SOME EFFECTS OF LITHIUM, SODIUM, POTASSIUM AND AMMONIUM IONS ON SODIUM CARRAGEENATE AND KAPPA CARRAGEENATE

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PREFACE

Carrageenin is the name given to the polysaccharide material which is commonly extracted from the seaweed, Chondrus Crispus, often called Irish Moss, (34) by the treatment of the dried material with boiling water and the precipitation of the product with ethanol. (27, 29) Carrageenin is a substance resembling a somewhat more familiar extractive from a seaweed, Gelidium Amansii, which is commonly called agar. (1, 14, 27) These substances are hydrophilic colloids of a polysaccharide nature and they have generally similar characteristics.

Carrageenin was first isolated in 1844 by Schmidt (30) and since then it has found many commercial uses. It is used in the preparation of many types of food such as puddings, ice cream, cake icings, and in chocolate milk drinks. Other important commercial uses of carrageenin are found in the pharmaceutical and detergent industries because of its ability to stabilize particles in liquids and solutions.

Carrageenin is able to form a soft heat reversible gel with water at a concentration of 3%. This soft gel melts between 27° and 30° C. Furthermore, a 5% water solution forms a rather rigid gel which melts at about 40° C. (12) The gels of carrageenin are much softer than those of agar and other such materials, consequently it can be used in products where a soft smooth texture is desirable. A peculiar property of carrageenin lies in the fact that its gelling ability is greatly enhanced by the addition of potassium and ammonium salts. This unusual behavior is also exhibited in varying degrees by cesium and rubidium salts (8, 21) Recent studies have been directed toward a better understanding of the effect of ions in general, and that of the potassium ion in particular upon the general properties of carrageenin, especially upon its gelling properties. The present work has been done in an attempt to extend these studies and to obtain information which might lead to a solution of the problem of why potassium and ammonium salts have their peculiar effects.

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INTRODUCTION

The actual structure of carrageenin has not as yet been completely elucidated. It can be classified as a polysaccharide containing sulfur. The nature of the sulfur content was investigated by Haas (12) and by Harwood (13), whose studies show that the sulfur exists as a sulfuric acid ester covalently bound to the polysaccharide chain. Associated with this esterified sulfate group are, predominantly, sodium ions. Potassium, calcium and magnesium ions, in smaller amounts, are also found associated with this group in the original extractive. Carrageenin is a colloidal electrolyte.

Johnson and Percival (16) have done much to establish the structure and composition of carrageenin. They and others (2, 23, 34, 35, 36) found that the major portion of the carrageenin polysaccharide is composed of D-galactose residues tied together at the number one and three carbon positions, with the esterified sulfate group located on the fourth carbon of the pyranose ring. These D-galactose groups are known from X-ray studies to be joined together by alpha glucoside linkages. (35) This general structure is shown in Fig. 1. This general type of structure is also found in various other seaweed polysaccharides such as agar and laminarin. (1)

Carrageenin can be separated into at least two main fractions; one of which gels while the other does not. These fractions have been named kappa and lambda carrageenin, respectively. (33) They cannot be resolved electrophoretically, but the two components can definitely be shown to exist by ultracentrifuge studies. (4) The kappa and lambda fractions can be separated from the original extractive because the kappa fraction is sensitive to the potassium ion. If potassium chloride solution is added to a solution of the original carrageenin which is too dilute to gel, a gelatinous precipitate of kappa carrageenin is formed. This precipitate can be collected by centrifuging, leaving the lambda fraction in solution. (33) The original Chondrus Crispus carrageenin seems to be composed of about 40% of the kappa fraction, 45% of the lambda fraction and about 5% of a material which has proved unrecoverable. Studies have shown that the fractions can be separated with negligible contamination.

Sulfate contents of the original extractive and of the kappa and lambda fractions were found by Smith and Cook (33) to be 29%, 24%, and 33%, respectively; and the corresponding specific optical rotations were 58°, 63° and 44°.

The structure of lambda carrageenin has not been specifically studied; however, its major constituent is the D-galactose residue mentioned previously. (31) Since the original carrageenin contains L-galactose and glucose, (2, 23, 24) it may well be that these sugar residues are also present in the lambda fraction. The kappa or gelling fraction contains the D-galactose residue together with 3,6-anhydro D-galactose. Its composition has been summed up as 20% 3,6-anhydro D-galactose, 25% sulfate and the remainder D-galactose. (31) The kappa fraction can be subfractionated by the addition of successive amounts of alcohol or potassium chloride solution followed by centrifuging. (31, 32) The compositions of the various subfractions seem to be the same, so far as the study has shown. There is, however, a change in viscosity which might be due to differences in the degree of dispersity of the particles. It seems probable that, superimposed upon a distribution due to particle size, there is a decreasing amount of branching with those particles which separate at higher alcohol concentrations. (31)

Since the gelling properties of carrageenin are of primary interest in this investigation it is important to develop a concept as to the structure of kappa carrageenin. From an analysis of the structure of the two sugar residues which make up this fraction it may be deduced that the D-galactose residue forms a polymer chain in which the units are probably joined together by alpha glucoside linkages. Furthermore, due to its configuration 3,6-anhydro D-galactose groups will probably be joined by beta glucoside linkages. If these two sugar units are to be composite parts of the same polysaccharide chain it would follow that an odd shaped chain should result. Based upon these concepts a possible structure of this material may be proposed. Such a possible structure as is shown in Fig. 2 might thus result. This would involve the succession: two

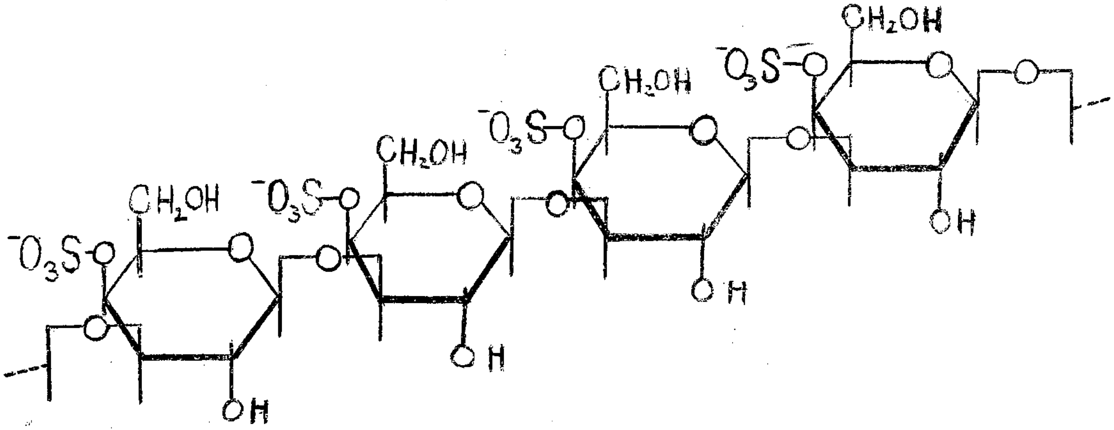


Figure 1: General Structure of Carrageenin.

