(5) G. C. Berry and T. A. Orofino, *J. Chem. Phys.*, **40,** 1614 (1964).
(6) E. F. Casassa and G. C. Berry, *J. Polym. Sci., Part A-2,* **4,** 881 (1966).
(7) W. Burchard, *Macromolecules,* **10,** 919 (1977).
(8) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971, p 212.
(9) B. E. Eichinger, *Macromolecules,* **5,** 496 (1972).
(10) B. E. Eichinger, *Macromolecules,* **10,** 671 (1977).
(11) A. Ben-Israel and T. N. E. Greville, "Generalized Inverses: Theory and Applications", Wiley-Interscience, New York, N.Y., 1974.
(12) S. Aronowitz and B. E. Eichinger, *J. Math. Phys. (Cambridge, Mass.),* **16,** 1278 (1975).
(13) R. Pecora, *J. Chem. Phys.,* **43,** 1562 (1965).
(14) J. M. Schurr, *Crit. Rev. Biochem.,* **4,** 371 (1977).

Ultrasonic Studies on Monovalent and Divalent Cation Salts of Carrageenans in Aqueous Solution

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It has been demonstrated that activity coefficients and osmotic coefficients of polyelectrolytes are much lower than those of simple salts, in aqueous solution at equivalent concentrations. This phenomenon of ion binding or ion condensation has received a variety of treatments,[1–5] the most comprehensive recent treatment being that of Manning,[6] who showed that in solutions of polyelectrolytes with a linear charge parameter, ξ, greater than 1, a fraction of monovalent counterions $(1 - \xi^{-1})$ will condense on the polyion in order to reduce the charge parameter to an effective value of 1. In general, equilibrium studies of the factors affecting counterion condensation in polyelectrolytes have proved particularly valuable in the development of a fundamental understanding of bulk physical properties and biological functions. However, a complete understanding of the mechanistic details of such processes can only be gained through kinetic studies, which can be carried out on these systems using ultrasonic relaxation methods. We report here our preliminary measurements on some carrageenan salts, characterized[2] by values of $\xi > 1$.

Experimental Section

The carrageenan samples in the appropriate counterion salt forms were prepared and estimated as described previously.[2] Ultrasonic absorption was determined at 298 K by the resonance interferometric technique developed by Eggers.[7] The electronic system was a modified version of a standard sweep level measuring set produced by Wandel and Goltermann.[8] Before measurements were taken, solutions of carrageenans were clarified by briefly subjecting them to a vacuum, in order to remove air bubbles.

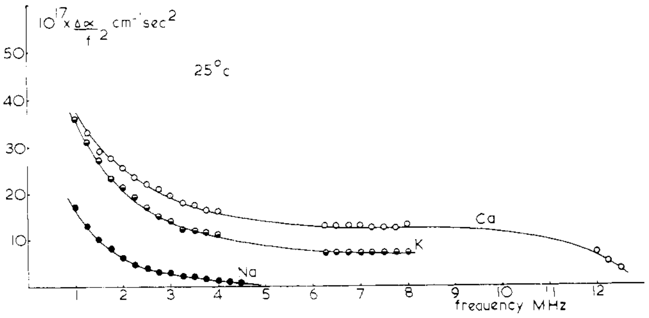

Figure 1. Plots of ultrasonic absorption ($\Delta\alpha/f^2$) vs. f for 0.04 N aqueous solutions of calcium, potassium, and sodium salts of κ-carrageenan.

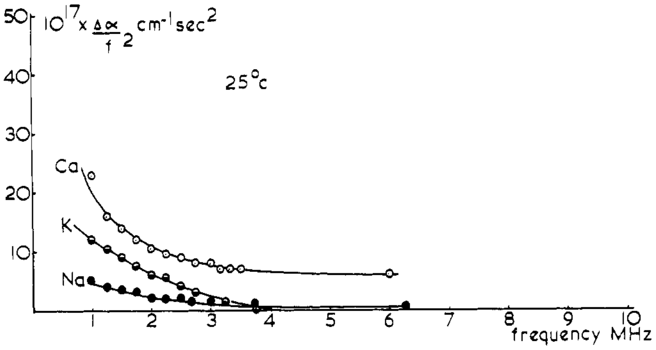

Figure 2. Plots of ultrasonic absorption ($\Delta\alpha/f^2$) vs. f for 0.04 N aqueous solutions of calcium, potassium, and salts of λ-carrageenan.

