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The Effect of Divalent Metals on the Properties of Alginate Solutions

I. Calcium Ions

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When increasing amounts of calcium ions are added to solutions of sodium alginate, the viscosity of the mixture and the volume of the precipitated gel pass through a maximum. The concentration of calcium ions corresponding to this maximum depends upon the concentration of sodium ions in the solution. Two different effects of the concentration of sodium ions are demonstrated, namely, a "salting-out" effect, and an effect upon the sodium-calcium ion-exchange equilibrium. Other factors influencing the concentration of calcium ions required for precipitation include the intrinsic viscosity of the sodium alginate, its concentration, and the raw material from which it was prepared.

It is well known that the addition of calcium ions to a solution of sodium alginate causes marked changes in the properties of the solution, namely an increase in viscosity, gel formation and precipitation. This reaction is important for the practical use of alginate but little work has been published in this field.

It has been shown by Haug[1] and by Müller[2] that alginates from different species vary in ion exchange properties. Haug has found that the selectivity coefficient, defined as

$$k = \frac{\mathrm{Ca_g} \times [\mathrm{Na_l}]^2}{[\mathrm{Ca_l}] \times \mathrm{Na_g}^2}$$

(where subscripts g and l refer to gel and liquid), depends on the relative amounts of guluronic and mannuronic acid residues in the alginate. The affinity for calcium increases with increasing amounts of guluronic acid residues in the alginate.

McDowell[3,4] has studied the precipitation of alginates from *Ascophyllum nodosum* and *Laminaria hyperborea* stipes by some divalent metals, including calcium. He observed visually when precipitation started, and found that the minimum amount of calcium needed was lower for alginates from *L. hyperborea* stipes than for those from *A. nodosum*. He made no attempt to determine the calcium content of the precipitates. The observed difference can thus be due either to different affinities of the alginates for calcium ions or to different solubilities of the sodium-calcium alginates. When sodium nitrate was added to the solution before the addition of calcium, McDowell found that it had a precipitation effect at high alginate concentrations; but in dilute solutions the dominating effect was that more calcium was needed to bring about precipitation, most probably because of the displacement of the ion exchange equilibrium.

A study of mixed calcium-sodium alginates has also been made by Mongar and Wassermann.[5,6] These authors dealt especially with the changes in physical properties occurring when calcium alginate fibres are allowed to swell in different salt solutions. They also determined some selectivity coefficients,[7] but gave no information about the species from which the alginate was prepared.

The nature of the linkage between calcium and alginate does not seem to be understood clearly. It has been suggested [5,8] that the divalent calcium ion is linked to carboxyl groups in different polymer molecules. Schweiger,[9] however, investigating the precipitation of acetylated alginate with divalent metals, found that free hydroxyl groups are essential for the precipitation. He then concludes that divalent metals are bound to alginate as a complex involving two carboxyl groups and two hydroxyl groups.

For practical purposes calcium is often used to increase the viscosity of alginate, to change the flow properties and to form gels. Several commercial alginate products contain small amounts of calcium. Some of the properties of two products of this type have recently been described in the literature,[10] although the presence of calcium in the products was not specifically mentioned.

In the present work we have investigated the effect of calcium ions on the viscosity of alginate solutions, in particular the effect of varying concentrations of calcium and sodium ions. The effect of the same factors on the gel volume has also been studied. In a subsequent paper the effect of other divalent metals will be described.

EXPERIMENTAL

Preparation and characterization of alginates. The preparation of alginate has been described earlier.[11] Alginates with different intrinsic viscosities were prepared by treating the algae with 1 N sulphuric acid at 40°C before alginate extraction. The determination of intrinsic viscosities, $[\eta]$, has been described previously.[12] The proportion of mannuronic to guluronic acid residues, M/G, was determined according to Haug and Larsen.[13] The results are corrected for different rates of breakdown of the two uronic acids during hydrolysis. The selectivity coefficient for the calcium-sodium ion exchange reaction, k, was determined by the method described earlier.[1] Values of M/G, k, and $[\eta]$ for the alginates used in this work are given in Table 1.

Preparation of sodium-calcium alginate solutions.

(a) *By addition of calcium to solutions of sodium alginate.* In order to obtain reproducible results in the viscosity measurement after addition of calcium to an alginate solution, standardized conditions for mixing the alginate solution and the calcium salts must be applied. It is particularly important to avoid large concentration gradients. We have adopted the following method of introducing calcium into the solution: Equal volumes

Table 1.