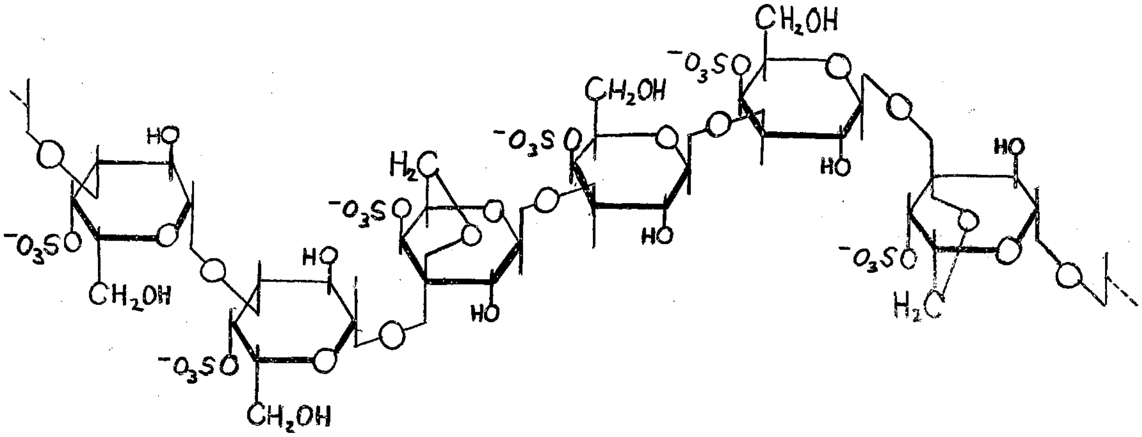


Figure 2: Proposed Structure of Kappa Carrageenin.

alpha linking residues - one beta linking residue, two alpha linking residues - one beta linking residue, and so on. This concept of the structure of the gelling fraction is quite different from that of Fig. 1; the earlier notion as to the structure of the original extractive. Undoubtedly the structure of kappa carrageenin must be different from that of the original material. It seems that the original material must be a mixture of these two forms. The structure shown in Fig. 2 involves a very "kinky" chain. Both polysaccharide chains, however, would be characterized by a restriction of free rotation about the glucoside linkages due to the presence of the sulfate group.

From X-ray studies conducted by Cook, (35) it is indicated that there is a periodic change in the orderly progression of the sugar units. Therefore, intermittently along the chain there would occur atomic spacings which are larger than those characteristic of the rest of the chain. These spacings, according to our concept as shown in Fig. 2, would be contiguous to the positions of the sulfate groups at the beta linkages. Cooks theory is that these spacing are just large enough to hold only the less hydrated potassium or ammonium ions and that they have the right configuration to do so. This would result in a forcing out of the water in such spaces, bringing about a change in the hydration and thus in the lyophilic nature of the polymer chain at these points. As will be shown later, this would result in the adherence of the particles at these points, and thus in gelation. Thus he accounts for the great gelling efficiency of potassium and ammonium ions.

The gelling properties of carrageenin are greatly affected by perchlorate ions. These ions readily disperse carrageenin gels, but if the dispersed gel is dialyzed free of perchlorate ions, the gel is again regenerated. (9) The fact that the perchlorate ion has a very low complexing ability, and that it is known to be a strong inhibitor of complexing may account for this effect. It may well be that the effect which any added ion produces may be associated with its complexing ability.

According to Rice (28) the pure calcium salt of carrageenin easily forms gels in aqueous solutions. This may be due to the ability of the divalent calcium ion to form cross linkages by associating itself with two esterified sulfate groups on different polysaccharide chains. This would be favorable to gel formation. On the other hand, such ions as those of aluminum, thallium and lanthanum shcw slight tendency to gel carrageenin. This may be due to their great tendency to form complexes. Thus is seems that a study of the effect here considered should be limited to simple monovalent cations.

Studies by Gulbier and Huber (11) and others have shown that the viscosity of a carrageenin solution is greatly decreased by the addition of small quantities of strong electrolytes. Upon adding more of the electrolyte the viscosity was lowered still more, but more slowly, until a nearly constant value was reached, after which the addition of further quantities caused little change. The first abrupt drop in viscosity with the addition of small quantities of electrolyte is found with many colloids. It is a matter of the lowering of zeta potential, commonly called the electrovisous effect. (36) Colloids show a certain resistance to flow due to their electrical charges. This is equivalent to an increased size of the particle, whence we have the effect of a removal of charge upon viscosity. This effect is found only with low concentrations of added electrolyte.

A second effect upon the viscosity of sols, on adding higher concentrations of electrolytes, is that of dehydration. This factor may often re-enforce the electroviscous effect. According to the accepted theory, dehydrated spots appear along the colloidal particles when an electrolyte is added. The particles become more lyophobic at these spots and so tend to adhere at such points. This causes the sol to coagulate to form a gel, a loose network or "brush heap" structure in which the space between the adhering particles is filled with solvent or very dilute sol. (17) The general diagram of such a structure would be somewhat as shown in Fig. 3. Here the dehydrated spots are represented by dark spots and the particles are crosshatched.

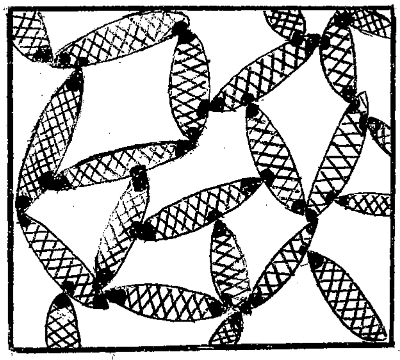


Figure 3: Diagram of Gel Structure

It has commonly been held that dehydration is brought about by an ion or other agent by an actual removal of water from the colloidal particle, as water is removed by alcohol added to the sol. It may well be, however, that the action of ions is different from that of a general dehydrating agent such as alcohol. If an actual removal of water is involved it would seem that the more highly hydrated ions should be more effective than those which are less hydrated. That is, for a series of ions the effectiveness should follow the lyotropic series. This series for the lithium, sodium and potassium ions is $Li^+ > Na^+ > K^+$ as determined by various methods. The effect of these ions in causing the gelling of carrageenin, agar and other polysaccharide colloids, however, have been found to fall in exactly the opposite order.

The theory of Cook presented above not only gives a more complete picture of the mechanism than does simple dehydration, but it is capable of explaining the apparent anomaly involved in the gelling of carrageenin. If a situation favorable for the acceptance of certain ions rather than others exists in a colloid particle then those ions will be preferentially taken up regardless of the particular degrees of hydration. The ability to cause gelling, then, becomes a specific property of the ions, not necessarily associated directly with their degrees of hydration.

Studies whose results aid in this connection were carried out by Rice. (Loc. Cit.) He investigated the effect of adding various salts in solution upon the viscosities of carrageenin sols. He found that the concentration of sodium, calcium and potassium chlorides necessary to cause flocculation varied little with the concentration of carrageenin. With a constant concentration of carrageenin, however, calcium and potassium chlorides were found to be about equally effective, and both were about 4.3 times as effective in flocculating carrageenin as was the sodium ion. He seems to have taken the "flocculation point" as the point at which a sudden break in the viscosity curve occurs.

