ance even if X-rays indicate that they do exist. The opposite is, of course, also possible.

Finally, it should be stressed that the theory has two conceptual errors built into it which, fortunately, act in opposite directions. Since the classical theory of elasticity is employed, it is mathematically quite feasible to obtain intercluster distances greater than the fully stretched length of a polymer chain; this is physically unreasonable. However, the tacit assumption is also made that chains are stretched between centers of clusters rather than between their surfaces. Since the latter possibility is much more likely, intercluster distances may well be greater than fully stretched chains without loss of physical reasonableness.

Symbols Used

d	distance between multiplets in cluster
e	electron charge
f	force needed to keep polymer chain at end-to-end distance h
h	end-to-end distance of polymer chain
$\overline{h^2}$	mean square end-to-end distance of polymer chain
$\overline{h_0^2}$	mean square end-to-end distance of freely jointed chain
K	dielectric constant of polymer
k	Boltzmann's constant
k'	($= W'/W$), dimensionless geometry-dependent factor giving the magnitude of the electrostatic energy released per ion pair in cluster formation.
l	length of repeat unit (1.54 Å for C–C bond)
M_c	average molecular weight of chain between ionic groups
M_0	molecular weight of repeat unit
N_{Av}	Avogadro's number
n	average number of ion pairs in cluster
n_0	average number of ion pairs in multiplet
r	distance between centers of charge in ion pair
r_m	radius of "amorphous" multiplet sphere
R	average distance between clusters
R_0	average distance between multiplets above cluster decomposition temperature T_c
s	number of ion pairs along one edge of a hypothetical cubic cluster
S_{ch}	area of hydrocarbon chain in contact with surface of "amorphous" multiplet
S_m	surface of amorphous multiplet of radius r_m
T_c	cluster decomposition temperature or cluster formation temperature
v_m	volume of multiplet of radius r_m
v_p	volume of ion pair
W	electrostatic work of ion-pair formation
W'	electrostatic work per ion pair in cluster collapse
W_{ch}	elastic work per chain in cluster formation
$1/(4\pi\epsilon_0)$	1 dyn cm^2/statcoulomb^2
ρ	density of polymer

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Interactions of Sodium and Potassium Ions with Sodium and Potassium Alginate in Aqueous Solution with and without Added Salt

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ABSTRACT: The interaction of sodium and potassium ions with sodium and potassium alginate were investigated by measuring the counterion activity coefficients in aqueous solutions of the polyelectrolytes with and without added simple electrolyte at 25°. In salt-free solutions, the counterion activity coefficients were found to increase with increasing dilution and the activity coefficients of potassium ions were higher than those of sodium ions throughout the concentration range. Counterion activity coefficients decreased with increasing polyelectrolyte concentration at constant simple salt concentration and decreased with decreasing salt concentration at a constant polyelectrolyte concentration. Deviations from the additivity rule were most pronounced when the salt and polymer concentrations were approximately equal. Good agreement was obtained when Manning's line-charge polyelectrolyte model was compared with the experimental results for the lowest simple salt concentration.

A previous publication[2] was devoted to an experimental study of the interactions of Na$^+$ and K$^+$ ions with κ-carrageenan and λ-carrageenan in aqueous solutions with and without added simple salt. Cation activity coefficients were determined using ion-selective glass electrodes. In the present paper, results of similar experiments are reported for the Na and K salts of alginic acid. The alginic acid used in this study was derived from *Macrocystes pyrifera*, a giant kelp which is extensively found in the coastal waters off the western United States. Structural investigations[3,4] have shown that alginic acid is a linear polymer of D-mannuronic

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(1) Taken from a portion of the Ph.D. thesis of T. J. P., Seton Hall University, 1968.

(2) T. Podlas and P. Ander, *Macromolecules*, **2**, 432 (1969).

(3) R. L. Whistler and W. M. Corbett in "The Carbohydrates, Chemistry, Biochemistry, Physiology," W. Pigman, Ed., Academic Press, New York, N. Y., 1957, Chapter 12.