Algae	M/G	*k*	[η]
L. digitata, Tarva 3/7-57	1.60	7.5	from 8 to 26
L. hyperborea stipes, Hustad 12/2-59	0.45	20.0	9.0 and 16.4
L. hyperborea » Vevang 15/12-61	0.60	20.0	10.6
A. nodosum, Flakk 15/8-62	1.70	7.0	10 and 10.6
A. nodosum, Være 2/3-59	1.66	8.3	9.0

(5 ml) of calcium salt (chloride or nitrate) and alginate solution containing the desired amount of sodium salt were mixed over a period of 1 min with gentle shaking. The shaking was continued for 1 min more, and the mixture allowed to stand. The viscosity increases rapidly in the first 5 to 10 min, and more slowly up to 24 h. In the present work, viscosity has been determined after 10 min, unless otherwise stated. All concentrations given refer to those of the mixtures.

(b) *By dissolving mixed sodium-calcium alginates.* Sodium-calcium alginate solutions, prepared as described in a), were precipitated with equal amounts of ethanol, washed with ethanol and ether, and dried overnight at 40°C. The preparations containing different amounts of calcium were dissolved in water overnight in a slowly moving shaker. Equal volumes of water or solutions of sodium salt were added and the shaking was continued for 1 h before viscosity measurements were taken.

Viscosity measurements. The viscosities were determined in two pipette viscometers (Table 2). The rate of shear and shear stress given in the table are maximum values at the capillary wall.[12] *t* is the flow time for the liquid passing through the capillary. No corrections for end effects were made, but correction for kinetic energy was applied when necessary.

Table 2.

Pipette No.	Volume, ml	Factor cSt/sec	Rate of shear, sec^{-1}	Shear stress, dyn/cm
1	2.89	0.164	$25200/t$	4100
2	1.55	4.15	$1170/t$	4850

Precipitation experiments. The preparation of sodium-calcium alginate mixtures was carried out by addition of calcium salt to sodium alginate solutions. The mixtures were allowed to stand 1 h before centrifugation. In order to obtain reproducible results in experiments with high concentrations of calcium, it was necessary to use mechanical stirring during the addition of the calcium salt. Stirring for 30 sec at 1000 rpm with a stirrer with a diameter of 2.5 cm was found to be convenient.

Centrifugation was carried out in a MSE centrifuge at 26 000 *g* for 30 min. When the gel was too loose to allow a separation of gel and liquid by decantation, the volume of the gel was found by pouring the contents of the centrifuge tubes slowly into a Buchner funnel (porosity 1). After standing for 1 h the amounts of material in the Buchner funnel and in the filtrate were determined by weighing. The time of 1 h was chosen because it was found that very little water was removed after 30 min.

The calcium content in the filtrate and the gel was determined by titration with EDTA.[14] The calcium in the gel was split off with excess 0.2 N hydrochloric acid before titration.

Thixotropic measurements. Solutions of sodium-calcium alginate prepared for viscosity measurements were stirred with the stirrer described above, and the viscosity measured at intervals. After 40 min the solutions were left standing and the viscosities determined at time intervals.

RESULTS

When calcium ions are added in increasing amounts to an alginate solution, the viscosity of the solution increases to a maximum value. Further addition of calcium leads to a decrease in the viscosity followed by precipitation. In Fig. 1 the results are given for solutions containing varying amounts of sodium nitrate. Using the above technique, both the values of the viscosities and the amount of calcium necessary to obtain the maximum viscosity were easily reproducible. The amounts of sodium ions present in the solutions markedly influence both the viscosity and the amount of calcium necessary to obtain the viscosity maximum. It should be noticed that at low concentration of sodium ions the viscosity maximum is displaced towards lower calcium concentrations with increasing amounts of sodium ions present, while the opposite is the case at higher concentration of sodium nitrate.