According to Overbeek and de Jong, (19) the affinity of a cation for the ionized group of an anionic colloidal electrolyte depends upon the valency, the polarizing power and the radius of the cation and upon the polarizability of the negatively charged group on the colloid. The effect of the valency of the cation has been mentioned above. If the dispersion medium is water the polarizability of the water associated with the cation must be taken into account. If the negative group on the colloid is more polarizable than the water the polarization energy will be added to the coulombic energy of the ions and a stronger bond will be formed. However, if the negative group is less polarizable than the water molecules, as is the case in sulfate colloids, the polarization energy will oppose the coulombic energy of the bond. Therefore, a less hydrated cation will have a greater affinity for the sulfate groups in a colloid than will a more highly hydrated one. These polarizability effects with sulfate colloids may be enhanced when hydroxyl groups are found near the sulfate group, as is the case with carrageenin. One would expect that the order of affinity of the cations which we have used would be NH_4^+, $K^+ > Na^+ > Li^+$ since this is the inverse order of their degrees of hydration. K^+ and NH_4^+ are approximately equally hydrated.

The ionic radii of the hydrated ions must also be taken into account. Different estimates of these values have been made. Thus Dean (7) gives "one estimate" without particular reference. The approximate radii in Angstrom units which he gives are for Li^+, 10.0; for Na^+, 7.9; for K^+, 5.3 and for NH_4^+, 5.4. Another estimate for the effective diameters of these ions taken from Klotz (18) gives in terms of $10^8 a_i$ the values 6 for Li^+; 4 - 4.5 for Na^+ 3 for K^+ and 2.5 for NH_4^+. It seems reasonable to take these values as indicating roughly the relative degrees of hydration of these ions in aqueous solution. A high degree of hydration is accompanied by a greater affinity for water and a lessened affinity for the colloid. On this basis we have again the above order for the affinities of the ions.

EXPERIMENTAL

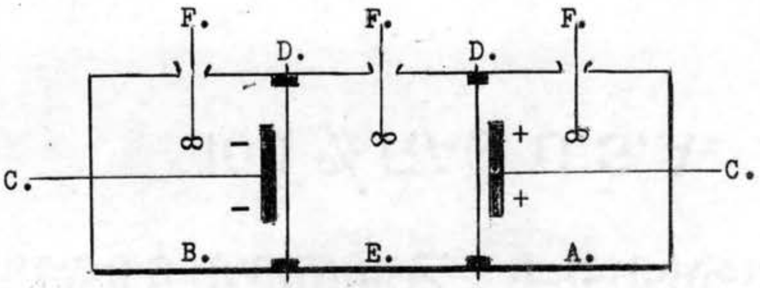
PREPARATION OF SODIUM CARRAGEENATE.

One difficulty which is encountered when working with natural products is in securing representative standard samples. The extractive from irish moss seaweed, commercial carrageenan, is no exception. It has been found that the composition of this material undergoes a seasonal variation, and that there is a change in composition when samples extracted from seaweed of different geographical origin are compared. (3) Most of the variations are related to differences in ash content. Irish moss gathered from January to May yields extractives which are higher in ash content than those gathered during the summer months. The difference lies in the percentage of calcium present. It cannot be stated unequivocally that the percentage in terms of equivalents of cations present is constant, though this is probably true. In ashing a sample for the purpose of analysis half of the sulfate is lost when sodium carrageenate is ignited, but there is no loss when the calcium salt is ignited. Thus the analyses which have been run may be faulty. In order to make sure of having a representative sample it seems necessary to replace all except one of the cations. For our experiments we have prepared sodium carrageenate.

The original carrageenin used in these experiments was supplied by the Seaplant Chemical Corporation of New Bedford, Massachusetts. It was "Seakem Type 3" which represents as well as possible the overall nature of their products.

Several ion exchange processes may be applied to colloidal materials such as these. An electrodialysis technique employed by Hoffmann and Gortner (15) to bring about ion exchange in agar seemed promising. The apparatus is sketched in Fig. 4. It consists of three chambers separated by semi-permeable membranes. Electrodes are placed just within the two end chambers, and these chambers contain water which is frequently renewed. The middle chamber contains the suspension of material, which is well stirred. On passing an electric current, moveable ions are carried out of the middle chamber. The sulfate ion is not removed since it is a component part of the agar. Cations are removed from the material and replaced by hydrogen ions from the dissociation of the solvent, water. Thus acid agar is produced in the process. It may be converted to a salt, such as the sodium salt, by treatment with the proper quantity of base.

This method was not feasible with carrageenin since acid carrageenin is unstable. The process had to be modified so as to introduce the sodium directly in place of others in our electrodialysis apparatus. The membranes used were a viscose product, artificial sausage casing. The electrodes were of graphite. The anode chamber was filled with sodium chloride or sodium nitrate solution, which was renewed from time to time. The cathode chamber



A. Anode Compartment
B. Cathode Compartment
C. Electrodes
D. Semi-permeable Membranes
E. Sol Compartment
F. Stirrers

Figure 4: Electrodialysis Apparatus

was filled with water. The middle chamber was filled with a 2% suspension of "Seakem Type 3". This suspension was stirred throughout the electrolysis. On electrolysis sodium ions were driven through the middle chamber where they could exchange with other ions present in the carrageenin. The process worked well in that the calcium ions were removed rapidly and finally went to a very low concentration in the sol after about eight hours electrolysis. The potential across the apparatus was 100 volts and the current that passed went from about 0.5 amperes at the start to 1.1 amperes at the end. There was considerable heating, and the product darkened progressively throughout the electrolysis. It seemed that the carrageenin was being degraded, so this method was abandoned after several trials.

A procedure for preparing sodium carrageenate suggested by Young (37) and by Goring (10) was tried with much better success. A 1% suspension of extractive ("Seakem Type 3") was put into collodion bags. These were suspended in a solution containing 0.04 moles NaCl per liter and a sodium acetate - acetic acid buffer to make the pH 5.5. (The sodium chloride solution was made slightly acid to insure the removal of calcium ion by dialysis. At higher pH values this ion tended to form compounds which clogged the pores of the collodion bag.) The outer solution was well stirred and renewed frequently. A small quantity of toluene was added to the outer solution to inhibit mold growth. At the end of ten days dialysis sodium oxalate tests showed that the calcium ion had been eliminated from the sol. The material was then dialyzed against running distilled water for eight days. At the end of this dialysis a silver nitrate test showed that the chloride ion was absent, so the product was assumed to be sodium carrageenate. The contents of the sacks were combined and evaporated to about one third the original volume in an air bath at a temperature of 75° C. or less. This was the stock solution for the experiments. It was stored in a brown glass bottle. This sodium carrageenate suffered no visible alteration on storage. Molds do not grow upon it, as they will upon preparations containing the calcium ion. The viscosity of a 0.1% solution was 7.78 relative to the viscosity of water, both at 25° C., at the start and at the end of six months. Five batches of sodium carrageenate were prepared in this manner. The concentration of the combined preparations was determined by evaporation of weighed samples at 75° C. until no further change in weight took place. It was found to be .95% carrageenate. About thirty grams in all were prepared.

The purity of the sodium carrageenate was established by ashing known weights of the above weighed samples. It was found to contain 28% sulfate, allowing for the fact that half the sulfate is lost on ignition. This compares as well as can be expected with the results of Smith and Cook, who found 29% sulfate.(33)

MEASUREMENT OF EFFECTIVE GELLING CONCENTRATIONS.

