROLYTE CONCENTRATION FOR AQUEOUS SOLUTIONS CONTAINING ADDED SIMPLE ELECTROLYTE AT 25°

m, NaCl	Monomolality × 10^2	a_+	$\gamma_\pm$	a_+^{calcd}	Δa_+
	Na κ-Carrageenan–NaCl				
0.00400	0.1049	0.00396	0.784		
	0.4106	0.00515	0.635	0.00603	17.0
	0.7000	0.00640	0.582	0.00738	15.2
	1.0970	0.00808	0.540	0.00921	13.9
	1.4820	0.00965	0.513	0.0109	12.9
	2.0040	0.0118	0.491	0.0132	12.1
	2.3920	0.0132	0.473	0.0149	13.2
0.00800	0.1366	0.00776	0.829		
	0.5838	0.00972	0.702	0.0104	7.0
	1.0470	0.0118	0.638	0.0125	5.9
	1.3320	0.0130	0.614	0.0138	6.1
	1.7340	0.0148	0.584	0.0156	5.4
	2.3250	0.0176	0.563	0.0182	3.4
0.04545	0.0589	0.0384	0.834		
	0.4952	0.0395	0.784	0.0405	2.5
	1.0240	0.0401	0.720	0.0430	7.2
	1.5010	0.0418	0.691	0.0451	7.9
	2.0790	0.0425	0.642	0.0477	12.2
	2.5400	0.0445	0.628	0.0497	11.6
0.09090	0.0940	0.0723	0.787		
	0.1254	0.0724	0.786		
	0.1874	0.0726	0.783		
	0.2498	0.0727	0.778	0.0725	1.1
	0.8503	0.0741	0.745	0.0763	2.9
	1.0300	0.0748	0.739	0.0772	3.2
	2.0610	0.0781	0.700	0.0817	4.6
	Na λ-Carrageenan–NaCl				
0.00400	0.1135	0.00396	0.771		
	0.4168	0.00493	0.604	0.00551	11.7
	0.6750	0.00578	0.538	0.00657	13.6
	1.0120	0.00675	0.478	0.00796	17.8
	1.4960	0.00856	0.451	0.00993	15.9
	2.0210	0.0105	0.434	0.0121	14.9
	2.5250	0.0123	0.420	0.0141	14.9
0.00800	0.1046	0.00780	0.862		
	0.2966	0.00820	0.748	0.00857	4.5
	0.5945	0.00905	0.649	0.00980	8.3
	0.7829	0.00953	0.602	0.0106	11.0
	1.2350	0.0111	0.545	0.0124	11.9
	1.8070	0.0136	0.522	0.0148	8.5
	2.5170	0.0172	0.521	0.0177	2.7
0.04545	0.2016	0.0386	0.813		
	0.4923	0.0392	0.778	0.0399	1.9
	1.0120	0.0398	0.716	0.0421	5.7
	1.4930	0.0410	0.679	0.0440	7.4
	1.9720	0.0426	0.654	0.0460	7.9
	2.5410	0.0445	0.628	0.0483	8.6
0.09090	0.1143	0.0722	0.784		
	0.1836	0.0727	0.784		
	0.2856	0.0714	0.762	0.0732	2.5
	1.0030	0.0743	0.736	0.0762	2.5
	1.5050	0.0757	0.714	0.0782	3.3
	2.5680	0.0786	0.674	0.0825	5.0
	K λ-Carrageenan–KCl				
0.00400	0.1693	0.00455	0.799		
	0.3416	0.00544	0.733		
	0.9594	0.00783	0.576	0.00793	12.7
	1.5540	0.0101	0.517	0.0105	3.7
	2.3500	0.0132	0.480	0.0137	4.0
	3.1640	0.0165	0.463		
0.00800	0.1343	0.00765	0.819		
	0.3239	0.00847	0.754		
	0.9498	0.0107	0.611	0.0114	6.9
	1.5800	0.0132	0.555	0.0142	7.2
	2.2110	0.0157	0.521	0.0167	6.6
	3.1800	0.0190	0.477		
0.04545	0.1433	0.0377	0.804		
	0.3535	0.0380	0.776		
	0.9178	0.0399	0.730	0.0414	3.8
	1.5840	0.0417	0.680	0.0443	6.2
	2.2820	0.0433	0.634	0.0471	8.8
	3.1580	0.0468	0.608		
0.09090	0.1592	0.0714	0.772		
	0.3546	0.0717	0.759		
	0.9743	0.0726	0.721	0.0749	3.1
	1.5620	0.0731	0.686	0.0774	5.8
	2.2130	0.0754	0.667	0.0801	6.2
	3.1250	0.0768	0.629		
	K κ-Carrageenan–KCl				
0.00400	0.1246	0.00450	0.858		
	0.2412	0.00533	0.831		
	0.6970	0.00783	0.714	0.00767[a]	−2.1
	1.2300	0.0100	0.613	0.0105	5.2
	1.8460	0.0123	0.548	0.0138	12.0
0.00800	0.0230	0.00800	0.867		
	0.2476	0.00846	0.808		
	0.7127	0.0107	0.707	0.0113[a]	5.6
	1.2470	0.0130	0.635	0.0142	8.9
	1.8170	0.0148	0.566	0.0172	16.0

[a] a_+^{p} obtained by extrapolation.

a_+^{s} is the counterion activity of the cations in simple salt solutions. The value of a_+^{s} is calculated from the known molal concentration of added salt and using extrathermodynamic assumptions.[5] The sum a_+^{p} and a_+^{s} equals a_+^{calcd}. To test the additivity rule given by eq 2, the per cent deviation from additivity can be defined as

$$\Delta a_+ = \frac{a_+^{\mathrm{calcd}} - a_+^{\mathrm{obsd}}}{a_+^{\mathrm{obsd}}} \times 100 \qquad (3)$$

The results presented in Table I appear to be in accord with those reported for other systems.[5] Values for Δa_+ were found to be lowest, *i.e.*, the additivity rule was best obeyed, when the ratio of simple salt to polyelectrolyte concentration was high. A few low values for Δa_+ were also found when the ratio of simple salt to polyelectrolyte concentration was low. However, in the sensitive region, the data indicate that the additivity rule holds to about 10% or worse.