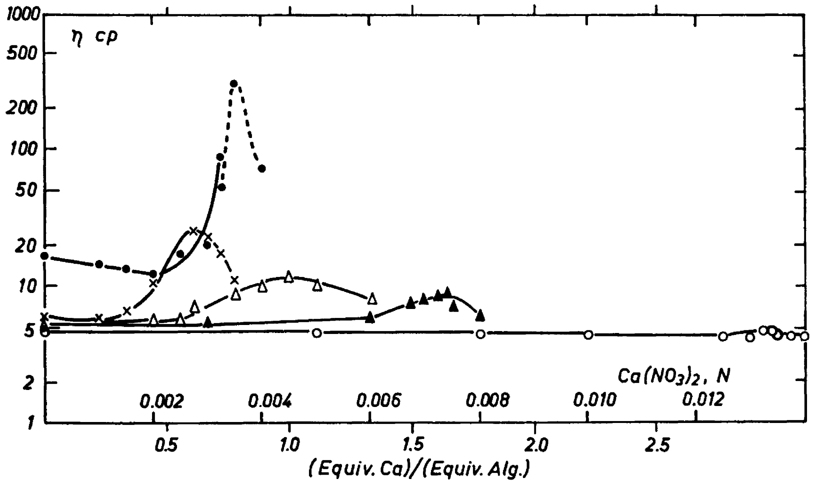

Fig. 1. Viscosity of 0.1 % (0.0045 N) solutions of sodium alginate containing different amounts of sodium nitrate after addition of various amounts of calcium nitrate. Alginate from *L. digitata*, Tarva 3/7-57, $[\eta] = 26.0$ (100 ml/g). $NaNO_3$: ● = 0 N; × = 0.05 N; △ = 0.1 N; ▲ = 0.2 N; ○ = 0.4 N. ——— = Pipette No. 1; - - - - = Pipette No. 2.

When calcium nitrate is added to a solution of sodium alginate there will be a cation exchange leading to liberation of sodium ions. The equivalents of free cations, consisting both of sodium and calcium ions ($Ca_1 + Na_1$), will be equal to the amount of calcium added. This leads to an increasing ionic strength when calcium is added to the solution, and is the cause of the slight decrease of viscosity observed at low calcium concentrations for the sample where no sodium nitrate is added. In order to investigate the effect of very small amounts of free cations, preparations of mixed sodium-calcium alginate were dissolved in water and mixed with solutions containing the desired amount of sodium nitrate. The viscosity as a function of the calcium content is given in Fig. 2.

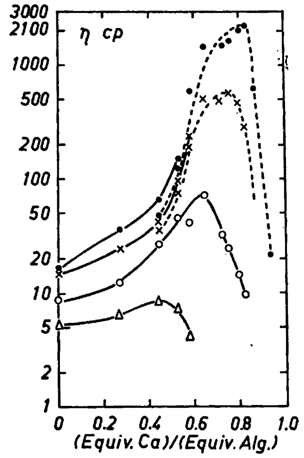

Fig. 2. Viscosity of 0.1 % solutions of mixed sodium-calcium alginates. Preparations of sodium-calcium alginates dissolved in water and mixed with sodium nitrate solutions of different strengths. Alginate from *L. digitata*, Tarva 3/7-57, $[\eta] = 26.0$. $NaNO_3$: ● = 0 N; × = 0.001 N; ○ = 0.005 N; △ = 0.05 N. ——— = Pipette No. 1; – – – – = Pipette No. 2.

A marked decrease of the viscosity and a significant displacement of the maximum towards lower values of calcium concentration is observed when the amounts of sodium ions are increased.

With sodium concentrations as high as 0.4 N, it is seen that the observed viscosity increase is very small, and with higher concentrations it vanishes (see Fig. 1). To investigate the effect of calcium at higher sodium ion concentrations the viscosity technique is thus not applicable. In this region of sodium ion concentration we have chosen to investigate, by centrifugation, the precipitation effect of calcium.

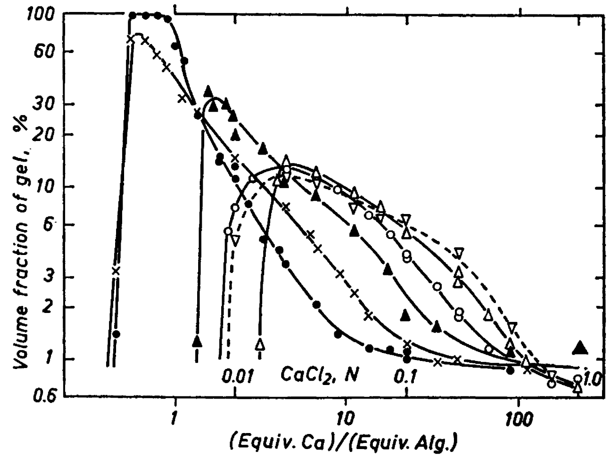

Fig. 3. Centrifugation of 0.1 % solutions of sodium alginate containing different amounts of sodium and calcium chloride. Alginate from *L. digitata*, Tarva 3/7-57, $[\eta] = 26.0$. NaCl: ● = 0 N; × = 0.05 N; ▲ = 0.2 N; ○ = 0.5 N; △ = 1.0 N; ▽ = 3.0 N.