The viscosities of colloidal systems have been used to study their structures and others of their features since the time of Graham, the father of colloid chemistry. A simple sol containing only very small particles has a viscosity which is almost the same as that of the solvent. This is true of gold sols and others like it. Solvation and the presence of electrical charges makes the viscosity to rise to some extent. If the sol has aggregated to form needle or threadlike particles the viscosity may increase greatly due to the fact that such particles interfere with the flow of the system through a narrow space. Brownian movement plays a large part in this effect. If the particles clump together to form large particles the system will be progressively immobilized, and if this process goes far enough flow may be quite prevented. The system will finally become plastic. Viscosity determinations enable one to detect more or less well these different states of the system, though it will very often be necessary to take into account other properties of the system to interpret the states with accuracy.

The application of viscosity data is somewhat different when it is desired to find gelling concentrations of added ions. The determinations require the use of a system in which the concentration of the dispersed material is held constant. To this system are added salts in progressive increasing concentrations, and the changes are followed by determining the viscosity after each addition. The common course of the changes is as follows. The relative viscosity of the system is a maximum when no salt has been added. The first small additions of salt to a negatively charged sol (such as carrageenin) reduces the negative charge upon the particles by adsorption of the positively charged cations. The viscosity falls rapidly as a result. Dehydration of the particles also probably occurs, with the same effect upon the viscosity. Finally the viscosity ceases to fall and clumping of the particles sets in. Further addition of the salt increases this clumping and causes a rise in the viscosity. The onset of this clumping may be taken as an indication that the sol has begun to gel, and the concentration of salt in the system where it begins may be taken as the gelling concentration for the salt which is involved.

Cannon - Fenske viscometers were used in measurements of viscosity. Sodium carrageenate sols of definite concentrations were prepared and the desired quantities of salt were added in all cases except when it was desired to determine the viscosity of the sol itself. 10 ml. portions were placed in the viscometer which was then clamped in the constant temperature bath. All runs were made at 25° C. After the usual fifteen minutes to come to temperature the efflux time of the sample was determined. Other runs were made at succeeding times. It was found that results checked well for the lower percentages of salt. Above a certain concentration, however, the efflux times became irregular and non-reproducible. In the range of lower salt concentrations the changes are due to the electroviscous effect, and probably in part also to dehydration. In the range of salt concentrations where efflux times were irregular, gelation was under way. The onset of this irregularity might be taken as the gelling concentration of the salt, but it cannot be determined with any reasonable accuracy. The irregularity results from the fact that different degrees of coagulation and formation of interlacing structures will result at different times. Then, too, with a thixotropic dispersed substance (carrageenin is such a substance) the structure will be disrupted by agitation such as comes from drawing the fluid up in the viscometer. This will introduce another complicating factor into the effux time. The following modification of the procedure was therefore introduced. The efflux time was taken about fifteen minutes after the viscometer and contents had been suspended in the bath. The fluid was then sucked up until its meniscus was just above the upper mark and the suction tube was clamped to maintain it in this position. After a sufficient time the tube was unclamped and the meniscus was allowed to fall, taking the efflux time. It was found that results checked satisfactorily if the fluid had been held high in the viscometer for some hours. A time which served for all the sols was eight hours, so this time was taken. Sets of efflux times for the various concentrations of salt present thus resulted.

For our purpose it was desired to determine relative viscosities. From the Poiseuille formula it follows that, other factors being held constant, the viscosity of a fluid at constant temperature is proportional to the product of the density of the fluid times its efflux time. The viscosity of any fluid relative to that of water taken as unity is given by the expression $\frac{\eta_1}{\eta_{H_2O}} = \frac{d_1 t_1}{d_{H_2O} t_{H_2O}}$ where d_1 and d_{H_2O} are the respective densities of the fluid and of water, respectively, and t_1 and t_{H_2O} are the respective efflux times. The density of each of the sols was taken as that of the salt solutions, since the carrageenin has a negligible influence upon the density of a suspension. The relative viscosities of the various sols was calculated using this formula.

When these relative viscosities were plotted against the corresponding salt concentrations a branching curve resulted. (Refer to Fig. 5) The gelling concentration for each salt was taken arbitrarily as the concentration at which branching of the curve as read from the graphs started.

The chloride salts were used in every case so that the specific effects of the respective cations might be clearly brought out. There is some evidence that nitrates and sulfates give essentially the same results as do chlorides, but this would not be true if the anions were adsorbed to different extents than is the chloride. Presumably the chloride ion would be adsorbed to the same extent for each concentration of salt for the dilute solutions which we used, regardless of the cation with which it is associated.

The data are presented in Tables I through VI, and represented graphically in Figures 5 through 10. The gelling concentrations are presented for the various salts in Table VII. The order of the gelling concentrations is, as will be seen, $K^+ > NH_4^+$ for sols containing 0.1% of sodium carrageenate. No gelling was found for Na^+ and Li^+ at this carrageenate concentration up to 0.3 moles of salt per liter. Gelling concentrations were found for both these ions on a 0.5% carrageenate sol, though they were much higher than those for K^+ and NH_4^+. This difference indicates that some other factor than those which we have discussed must be effective in producing gelling with Na^+ and Li^+. The overall order of effectiveness is $K^+ > NH_4^+ > Na^+ > Li^+$. This the order which is predicted on several different grounds above, but the reverse of the lyotropic series for these ions.

The theory of gelation proposed by Cook is well substantiated for the potassium ions, but it cannot hold for the sodium and lithium ions. The gelation by the latter two ions must be explained in some other manner.

THE SALTS OF KAPPA CARRAGEENATE.

It was of interest to prepare various salts of kappa carrageenate and to try to characterize them. The sodium carrageenate previously used was taken as the starting material. Following the procedure developed by Smith, (33) a 0.15% solution was prepared and molar KCl solution was added dropwise with rapid stirring until the KCl concentration reached 0.2 molar. The resulting precipitated material was collected using a Sharples Supercentrifuge. It was dialyzed

TABLE I: Data for Determination of Effective Gelling Concentration of Potassium Chloride on 0.1% Sodium Carrageenate Sol.

Concentration on KCl (moles/liter)	Flow Times* (seconds)		Relative Viscosity @ 25° C.	
	Initial	After setting 8 hours	Initial	After setting 8 hours
0.00000	414	--	7.78	--
0.00115	277	--	5.18	--
0.00231	227	--	4.24	--
0.00625	169	--	3.16	--
0.01250	145	--	2.74	--
0.01790	141	154	2.63	2.91
0.02030	142	162	2.67	3.05
0.02500	145	177	2.74	3.33
0.03590	170	190	3.18	3.56
0.05000	154	196	2.90	3.70
0.08240	149	170	2.80	3.19
0.10000	134	149	2.49	2.80

*as determined by a Fenske-Cannon viscometer, size 100 with a flow time for water of 53.4 seconds @ 25°C.

TABLE II: Data for Determination of Effective Gelling Concentration of Ammonium Chloride on 0.1% Sodium Carrageenate Sol.