Results

In the use of the ultrasonic method to study the chemical relaxation of the very fast reactions, it is necessary to interpret macroscopic measurements in terms of the microscopic behavior of the systems being investigated. Previous work has shown that the relaxation spectra of polyelectrolytes are characterized by a distribution of relaxation times resulting from the perturbation of equilibria involving counterion condensation as well as fast processes associated with the polymer chain.[9] In an attempt to resolve the relaxation effects, it has been suggested[10] that the contribution to the excess sound absorption arising from counterion condensation equilibria, $\Delta\alpha$, in any particular salt of a polyanion, can be obtained from expression 1, f being ultrasonic frequency.

$$\frac{\Delta\alpha}{f^2} = \left(\frac{\alpha}{f^2}\right)_s - \left(\frac{\alpha}{f^2}\right)_t \qquad (1)$$

Where $(\alpha/f^2)_s$ is the measured sound absorption in a solution of a particular metal ion salt of the polyanion and $(\alpha/f^2)_t$ is the corresponding sound absorption measured in a solution having the same concentration of the tetramethylammonium salt of the polyanion. This equation is based on the assumptions that the volume changes associated with the counterion condensation process in the TMA salts are zero,[10] and that the other relaxation processes associated with the polymer chain are not affected by the counterion. The relaxation data for all the solutions have been determined on this basis.

The measurements were carried out over the frequency range 1–12 MHz. In all cases, $\Delta\alpha/f^2$ was found to decrease with increasing frequency as shown in Figures 1 and 2, indicating the presence of a relaxation. Due to the high viscosities of the solutions, concentrations were limited to 4×10^{-2} N. One consequence of being limited to such low concentrations of polyions is that the observed variations of $\Delta\alpha/f^2$ with frequency are extremely small. In addition, since $\Delta\alpha/f^2$ is apparently proportional to concentration, as shown in Figures 3 and 4, the effect becomes weaker as the concentration is lowered. In all cases, the observed relaxations are characterized by more than one relaxation time and the variation of $\Delta\alpha/f^2$ with frequency can be described by an equation[11] involving a distribution of relaxation times and which contains four adjustable parameters. However, as a result of our narrow frequency range and the limitations imposed by the low concentrations of polyions which result in a weak relaxation amplitude, we are not justified in using the detailed results obtained from the analysis of the data. However, for the purpose of the following discussion, several noteworthy features of the relaxation data are summarized below.

(i) For the two concentrations studied, $\Delta\alpha/f^2$ was found to be proportional to polyion concentration, as shown in Figures 3 and 4.

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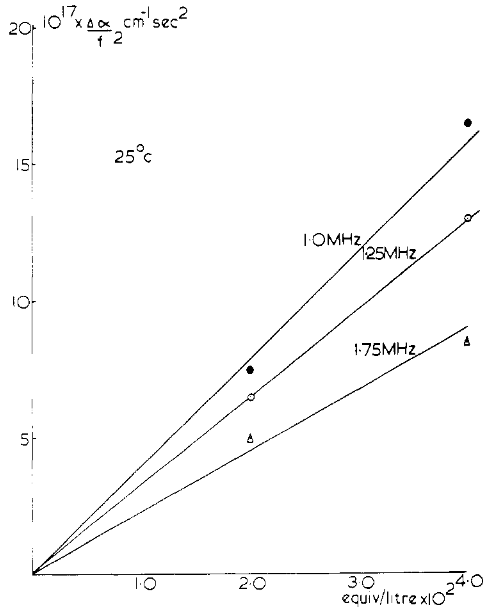

Figure 3. Variation of ultrasonic absorption ($\Delta\alpha/f^2$) at particular frequencies for sodium salts of κ-carrageenan as a function of polyanion concentration.

(ii) For all of the compounds studied there is a relaxation process centered at around 1 MHz.

(iii) The amplitude of the relaxation process depends on the nature of the counterion and polyelectrolyte.

(iv) For all of the compounds studied the values of $\Delta\alpha/f^2$ at the highest measured frequency are greater than zero.