Fig. 3 gives the volume fraction of gel as a function of the calcium concentration in the mixture. The concentration of sodium ions is varied from 0 to 3.0 N. The figure shows that the volume fraction of gel goes through a maximum with increasing calcium concentration in the same way as the viscosity values in Fig. 1. The calcium concentrations giving maximum volume fraction of gel are the same as those giving the maximum viscosity shown in Fig. 1.

In Figs. 1—3 the alginate concentration and intrinsic viscosity have been kept constant. In Tables 3 and 4 the effect of these properties on the viscosity-increase in the presence of calcium ions is investigated. Table 3 shows the effect of alginate concentration on the maximum viscosities and the amount of calcium necessary to obtain viscosity maxima. The sodium nitrate concentration and the intrinsic viscosity are kept constant. In Table 4 the intrinsic viscosity is varied, other conditions being kept constant. The tables show that the amount of calcium necessary to obtain maximum viscosity (expressed as equiv. of calcium to equiv. of alginate) decreases both when the alginate concentration and when the intrinsic viscosity is increased. The ratio between the maximum viscosity and the viscosity without calcium also increased in the same way.

The effect of varying intrinsic viscosities was also investigated by precipitation experiments. The results are given in Fig. 4 and show that the

Table 3. The amount of calcium sufficient to give maximum increase in viscosity at different concentrations of alginate. Alginate: *Laminaria digitata*, Tarva 3/7-57, $[\eta] = 19.6$. Sodium nitrate concentration: 0.05 N.

Concentration of alginate, g/100 ml	0.1	0.2	0.3
Viscosity without calcium, cp	4.77	12.5	35
Added calcium at maximum viscosity, equiv./l	0.00275	0.0035	0.0040
$\frac{\text{Equiv.calcium}}{\text{Equiv.alginate}}$	0.612	0.389	0.296
Equiv. fraction of alginate bound to calcium, Ca_g (calculated values)	0.500	0.356	0.212
The maximum viscosity, cp	12.3	207	3170
$\frac{\text{Maximum viscosity}}{\text{Viscosity without calcium}}$	2.58	16.5	90.6

Table 4. The amount of calcium sufficient to give maximum increase in viscosity at different values of intrinsic viscosities. Alginate: *Laminaria digitata*, Tarva 3/7-57, 0.2 g/100 ml. Sodium nitrate concentration: 0.05 N.

Intrinsic viscosity, 100 ml/g	8.0	9.2	11.6	19.6
Viscosity without calcium, cp	4.31	4.49	5.65	12.5
Added calcium at maximum viscosity, equiv./l	0.0050	0.0045	0.0040	0.0035
Equiv. fraction of alginate bound to calcium, Ca_g (calculated values)	0.483	0.443	0.401	0.356
The maximum viscosity, cp	25.2	32	48	207
$\frac{\text{Maximum viscosity}}{\text{Viscosity without calcium}}$	5.9	7.1	8.5	16.5

maximum volume fraction of gel increases with increasing intrinsic viscosities. The range of calcium concentrations where the water content of the gel is high also increases. The same effect was observed in experiments where the alginate concentration was increased.

In all the experiments above the alginates were prepared from the same alga, *Laminaria digitata*. Fig. 5 shows some centrifugation experiments where alginates from different species of brown algae are compared. The figure shows that the range of calcium concentrations giving a gel with high water content increases in the sequence *Laminaria hyperborea* stipes, *Laminaria digitata, Ascophyllum nodosum.*

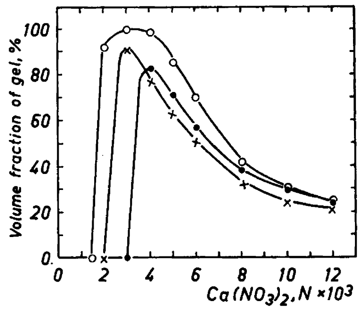

Fig. 4. Centrifugation of 0.2 % solutions of sodium-calcium alginates with different values of intrinsic viscosity. The sodium nitrate concentration is 0.05 N.
Alginate from *L. digitata*, Tarva 3/7-57. ● $[\eta] = 9.0$; × $[\eta] = 14.2$; ○ $[\eta] = 24.5$.