Concentration of NH_4Cl (moles/liter)	Flow Times* (seconds)		Relative Viscosity @ 25° C.	
	Initial	After setting 8 hours	Initial	After setting 8 hours
0.00000	414	--	7.78	--
0.00122	276	--	5.18	--
0.00234	224	--	4.22	--
0.00607	173	--	3.26	--
0.01250	127	--	2.40	--
0.03900	130	--	2.45	--
0.04380	130	--	2.45	--
0.05000	127	--	2.40	--
0.05850	128	--	2.42	--
0.06330	122	138	2.30	2.61
0.06820	123	152	2.32	2.87
0.08270	145	172	2.74	3.20
0.10000	147	175	2.78	3.24
0.10700	142	173	2.68	3.22

*as determined by a Fenske-Cannon viscometer, size 100 with a flow time for water of 53.4 seconds @ 25° C.

TABLE III: Effect of Sodium Chloride on the Relative Viscosity of a 0.1% Sodium Carrageenate Sol.

Concentration of NaCl (moles/liter)	Flow Time* (seconds)	Relative Viscosity (@ 25° C.)
0.00000	414	7.78
0.00120	271	5.07
0.00250	221	4.15
0.00490	176	3.23
0.00990	148	2.26
0.01980	129	2.44
0.02500	126	2.38
0.05000	114	2.14
0.10000	105	1.96
0.30000	103	1.93

*as determined by a Fenske viscometer, size 100 with a flow time for water of 53.4 seconds @ 25° C.

TABLE IV: Data for Determination of Effective Gelling Concentration of Sodium Chloride on 0.5% Sodium Carrageenate Sol.

Concentration of NaCl (moles/liter)	Flow Times* (seconds)		Relative Viscosity @ 25° C.	
	Initial	After setting 8 hours	Initial	After setting 8 hours
0.000	300	--	25.6	--
0.162	132	--	11.5	--
0.203	150	--	12.9	--
0.223	156	165	13.4	14.2
0.235	167	190	14.4	16.4
0.262	174	200	15.0	17.3
0.308	188	219	16.2	18.9
0.325	190	220	16.4	19.0
0.365	187	217	16.1	18.7
0.406	183	223	15.8	19.3

*as determined by a Fenske-Cannon viscometer, size 200 with a flow time for water of 11.7 seconds at 25° C.

TABLE V: Effect of Lithium Chloride on the Relative Viscosity of a 0.1% Sodium Carrageenate Sol.

Concentration of LiCl (moles/liter)	Flow Time* (seconds)	Relative Viscosity (@ 25° C.)
0.00000	414	7.78
0.00123	290	5.45
0.00368	212	3.96
0.00613	184	3.44
0.00125	153	2.88
0.02500	130	2.43
0.05000	117	2.11
0.10000	108	2.03
0.30000	107	2.02

*as determined by a Fenske viscometer, size 100 with a flow time for water of 53.4 seconds @ 25° C.

TABLE VI: Data for Determination of Effective Gelling Concentrations of Lithium Chloride on 0.5% Sodium Carrageenate Sol.

Concentration of LiCl (moles/liter)	Flow Times* (seconds)		Relative Viscosity @ 25° C.	
	Initial	After setting 8 hours	Initial	After setting 8 hours
0.0000	300	--	25.6	--
0.1793	150	--	12.9	--
0.2330	150	--	12.9	--
0.2510	166	--	14.3	--
0.2690	170	178	14.6	15.1
0.2865	168	177	14.5	15.2
0.3045	168	182	14.5	15.7
0.3225	180	192	15.5	16.5
0.3585	217	240	18.7	20.6
0.4130	195	240	16.8	20.6

*as determined by a Fenske-Cannon viscometer, size 200 with a flow time for water of 11.7 seconds at 25°C.

Figure 5: Effect of K^+ on 0.1% Sodium Carrageenate.

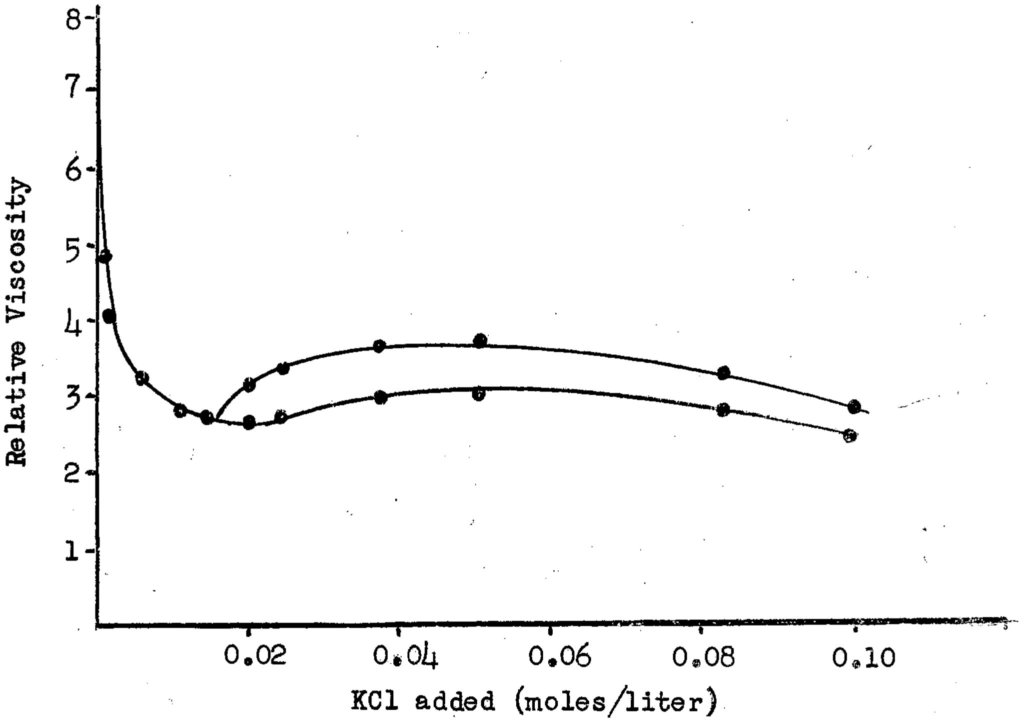


Figure 6: Effect of NH_4^+ on 0.1% Sodium Carrageenate.