Discussion

The results in Figures 3 and 4 are consistent with previously reported results for polyanion salts and similar to results obtained in investigation of ion-pair formation in aqueous solutions of divalent metal ion sulfates.[12] The interpretation of such results is that counterion condensation arises from monomolecular processes.[10] The low-frequency relaxations are all characterized by prominent inflection points in the $\Delta\alpha/f^2$ against frequency relaxation curves, at approximately 1 MHz. This implies that the kinetics of the process being perturbed by the sound wave at this frequency are independent of the counterion. On the basis of previous work,[10] we can reasonably assign this low-frequency phenomenon to the perturbation of the equilibrium associated with inner-sphere complex formation (contact ion pairs) where it has been shown that the relaxation frequency depends only slightly on the nature and valency of the counterion. Further evidence supporting this assignment is the apparent dependence of the amplitude of the relaxation process on the nature of the counterion. Indeed if we assume that the relaxation frequencies associated with the inner-sphere complex formation are reasonably constant for the different salts, then the magnitude $\Delta\alpha/f^2$ at this frequency is directly proportional to $(\Delta V^0)^2$, where ΔV^0 is the volume change associated with this process.[9,10] Thus we get an order of the volume change upon counterion condensation for both the κ and λ fractions, Ca > K > Na. The affinity sequence K > Na has also been observed for binding to dextran sulfate.[13] The interpretation in terms of the greater ease of replacement of the water of hydration in K^+(aq) compared with Na^+(aq) is consistent with our observation of a greater colume change. Since the relaxation frequency depends only little on the polyion nature for the low-frequency relaxational process,[10] it should also be valid to compare the values of $\Delta\alpha/f^2$ at the same low frequencies for λ and κ carrageenans (average separation between charged sites 0.33 and 0.51 nm, respectively) and make some inferences about the volume changes and the binding mechanism. It has been observed[14] that increase in the linear charge density of a polyanion causes an increase in the value of $\Delta\alpha/f^2$. In addition, the volume change brought about by release of electrostricted water depends not only on the intrinsic electrostriction of the charged group but also on the *minimum* distance between charges sites.[15] X-ray diffraction data[16] on oriented fibers of the calcium salt of ι-carrageenan, very similar in conformation to κ-carrageenan, showed sulfate groups, in pairs, surprisingly close together, in a double-helical conformation. In our solutions we can expect a high percentage of the κ-carrageenan to be in the double-helical conformation.[17] Cation interaction with κ-carrageenans in the double-helical state might therefore lead to greater loss of electrostricted water relative to the equivalent solutions of λ-carrageenan. This alone could result in the larger relative $\Delta\alpha/f^{2\prime}$ (and hence ΔV^0) values we see for the κ-carrageenan compared to corresponding λ-carrageenan solutions (Figures 1 and 2). Specific cation interactions with the double-helical residues of the carrageenans will lead to extensive loss of the cation hydration shell.[16] The greater interaction of the potassium counterion in the κ-carrageenan system, compared with the sodium counterion, is demonstrated by the formation of the so-called "tie points" or double helices, bringing about gellation of the polysaccharide.[18,19] We thus conclude that for λ-carrageenan, the indicated volume changes on cation binding $Ca^{2+} > K^+ > Na^+$ correlate well with the degree of ion binding data obtained from emf measurements,[2] with ion selective electrodes. This can be explained on the basis of the polarizability of the sulfate group and binding of a hydrated cation. The same order was found for the degree of ion binding of these cations to κ-carrageenan. While it would appear to be sufficient to account for this in terms of electrostatic binding of hydrated cations to give an order $Ca^{2+} > K^+ > Na^+$, site binding of cations to κ-carrageenan is inferred from the ultrasonic relaxation study. Site binding by κ-carrageenan might be expected to lead to a reversal of the order of degree of alkali metal ion binding observed for the fraction, with the smallest crystallographic ion binding most strongly to the carrageenan, as is the case with the carboxymethylcellulose in its interaction with alkali metal ions.[14,20] This would suggest an order $Ca^{2+} > Na^+ > K^+$. However, the specific ionic effects observed with K^+ and thus gelling polyanions, leading to extensive loss of

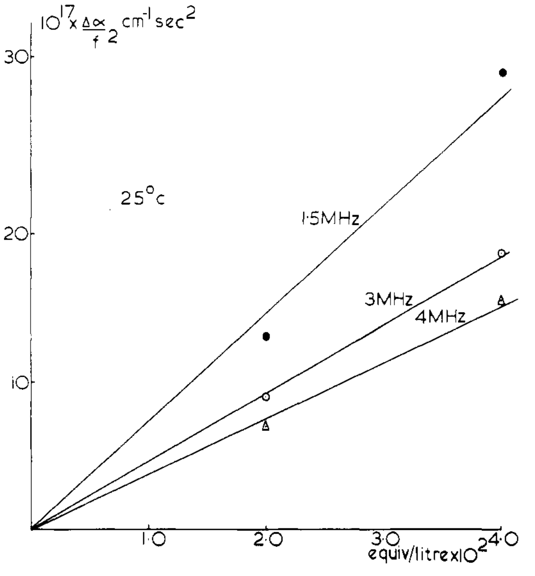

Figure 4. Variation of ultrasonic absorption ($\Delta\alpha/f^2$) at particular frequencies for calcium salts of κ-carrageenan as a function of concentration.

the cation hydration shell,[16] would account for the observed order $Ca^{2+} > K^+ > Na^+$. Further, Daoust and Hade,[21] in investigating the effect of cation size on heats of dilution of polystyrene sulfonate, found that the degree of *site* binding in that case was $Ca^{2+} > K^+ > Na^+$. We conclude site binding is a significant factor in counterion binding to κ-carrageenan but not with λ-carrageenan.