(4) E. T. Davidson, "Carbohydrate Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1967.

acid units and its epimer, L-guluronic acid, linked by β-1,4 bonds. The structure of alginic acid is known with more certainty than those of κ-carrageenan and λ-carrageenan, and it was thought that successful application of experimental results to polyelectrolyte theory might be more readily attained.

Experimental Section

Sodium and potassium alginates were donated by the Kelco Company, Clark, N. J. Flame photometry measurements showed evidence of a trace of Ca^{2+}, less than 0.5%, but no other contaminating cations could be detected. Equivalent weights and water contents of the polymers were determined as was previously described.[2]

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

The apparatus and experimental methods for determining single ion activities have been described previously.[2] All measurements were performed at 25°.

Results and Discussion

Single Ion Activity Coefficients in Pure Aqueous Polyelectrolyte Solution. Figure 1 gives the results of the measurements of counterion activity coefficients as a function of sodium alginate and potassium alginate concentration. Concentrations of polyelectrolyte are expressed throughout this discussion as equivalents per kilogram of solvent. For both polyelectrolytes, the values of the counterion activity coefficients, γ_+, increased with increasing dilution. Also, γ_{K^+} is higher than γ_{Na^+} throughout the concentration range.

To estimate the amount of ion binding for polyelectrolyte solutions without added salt, eq 1 has been used,[2,5] where f is operationally defined as the degree of

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

ion binding. From eq 1 and Figure 1, it is evident that the degree of ionic binding is greater when Na^+ is the counterion as compared to K^+, *i.e.*, the binding is greater when crystallographic ion radius is smaller. The same order of binding was obtained for the sodium carrageenan and potassium carrageenan.[2] Apparently, the hydration layer of the counterions is being penetrated by the carboxyl groups on the alginate polyions; similar conclusions were made concerning the sulfate groups on the carrageenan polyions.

Manning[6] recently derived laws valid for dilute solutions of polyelectrolyte employing an infinitely thin line charge as the model for the real polyelectrolyte chain. For a salt-free polyelectrolyte solution, Manning's model gives

$$\gamma_+ = e^{-1/2\xi^{-1}} = (2.718)^{-1/2\xi^{-1}} \qquad \xi > 1 \qquad (2)$$

where the charge density parameter $\xi = e^2/\epsilon kTb$, with e the protonic charge, ϵ the dielectric constant of pure solvent, k the Boltzmann constant, T the absolute temperature, and b the distance between charges. For water at 25°, the value of ξ is $7.135b^{-1}$, where b is in ångström units. Using the reported value[7] of $b = 5.0$ Å for sodium alginate, $\xi = 1.427$ and the theoretical value of γ_+ for alginate salts obtained from eq 2 is 0.43. At the lowest concentration of sodium alginate (1.2040×10^{-2} monomolal) and of potassium alginate (3.943×10^{-3} monomolal), experimental values of $\gamma_{Na^+} = 0.51$ and $\gamma_{K^+} = 0.52$, respectively, were obtained. The discrepancy between the experimental and theoretical values for γ_+ may be due to the breakdown of local rodlike structure, as was suggested by Manning.[6] However, it should be noted that the previously reported results[2] for γ_+, for Na and K salts of λ-carrageenan ($\xi = 1.50$) and of κ-carrageenan ($\xi = 1.05$) agree with the theoretical values calculated from eq 2 to better than 10% for the lowest concentration of polyelectrolyte.

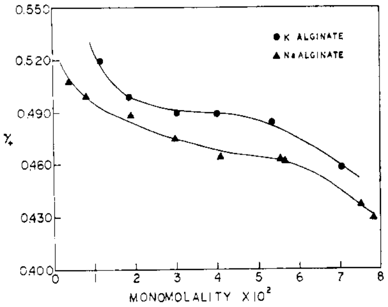

Figure 1. Counterion activity coefficients as a function of sodium alginate and potassium alginate in aqueous solutions at 25°.