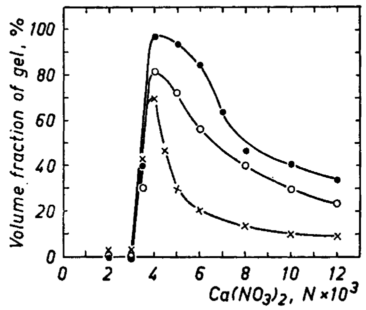

Fig. 5. Centrifugation of 0.2 % solutions of sodium-calcium alginates from different species, all with intrinsic viscosity of 9. The sodium nitrate concentration is 0.05 N. ● = *A. nodosum*, Være 2/3–59; ○ = *L. digitata*, Tarva 3/7-57; × = *L. hyperborea* stipes, Hustad 12/2-59.

In order to determine whether the difference between alginates from different species also appears in the viscosity measurements, alginates from *L. hyperborea* stipes and *A. nodosum* were compared. The results are given in curve 1, Figs. 6 a and 6 b. The time of standing before viscosity measurements in this case was 20 h. Except for a difference in the maximum viscosity, the two alginates seem to be very similar. McDowell,[4] however, shows that on solution of mixed sodium-calcium alginates with low calcium content, alginate from *A. nodosum* gives much higher viscosity than that from *L. hyperborea* stipes. Mixed sodium-calcium alginates were therefore dissolved in solutions of the same salt concentrations as in the previous experiment. Results are given in curve 2, Figs. 6 a and 6 b. Comparing curve 1 and 2 in these two figures, it may be seen that the two different methods of making solutions of mixed sodium-calcium alginates give solutions with different viscosities. At low calcium content the viscosity is higher when the solution is prepared by dissolving mixed sodium-calcium alginate than when calcium is added to a sodium alginate solution. This difference is particularly pronounced for the alginate prepared from *Ascophyllum nodosum.*

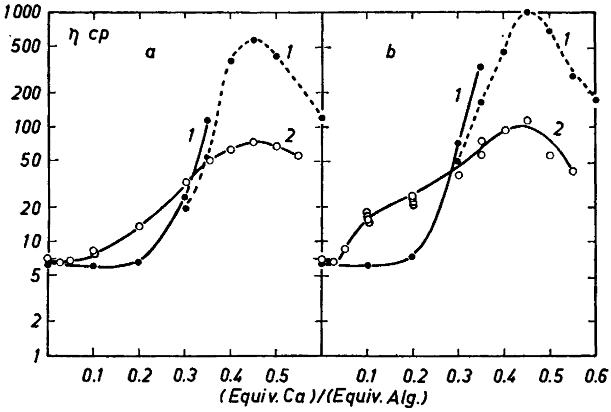

Fig. 6. Viscosity of 0.2 % solutions of sodium-calcium alginates with concentration of free cation ($Ca_l + Na_l$) equal to 0.01 N. Comparison between alginates prepared from different species and between solutions prepared in two different ways.
a) *L. hyperborea* stipes, Vevang 15/12-61, $[\eta] = 10.6$;
b) *A. nodosum*, Flakk 15/8-62, $[\eta] = 10.6$.
Curves 1: Addition of calcium nitrate to solutions of sodium alginate.
Curves 2: Dissolving mixed sodium-calcium alginates.

A comparison between the two methods of preparing solutions of sodium-calcium alginates with an equivalent fraction of calcium, Ca_g, equal to 0.1, was carried out for several alginate samples prepared from *L. hyperborea* stipes, *L. digitata* and *A. nodosum*. For alginates from *L. hyperborea* stipes, the solution prepared by dissolving the mixed sodium-calcium alginate had a viscosity of 1 to 1.7 times the viscosity of solutions prepared by calcium addition. For alginates from *L. digitata* and *A. nodosum* the corresponding ratio was 2 to 5. This difference between the alginates may be caused by the difference in uronic acid composition.

When measuring solutions of mixed sodium-calcium alginates with high viscosities irregular flow was observed and the reproducibility was low. If the solutions were stirred with a highspeed mechanical stirrer the viscosity decreased markedly. The decrease was irreversible as no rise in viscosity was observed when the solutions were left standing. The result of one experiment is given in curve 5, Fig. 7.