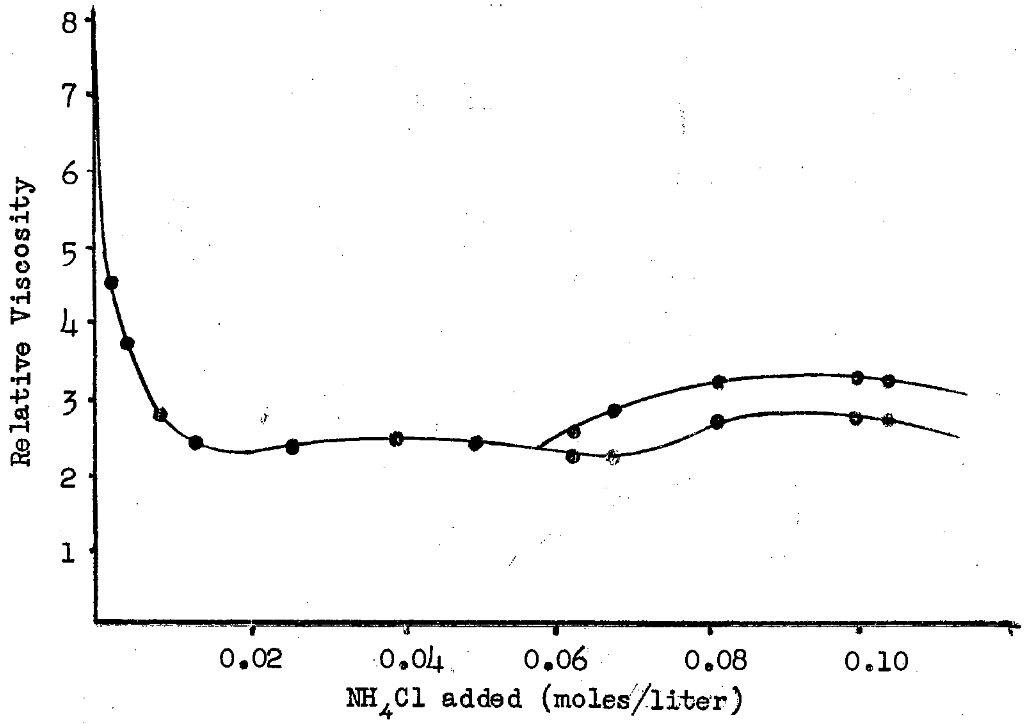


Figure 7: Effect of Na+ on 0.1% Sodium Carrageenate.

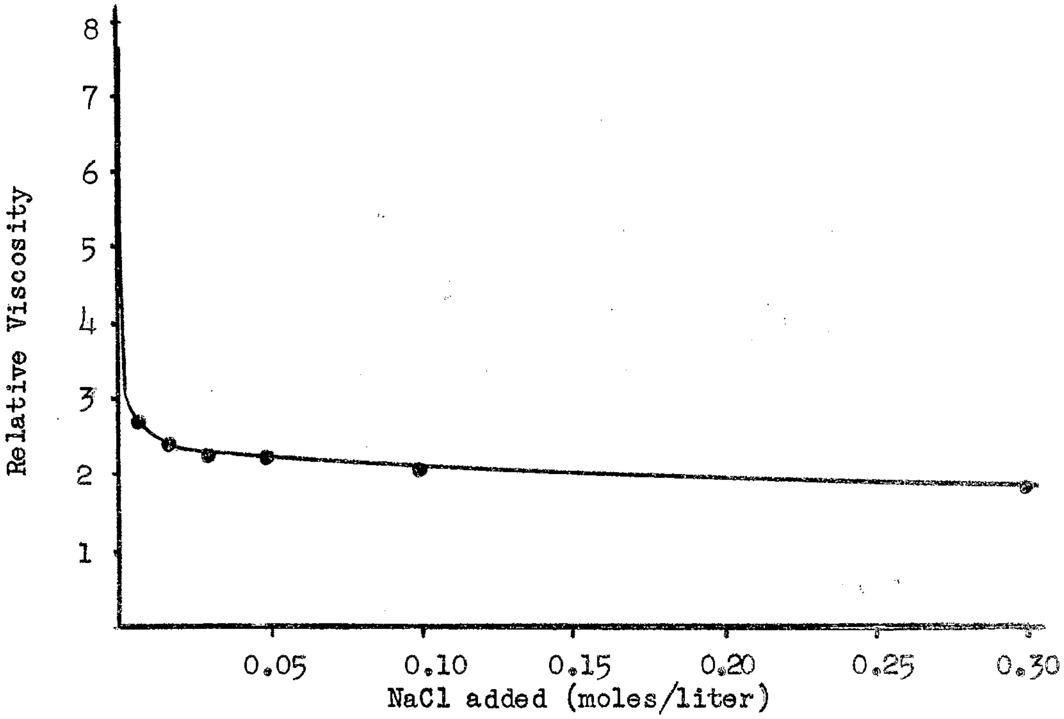


Figure 8: Effect of Na+ on 0.5% Sodium Carrageenate.

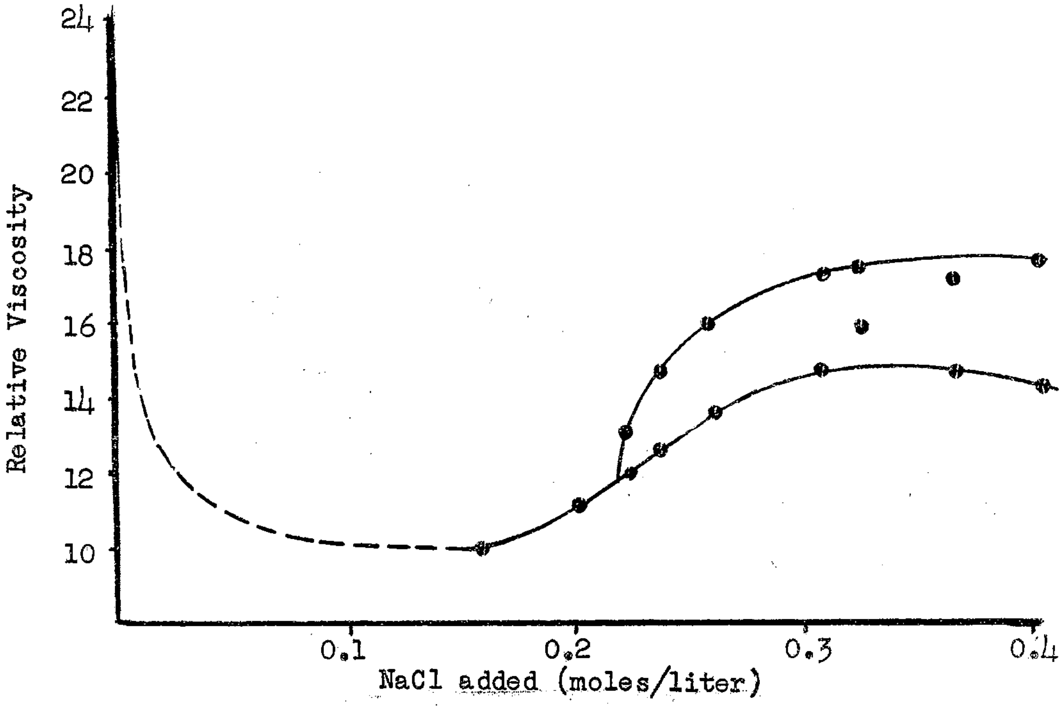


Figure 9: Effect of Li+ on 0.1% Sodium Carrageenate.