Single Ion Activity Coefficients for Polyelectrolyte Solutions with Simple Electrolyte. The data in Table I illustrate the γ_{Na^+} and γ_{K^+} trends as a function of polyelectrolyte concentration at several concentrations of simple salt. Values of γ_{Na^+} are generally lower than those of γ_{K^+}. This behavior was also noted for carrageenan solutions,[2] and has been found to be a common phenomena with polyelectrolyte solutions. It is evident from Table I that the counterion activity coefficients decrease with increasing polymer concentration at constant simple salt concentration, and decrease with a decrease in the simple salt concentration at a constant polymer concentration. This has been found to be fairly common polyelectrolyte behavior and has been usually explained by considering the effect of shielding of the charges on the polyion by the ions of the simple salt.[2,8,9]

The empirical additivity rule for cationic activities in polyelectrolyte-salt solutions is

$$a_+^{\text{obsd}} = a_+^{\text{p}} + a_+^{\text{s}} \qquad (3)$$

where a_+^{p} is the counterion activity for cations of the polyelectrolyte in pure polyelectrolyte solution, and a_+^{s} is the counterion activity of the cations in simple salt solutions. To test the additivity rule given by eq 3, the per cent deviation from additivity can be defined as[2,5]

$$\Delta a_+ = \frac{a_+^{\text{calcd}} - a_+^{\text{obsd}}}{a_+^{\text{obsd}}}(100) \qquad (4)$$

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[5] J. W. Lyons and L. Kotin, *J. Amer. Chem. Soc.*, **87**, 1670 (1965).

[6] G. S. Manning, *J. Chem. Phys.*, **51**, 924 (1969).

[7] K. J. Palmer and M. B. Hartzog, *J. Amer. Chem. Soc.*, **67**, 1865 (1969).

[8] S. A. Rice and M. Nagasawa, "Polyelectrolyte Solutions," Academic Press, New York, N. Y., 1961.

[9] H. Morawetz, "Macromolecules in Solution," Interscience Publishers, New York, N. Y., 1965, Chapters 6–9.

TABLE I

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

Salt, *m*	Monomolality × 10^2	a_+	γ_+	a_+^{calcd}	Δa_+
	Sodium Alginate-NaCl				
0.00400	0.3805	0.00560	0.717	0.00568	1.5
	0.8596	0.00800	0.635	0.00804	0.5
	1.8310	0.0126	0.565	0.0126	0.3
	2.7900	0.0170	0.533	0.0171	0.3
	4.1690	0.0227	0.497	0.0233	2.6
	5.7490	0.0296	0.481	0.0303	2.4
	7.7240	0.0366	0.450	0.0377	2.9
0.00800	0.4127	0.00937	0.773	0.00940	0.3
	0.7126	0.0107	0.707	0.01088	1.7
	1.9630	0.0167	0.604	0.0168	0.7
	2.8630	0.0206	0.562	0.0209	1.6
	4.2270	0.0264	0.525	0.0271	2.6
	5.7080	0.0326	0.501	0.0337	3.4
	7.8410	0.0407	0.471	0.0416	2.1
0.04545	0.3797	0.0390	0.792	0.0380	2.1
	0.8293	0.0410	0.763	0.0420	2.5
	1.9170	0.0445	0.689	0.0472	6.0
	2.7510	0.0478	0.655	0.0510	6.7
	4.0010	0.0520	0.608	0.0567	9.0
	5.7070	0.0574	0.560	0.0643	12.0
	7.6200	0.0630	0.518	0.0714	13.3
0.09090	0.2254	0.0725	0.778		
	0.5753	0.0738	0.764	0.0749	1.5
	1.6950	0.0774	0.718	0.0803	3.7
	2.8010	0.0809	0.680	0.0854	5.6
	3.7610	0.0841	0.654	0.0897	6.7
	5.4020	0.0894	0.617	0.0971	8.6
	7.9390	0.0968	0.568	0.1065	10.0
	Potassium Alginate-KCl				
0.00400	0.2003	0.00482	0.083		
	0.6407	0.00700	0.673		
	1.5490	0.0116	0.595	0.0116	0.0
	2.5010	0.0163	0.562	0.0161	−1.2
	3.8380	0.0214	0.505	0.0226	5.6
	6.5890	0.0332	0.476	0.0343	3.3
0.00800	0.2034	0.00805	0.802		
	0.5712	0.00980	0.715		
	1.5960	0.0151	0.630	0.0154	1.7
	2.5010	0.0192	0.582	0.0197	2.6
	5.0830	0.0295	0.501	0.0320	8.5
	6.5880	0.0365	0.494	0.0379	3.8
0.04545	0.2173	0.0390	0.819		
	0.6227	0.0407	0.788		
	1.5220	0.0442	0.728	0.0451	2.0
	2.5380	0.0478	0.675	0.0499	4.4
	3.6420	0.0527	0.644	0.0533	4.9
	4.9090	0.0567	0.600	0.0613	8.1
	6.5550	0.0622	0.560	0.0689	9.2
0.09090	0.1793	0.0725	0.782		
	0.7012	0.0757	0.773		
	1.5220	0.0777	0.732	0.0783	0.8
	2.7290	0.0814	0.689	0.0841	3.3
	3.6520	0.0845	0.663	0.0886	4.9
	4.9970	0.0881	0.625	0.0949	7.7
	6.6210	0.0919	0.585	0.1013	10.2