Coion activities a_{Cl^-} and activity coefficients γ_{Cl^-} are given in Table II. The coion behavior is similar to that reported for other polyelectrolytes.[13] The γ_{Cl^-} values are only slightly affected by the presence of polyelectrolyte. They are a little lower when compared to the activity coefficients of pure salt solutions. This decrease is greater as the salt concentration decreases, and

Table II

Coion Activities and Activity Coefficients as a Function of Polyelectrolyte Concentration for Aqueous Solutions Containing Added Simple Electrolyte at 25°

m, NaCl	Monomolality × 10^2	a_{Cl^-}	γ_{Cl^-}
	Na λ-Carrageenan–NaCl		
0.00400	0.1135	0.00366	0.915
	0.3173	0.00359	0.898
	0.4168	0.00352	0.880
	0.6750	0.00350	0.875
	1.4960	0.00341	0.853
	2.0210	0.00334	0.835
	2.5250	0.00330	0.825
0.00800	0.0927	0.00726	0.907
	0.3185	0.00719	0.898
	0.4926	0.00706	0.883
	0.9113	0.00687	0.859
	1.4910	0.00684	0.855
	2.0120	0.00682	0.852
	2.5210	0.00676	0.845
0.04545	0.0518	0.0373	0.820
	0.1447	0.0370	0.814
	0.2308	0.0368	0.810
	0.4942	0.0368	0.810
	1.0170	0.0367	0.807
	1.5010	0.0367	0.807
	1.9830	0.0365	0.803
	2.5410	0.0364	0.801
0.09090	0.0516	0.0706	0.777
	0.1442	0.0705	0.775
	0.2300	0.0701	0.771
	1.0030	0.0690	0.759
	1.5050	0.690	0.759
	1.9630	0.0682	0.750
	K λ-Carrageenan–KCl		
0.00400	0.1703	0.00364	0.910
	0.3186	0.00362	0.905
	0.9496	0.00344	0.860
	1.5697	0.00338	0.845
	2.1830	0.00335	0.838
0.00800	0.1614	0.00723	0.904
	0.3104	0.00715	0.894
	0.9609	0.00706	0.883
m, MaCl	Monomolality × 10^2	a_{Cl^-}	a_{Cl^-}
	1.5890	0.00687	0.859
	2.2660	0.00682	0.853
	2.8310	0.00670	0.838
0.04545	0.1639	0.0374	0.823
	0.3040	0.0373	0.821
	0.9156	0.0372	0.818
	1.6040	0.0367	0.807
	2.3540	0.0365	0.803
	3.1870	0.0365	0.803
0.09090	0.2892	0.0700	0.770
	0.8521	0.0700	0.770
	1.4870	0.0697	0.767
	2.0270	0.0694	0.763
	2.9920	0.0694	0.763
	Na κ-Carrageenan–NaCl		
0.00800	0.0993	0.00723	0.903
	0.1384	0.00717	0.896
	0.2768	0.00713	0.891
	0.9049	0.00690	0.862
	1.4980	0.00674	0.842
	2.0150	0.00671	0.839
	2.5040	0.00669	0.836
0.04545	0.0943	0.0371	0.816
	0.1880	0.0371	0.816
	0.3218	0.0370	0.814
	0.4952	0.0368	0.810
	1.0240	0.0364	0.801
	1.5010	0.0363	0.799
	2.0790	0.0360	0.792
	2.5400	0.0360	0.792
0.09090	0.0629	0.0703	0.773
	0.1272	0.0701	0.771
	0.3218	0.0699	0.769
	0.5038	0.0698	0.768
	1.0540	0.0693	0.762
	1.5090	0.0693	0.762
	2.0270	0.0690	0.759
	2.5260	0.0690	0.759

as the polymer concentration increases, but it not of the order of magnitude of the decrease in counterion activity coefficients.

When the concentration of the bound counterions is high, and when there is sufficient shielding by the small ions, the repulsion of the coions by the polyions of the same charge is reduced. Therefore, at high salt concentrations, γ_{Cl^-} values are practically unaffected by the polyelectrolytes. As the concentration of salt is decreased, the relative lowering of γ_{Cl^-} increases. If the binding of the counterions by the polyions is imagined to be insignificant, the repulsion of the byions by the polyions would have the effect of raising γ_{Cl^-}; this is contrary to the experimental results. The decrease in γ_{Cl^-} can be attributed to the increased ionic strength as polyelectrolyte is added to the system. There are, of course, repulsions between the negatively charged chloride ions and the "free" fixed charges on the polyions, but the net effect is a lowering of γ_{Cl^-} as the effect of the increased ionic strength overrides the repulsive effects. At the lowest concentration of added salt, γ_{Cl^-} values for the potassium carrageenans are higher than for the sodium carrageenans. This is a consequence of the higher values of γ_+ obtained with the potassium salts and greater repulsions between negative charges on the polyion and the mobile chloride ions.

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