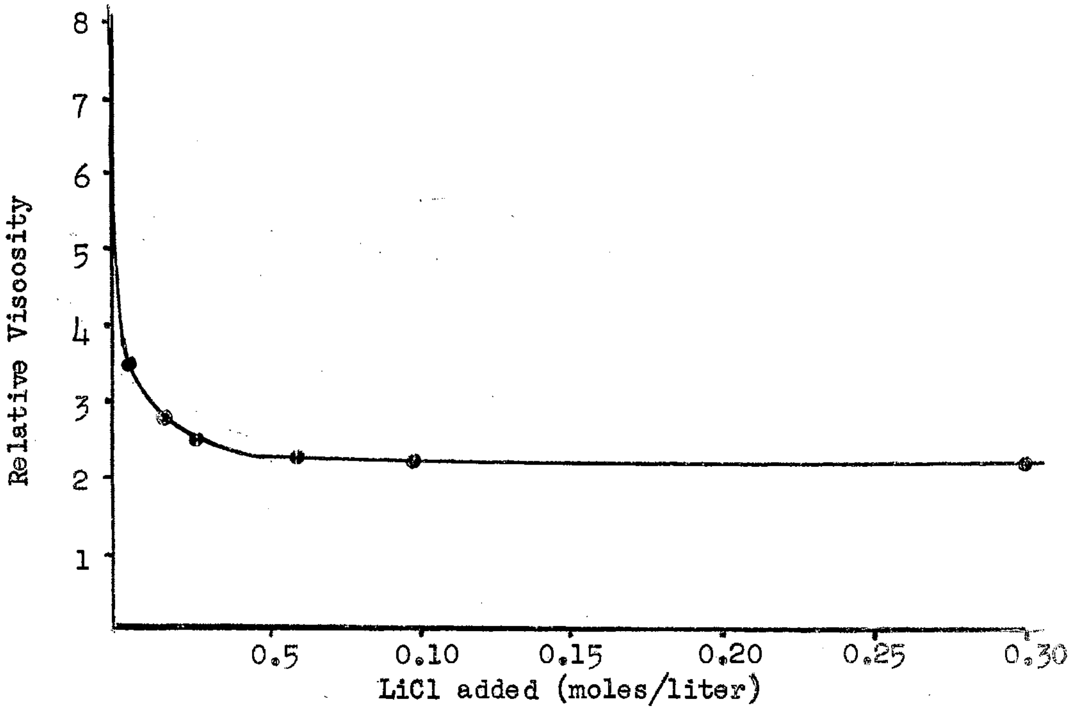


Figure 10: Effect of Li+ on 0.5% Sodium Carrageenate.

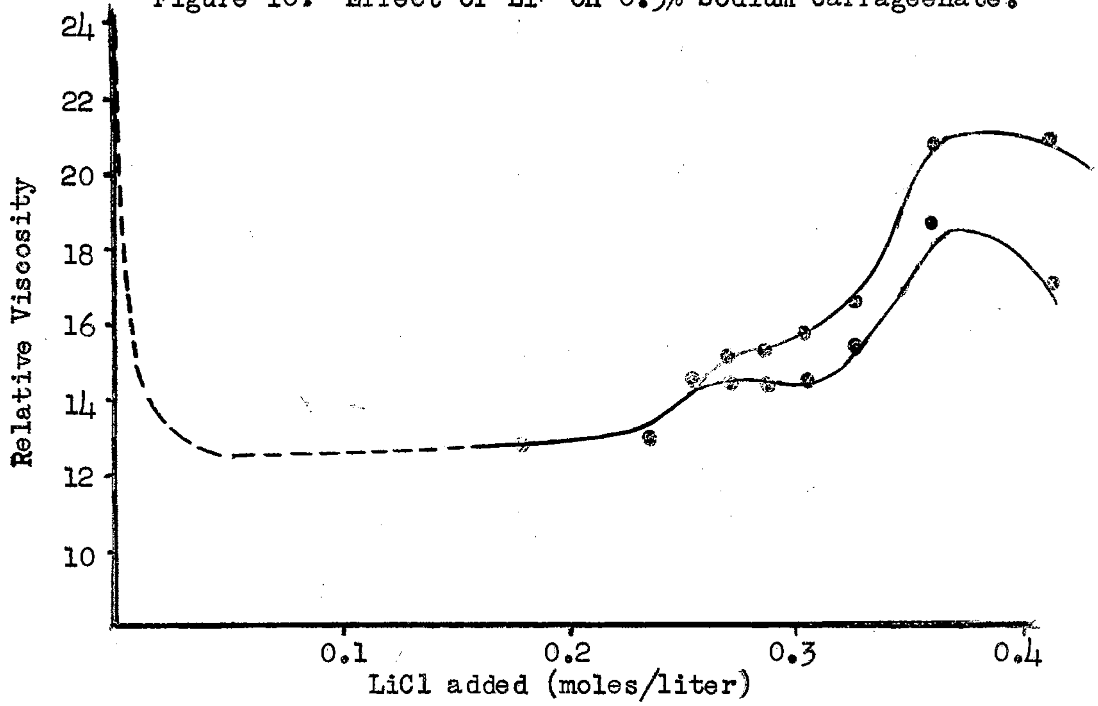


TABLE VII: Effective Gelling Concentrations of Various Salts.

Salt Added	Percent Sodium Carrageenate	Moles/liter Effective Gelling Concentration
KCl	0.1	0.0165
NH_4Cl	0.1	0.0575
NaCl	0.1	---
NaCl	0.5	0.228
LiCl	0.1	---
LiCl	0.5	0.260

using sodium chloride to reconvert it to the sodium salt, which is soluble, for four days and then diluted to 0.15%. It was then reprecipitated as above with KCl and again recovered. The purpose of this step was to make sure that the lambda fraction had been completely eliminated. A portion of it was then again converted to sodium kappa carrageenate by dialysis as above described. Attempts to convert other portions to potassium kappa carrageenate and lithium kappa carrageenate were made by dialysis against the corresponding chlorides. The displacement seemed to occur very readily with the potassium ion, but it went very poorly with the lithium ion. Considering the apparent ease of displacement it seems that kappa carrageenate has a greater affinity for the potassium ion than for the sodium ion and that it has but little affinity for the lithium ion.

Many equations have been proposed to give the relation between the viscosity of a sol and its concentration. One of the best is that of Staudinger (5) $\eta_{sp} = \eta_r - 1 = KMc$ where η_{sp} is the so-called specific viscosity, η_r is the relative viscosity, M is the molecular weight of the substance (essentially a polymer), K is a constant characteristic of the substance and c is its concentration. The equation may be divided through by c, giving $\frac{\eta_{sp}}{c} = [\eta] = KM$ where $[\eta]$ is the value which is found by plotting the data and extrapolating to $c = 0$: the so called intrinsic viscosity. The coefficient K varies only slightly with the molecular weight, so this last equation may be used to make a fairly reasonable estimate of molecular weight if K can be determined for one sample of known molecular weight. Molecular weights of colloids cannot be directly found from viscosity data. Osmotic and other methods must be employed for this purpose. Nevertheless, it should be possible to estimate relative molecular weights for different colloids, and so to compare them roughly with one another.

The relative viscosities of sodium, potassium and lithium kappa carrageenate have been found by the same method as was used in the work previously described using an Ubbelohde viscometer. (6) The concentrations, efflux times, specific viscosities and values of $\frac{\eta_{sp}}{c}$ are given in Tables VIII, IX and X in columns 1, 2, 3 and 5 for the three salts. The plots of $\frac{\eta_{sp}}{c}$ against c give pronounced curves which show very rapid rises at low concentrations. They cannot be satisfactorily extrapolated to give values of $[\eta]$ lim, but it is evident from their courses that if this could be done the value for sodium kappa carrageenate would lie high, that for the lithium salt would be much lower and that for the potassium salt would be lowest of all. A plot which gives a nearly straight line is that of $\frac{\eta_{sp}}{c}$ against $1/\sqrt{c}$. (20) These plots are shown in Figures 11, 12 and 13. We have found no viscosity equation relating these two quantities. It will be noted, however, that the curves extrapolate to 14.0 for sodium kappa carrageenate, to 6 for the lithium salt and to 3 for the potassium salt.

This work shows that potassium, sodium and lithium kappa carrageenates are three quite different entities.