Lyons and Kotin[5] have concluded from an experimental investigation using several polyelectrolytes that the additivity rule for the counterion is not valid. The results presented in Table I indicate once again[2,5] that while the additivity rule is best obeyed when the ratio of salt to polyelectrolyte concentration is high, poorer agreement with additivity was obtained in the more sensitive region where the simple salt and polyelectrolyte concentrations are approximately equal. Manning[6] has recently shown from his model that the additivity rule for the mean activity coefficient is restricted to the condition of excess salt.

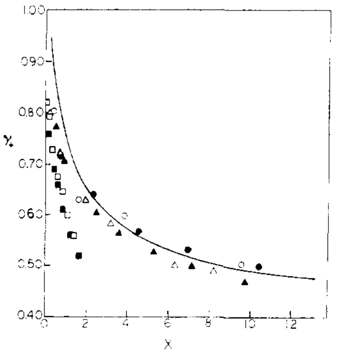

Figure 2. Comparison of the theoretical curve (solid line) for γ_+ calculated from eq 5 and the experimental points for sodium alginate in NaCl [●, 0.004 *M;* ▲, 0.008 ■; 0.04545 *m*] and potassium alginate in KCl [○, 0.004 *m;* △, 0.008 *m;* □, 0.04545 *m*].

To compare the measured values of the counterion activity coefficient with those calculated from Manning's theory, eq 45 in ref 6 was used, where $X = n_e/n_s$

$$\gamma_+ = (\xi^{-1}X + 1)(X + 1)^{-1} \times \exp[-{}^1\!/_2\xi^{-1}X/(\xi^{-1}X + 2)] \quad (5)$$

and n_e and n_s are the equivalents of the polyelectrolyte and simple salt, respectively, per kilogram of solvent and $\xi > 1$. The results are shown in Figure 2, where the solid line represents the theoretical results calculated from eq 5 and the points are the experimental values obtained for polyelectrolyte solution in different NaCl and KCl concentrations. It is evident from Figure 2 that the correlation between the experimental and theoretical values for γ_+ are excellent for the lowest concentrations of simple salt employed, *i.e.*, 0.004 and 0.008 *m*, irrespective of the counterion used. In accordance with the theory, the measured values of γ_+ are the same for fixed values of *X*. However, as the concentration of simple salt increases, the correlation between the theoretical and experimental results get progressively poorer. This is to be expected inasmuch as Manning's theory implies that the simple salt be so dilute that the ionic activity coefficients would be equal to unity were it not for the presence of the polyion.