The observation that at the highest operating frequency $\Delta\alpha/f^2 \neq 0$ means that a further relaxation process occurs at even higher frequencies since, in the interpretation of eq 1, $\Delta\alpha/f^2$ should equal zero when all of the processes have relaxed. This further relaxation process has an extremely weak amplitude, indicating that more than one step occurs in the cation condensation phenomenon.

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References and Notes

(1) T. J. Podlas and P. Ander, *Macromolecules*, **3**, 154 (1970).
(2) G. Pass, G. O. Phillips, and D. J. Wedlock, *Macromolecules*, **10**, 197 (1977).
(3) R. Fernandez-Prini, E. Baumgartner, S. Libermann, and A. E. Lagos, *J. Phys. Chem.*, **73**, 1420 (1969).
(4) B. N. Preston, J. McK. Snowden, and K. T. Houghton, *Biopolymers*, **11**, 1645 (1972).
(5) J. D. Wells, *Proc. R. Soc. London, Ser. B*, **183**, 399 (1973).
(6) G. S. Manning, *J. Chem. Phys.*, **51**, 934 (1969).
(7) F. Eggers, *Acoustics*, **19**, 323 (1968).
(8) R. A. Pethrick and E. Wyn-Jones, *Ultrasonics*, **10**, 228 (1972).
(9) G. Atkinson, E. Baumgartner, and R. Fernandez-Prini, *J. Acoust. Soc. Am.*, **93**, 6436 (1971).
(10) R. Zana and C. Tondre, *Biophys. Chem.*, **1**, 367 (1974).
(11) R. A. Pethrick, *J. Macromol. Sci., Part C*, **9**, 91 (1973).
(12) M. Eigen and K. Tamm, *Electrochemistry*, **66**, 107 (1962).
(13) I. Satake, M. Fukuda, T. Ohta, K. Nakamura, N. Fujita, A. Yamauchi, and H. Kimizuka, *J. Polym. Sci., Polym. Phys. Ed.*, **10**, 2343 (1972).
(14) R. Zana, C. Tondre, M. Rinaudo, and M. Milas, *J. Chim. Phys. Phys.-Chim. Biol.*, **68**, 1258 (1971).
(15) C. Tondre and R. Zana, *J. Phys. Chem.*, **76**, 3451 (1972).
(16) S. Arnott and W. E. Scott, *J. Mol. Biol.*, **90**, 253 (1974).
(17) T. C. M. Dea, A. A. McKinnon, and D. A. Rees, *J. Mol. Biol.*, **68**, 153 (1972).
(18) D. B. Smith and W. H. Cook, *Arch. Biochem. Biophys.*, **45**, 232 (1953).
(19) M. Glicksmann, "Gum Technology in the Food Industry", Academic Press, New York, N.Y., 1969.
(20) G. Pass, G. O. Phillips, and D. J. Wedlock, *J. Chem. Soc., Perkin Trans. 2*, 1229 (1977).
(21) H. Daoust and A. Hade, *Macromolecules*, **9**, 608 (1976).

Linear Poly(*N*-alkylethylenimine)s

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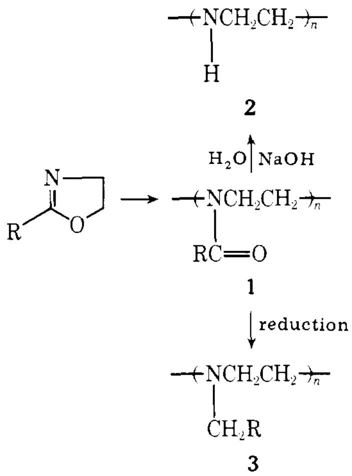
Poly(*N*-alkylethylenimine)s may be prepared by the ring-opening polymerization of *N*-alkylethylenimines.[1] The polymerization of *N*-alkylethylenimines, however, normally is accompanied by side reactions such as a reaction between the growing species and the amino group of the produced polymer chain and usually does not yield poly(*N*-alkylethylenimine)s having clear-cut structures in quantitative yield.[2] In some cases cyclic oligomers are also produced. Production of polymer and/or oligomer depends upon the monomer structure, the nature of initiator, and the polymerization conditions.[2]