TABLE VIII: Determination of Viscosity a $\lim\limits_{\frac{1}{\sqrt{C}} \to 0} \frac{\eta_{sp}}{C}$ of Sodium Kappa Carrageenate.

Concentration (grams/100 mls. water)	Flow Times* (seconds)	η_{sp} @ 25° C.	$\frac{1}{\sqrt{C}}$	$\frac{\eta_{sp}}{C}$
0.3160	976	9.84	1.78	31.1
0.2105	753	7.37	2.18	35.0
0.1580	636	6.07	2.51	38.4
0.1054	510	4.67	3.08	44.3
0.0791	440	3.89	3.54	49.2
0.0574	374	3.16	4.17	55.1
0.0421	317	2.53	4.87	60.1

*as determined by an Ubbelohde capillary viscometer with a flow time for water of 88 seconds @ 25° C.

TABLE IX: Determination of Viscosity as $\lim\limits_{\frac{1}{\sqrt{C}} \to 0} \frac{\eta_{sp}}{C}$ of Potassium Kappa Carrageenate.

Concentration (grams/100 mls. water)	Flow Times* (seconds)	η_{sp} @ 25° C.	$\frac{1}{\sqrt{C}}$	$\frac{\eta_{sp}}{C}$
0.2690	260	1.99	1.92	7.40
0.1782	220	1.44	2.36	8.07
0.1344	203	1.26	2.72	9.36
0.0770	169	0.88	3.61	11.40
0.0499	150	0.67	4.48	13.20

*as determined by an Ubbelohde capillary viscometer with a flow time for water of 88 seconds @ 25° C.

TABLE X: Determination of Viscosity as $\lim_{\frac{1}{\sqrt{c}} \to 0} \frac{\eta_{sp}}{C}$ of Lithium Kappa Carrageenate.

Concentration (grams/100 mls. water)	Flow Times* (seconds)	η_{sp} @ 25° C.	$\frac{1}{\sqrt{C}}$	$\frac{\eta_{sp}}{C}$
0.2500	413	3.58	2.00	14.3
0.1665	340	2.78	2.46	16.7
0.1250	292	2.24	2.83	17.9
0.0833	246	1.73	3.48	20.8
0.0714	230	1.56	3.75	21.8
0.0556	210	1.33	4.25	23.9
0.0417	190	1.11	4.90	26.6
0.0333	178	0.98	5.50	29.4

*as determined by an Ubbelohde capillary viscometer with a flow time for water of 88 seconds @ 25° C.

Figure 11: Plot of $\frac{\eta_{sp}}{C}$ vs. $C^{-\frac{1}{2}}$ for Sodium Kappa Carrageenate.

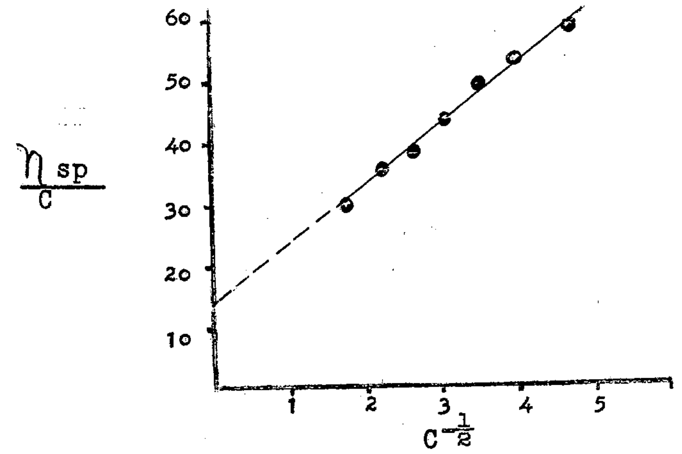


Figure 12: Plot of $\frac{\eta_{sp}}{C}$ vs. $C^{-\frac{1}{2}}$ for Potassium Kappa Carrageenate.

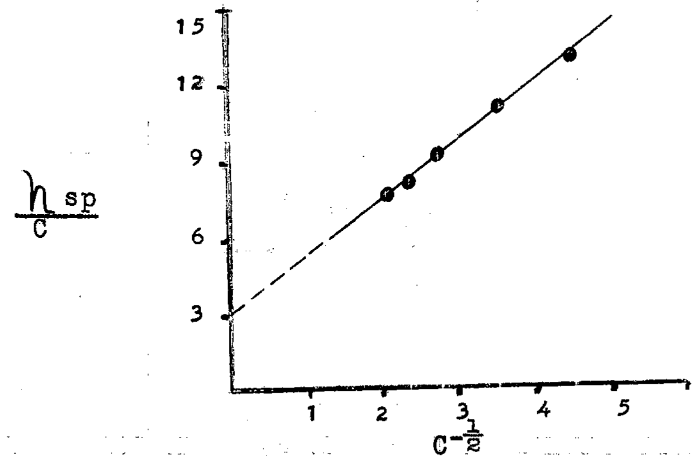
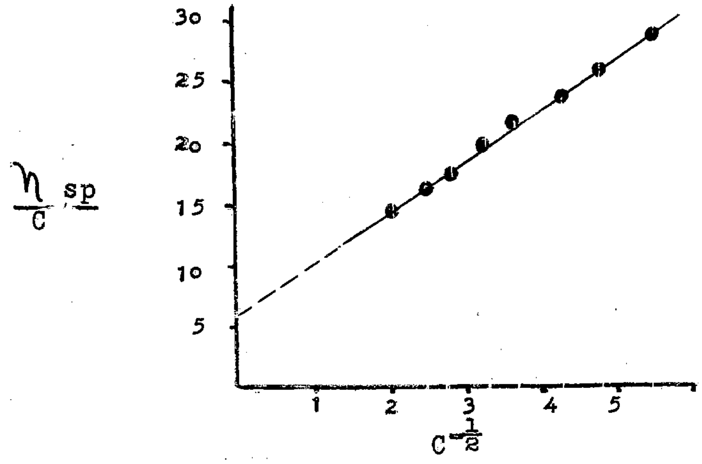


Figure 13: Plot of $\frac{\eta_{sp}}{C}$ vs. $C^{-\frac{1}{2}}$ for Lithium Kappa Carrageenate.



An equation given by Papkov (22), $\ln \eta_r = kc^a$ is closely followed by our data for the three salts of kappa carrageenin. The respective equations are $\ln \eta_r = 3.35\ c^{0.30}$ for the sodium salt; $\ln \eta_r = 1.95\ c^{0.42}$ for the potassium salt and $\ln \eta_r = 2.76\ c^{0.40}$ for the lithium salt.

SUMMARY

Carrageenin, its properties and some of the work which has been done upon it are discussed. Sodium carrageenate has been prepared and the gelling concentrations of K^+, NH_4^+, Na^+ and Li^+ for it have been determined. The order of gelling efficiencies is the reverse of that found in the lyotropic series. The gelling by potassium and ammonium ions may be explained by current theories, but that by the sodium and lithium ions cannot. Salts of kappa carrageenin have been prepared and their relative viscosities have been determined for the lower concentrations. The results are well expressed by the equation of Papkov. The equation of Staudinger does not give satisfactory results. It seems that the sodium, potassium and lithium salts of kappa carrageenate are very different in nature. More work will be required to make clear the effects which have been studied.

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