Mean activity coefficients for the simple salts were not determined in this study because of experimental difficulty encountered in evaluating γ_{Cl^-}. Donnan equilibrium measurements[10] of several salts of alginic acid in aqueous salt solutions indicated that the mean activity coefficient of the simple salt was found to be independent of the polyelectrolyte concentration and of the simple salt concentration.

Manning's theory was applied to the experimental results[2] obtained for sodium and potassium λ-carrageenan

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(10) A. Katchalsky, R. E. Cooper, J. Upadhyay, and A. Wasserman, *J. Chem. Soc.*, 5198 (1961).

and κ-carrageenan in salt free and in aqueous NaCl and KCl solutions. Values of[2] b = 4.75 Å for λ-carrageenan and b = 6.8 Å for κ-carrageenan gives $\xi = 1.50$ and 1.05, respectively. From eq 2, theoretical values of γ_+ for γ_+ for λ-carrageenan and κ-carrageenan are 0.41 and 0.58, respectively. Comparing these theoretical values with the experimental ones obtained at the *lowest* concentration indicates good quantitative agreement. Values of γ_+ for sodium and potassium λ-carrageenan at 2.17×10^{-3} and 6.47×10^{-3} monomolal are 0.43 and 0.44, respectively. Values of γ_+ for sodium and potassium κ-carrageenan at 2.44×10^{-3} and 7.19×10^{-3} monomolal are 0.61 and 0.56, respectively.

In aqueous solutions of simple salt the linear λ form gave results more in accord with theory than the branched κ form, which should be expected. As was observed for the alginate system, better agreement between theory and experiment was obtained as the added salt concentration was lowered. Agreement was very poor in 0.04545 and 0.0909 *m* added salt. When 0.004 and 0.008 *m* added salts are employed, plots of γ_+ and γ_- *vs.* X indicate that the theoretical curves are above and below the experimental points for the counterions and coions, respectively. This is illustrated in Figure 3. These effects tend to cancel each other, so that good correlation results when $\gamma_\pm$ *vs.* $\sqrt{X}$ is plotted for λ-carrageenan in 0.004 and 0.008 *m* added salt. Also it is noted from Figure 3 that while $\gamma_{K^+} > \gamma_{Na^+}$ for all X values, they tend to approach one another as X goes to zero.

Critical evaluation of Manning's theory is premature at the present time inasmuch as more detailed investigations are needed on polyelectrolyte systems which are more in accord with the model. However, good correlation between theory and experiment is obtained for the trends in the concentration dependence of the single ion activity coefficients in dilute simple salt solutions.

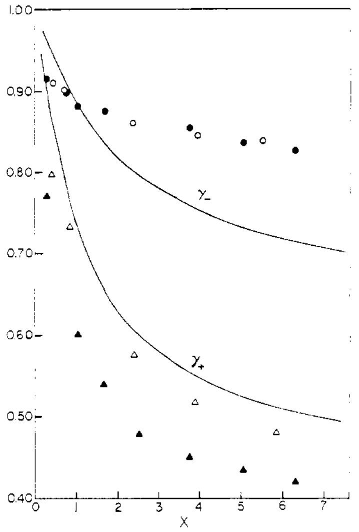

Figure 3. Comparison of the theoretical curves (solid lines) for γ_+ calculated from eq 5 and for γ_- calculated from eq 47 of ref 6 for sodium λ-carrageenan in 0.004 *m* NaCl (filled symbols) and potassium λ-potassium carrageenan in 0.004 *m* KCl (open symbols).

No provision is made in the theory for the different pendant charges of polyions or of counterions. The theory should be extended to include a "distance of closest approach" parameter so as to render the model more realistic.

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