In this paper we wish to report a new method of the preparation of linear poly(*N*-alkylethylenimine)s. Previously we reported the preparation of linear, crystalline polyethylenimine **2** by the alkaline hydrolysis of poly(*N*-formylethylenimine) **1** (R = H) which is obtained by the isomerization polymerization of unsubstituted 2-oxazoline.[3] Reductions of poly(*N*-acylethylenimine)s **1** are expected to give poly(*N*-alkylethylenimine)s **3**. The present paper describes the results, in which $LiAlH_4$ and AlH_3 were used as reducing agents.



R = H, alkyl, aryl

Experimental Section

Reagents. 2-Oxazoline was prepared and purified as reported previously.[4] 2-Propyl-2-oxazoline and 2-phenyl-2-oxazoline were prepared according to the literature.[5] Commercial reagents of 2-methyl-2-oxazoline (Aldrich Co.) and all solvents were dried and distilled under nitrogen. $LiAlH_4$ was commercial reagent and was used without further purification. AlH_3 was prepared according to the method of Yoon and Brown.[6]

Polymerization. The polymerizations of 2-oxazolines were carried out in acetonitrile using ethyl trifluoromethansulfonate as an initiator at room temperature 100 °C under nitrogen. Polymers obtained were purified by reprecipitation (chloroform solvent–ethyl ether nonsolvent) and subjected to a molecular weight determination by vapor pressure osmometer (Hitach Perkin-Elmer Model 115).

Reduction with $LiAlH_4$. A typical experiment (No. 3) proceeded as follows. Poly(*N*-acetylethylenimine) ($\overline{M}_n$ = 7600), 1.0 g (11.8 mmol), was dissolved in 19 mL of CH_2Cl_2. $LiAlH_4$, 0.34 g (9.0 mmol), in ethyl ether, 2.5 mL, was added to the solution. The mixture was stirred at 40 °C for 68 h under nitrogen. The reaction was stopped by the addition of 0.63 mL of water. The organic layer was filtered and the reduced polymer was obtained by the evaporation of the filtrate (0.36 g, 43%).

Reduction with AlH_3. A typical experiment (No. 5) was performed as follows. Poly(*N*-acetylethylenimine) ($\overline{M}_n$ = 4480), 0.5 g (5.9 mmol), was dissolved in 39 mL of CH_2Cl_2. To this solution, 5.2 mL of AlH_3–THF solution (AlH_3 7.08 mmol) was added at 0 °C under nitrogen. After stirring for 6 h, the reaction mixture was hydrolyzed with 5 mL of water and 1 g of NaOH in 30 mL of water was added. The organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2. The combined CH_2Cl_2 solution was filtered and evaporated to dryness under vacuum, polymer yield 0.25 g (59%). The product poly(*N*-ethylethylenimine) was converted into HCl salt with an excess of diluted hydrochloric acid and the HCl salt was reprecipitated from the aqueous solution with addition of ethanol. The HCl salt was dried at 70 °C in vacuo and subjected to elemental analysis. Anal. Calcd for $(C_4H_9N{\cdot}HCl)_n$: C, 44.66; H, 9.37; N, 13.02. Found: C, 44.02; H, 9.74; N, 12.95.

Reduction of Poly(*N*-formylethylenimine). A mixture of 0.50 g (7 mmol) of poly(*N*-formylethylenimine), 1.1 mL (25 mmol) of 85% formic acid, and 2.3 mL (28 mmol) of 37% aqueous formaldehyde solution was heated at 100 °C under nitrogen. After 68 h the reaction mixture was cooled and 2.5 mL of concentrated hydrochloric acid was added. Heating at 100 °C was continued for another 5 h. Then, water and formic acid were distilled off at 50 °C under reduced pressure. The residue was dissolved in a small portion of water, made strongly basic with sodium hydroxide, and extracted with CH_2Cl_2. The CH_2Cl_2 solution was evaporated to give 0.23 g (58%) of polymer. The elemental analysis of the product was performed with its HCl salt as described above. Anal. Calcd for $(C_3H_7N{\cdot}HCl)_n$: C, 38.52; H, 8.62; N, 14.97. Found: C, 38.14; H, 8.83; H, 14.41.

Purification of Reduced Polymers. Poly(*N*-benzylethylenimine) was purified by reprecipitation by pouring its CH_2Cl_2 solution into *n*-hexane. The other polymers did not precipitate well in *n*-hexane.

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