Fig. 7 also shows the results of similar determinations of the thixotropic properties of sodium-calcium alginate solutions prepared by addition of calcium to dissolved sodium alginate (curves 1—4, Fig. 7). In all cases an increase of viscosity was observed when the solutions were left standing, which indicated a marked difference between solutions prepared in the two different ways described above. It should be noticed, however, that the viscosity of the solutions represented by curves 3 and 4 (Fig. 7) does not return to the original value on standing, in contrast with the solutions corresponding to curves 1 and 2. The two latter solutions contain less calcium than the amount necessary to give maximum viscosity, the former (curves 3 and 4) contains more calcium.

DISCUSSION

When calcium ions are added to a solution of sodium alginate the viscosity of the solution increases (Fig. 1). The increase in viscosity is due to the formation of a loose gel, as shown by the centrifugation experiment (Fig. 3) and by the marked thixotropy of the mixtures (Fig. 7). Further addition of calcium leads to a decrease of viscosity and gel volume, and the viscosity is irreversibly decreased when the solutions are stirred. The amount of calcium necessary to obtain maximum viscosity and gel volume has been found to be a well reproducible quantity, and for the sake of convenience we shall designate it Ca_{max}.

As shown in Figs. 1 and 2 small amounts of sodium ions displace Ca_{max} towards lower values, while large amounts displace it towards higher values.

A further analysis of the effect of sodium ions on solutions of sodium-calcium alginates requires the equivalent fraction of calcium bound to the alginate to be known. The selectivity coefficient of the ion exchange reaction has been determined for the alginate from *L. digitata*. The selectivity coefficient was found to be 7.5 (concentrations in the gel phase calculated as equivalent fractions and in the liquid phase as normalities). In order to check whether these values of the selectivity coefficient may be used in our case, the amount of calcium in the gel was determined in some of the centrifugation experiments. The calcium content of a volume of the liquid phase equal to the gel volume was subtracted from the total calcium content of the gel phase. This gave

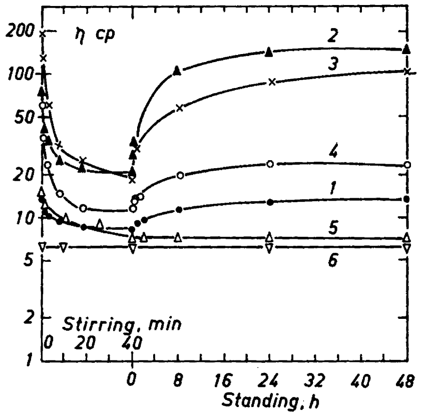

Fig. 7. Thixotropic properties of 0.2 % solutions of sodium-calcium alginates containing 0.01 N of free cations.
Alginate from *A. nodosum*, Flakk 15/8-62, $[\eta] = 10$.
$Ca(NO_3)_2$: 1 = 0.003 N; 2 = 0.004 N; 3 = 0.005 N; 4 = 0.006 N. 5 = Dissolved mixed sodium calcium alginate with $Ca_g = 0.1$. 6 = Sodium alginate.

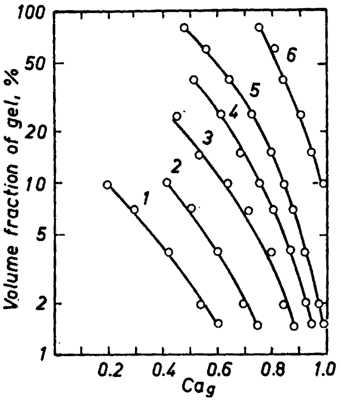

Fig. 8. Volume fraction of gel as a function of Ca_g at different concentrations of free cations (calculated from Fig. 3).
$(Ca_l + Na_l)$: 1 = 1.0 N; 2 = 0.5 N; 3 = 0.2 N; 4 = 0.1 N; 5 = 0.05 N; 6 = 0.01 N.

Table 5. Comparison between values of Ca_g determined analytically and calculated using a chosen selectivity coefficient. Alginate: *Laminaria digitata*, Tarva 3/7-57.

Added salt, equiv./l Sodium chloride	Calcium chloride	Ca_g (determined)	Ca_g (calculated) $k = 1$	$k = 7$	$k = 14$
0	0.01	0.961	0.95	0.97	0.985
0.05	0.01	0.79	0.56	0.78	0.83
0.2	0.01	0.47	0.161	0.435	0.54
0.05	0.02	0.856	0.68	0.855	0.895
0.05	0.03	0.895	0.74	0.88	0.92
0.05	0.04	0.925	0.76	0.90	0.93
0.05	0.05	0.89	0.78	0.91	0.935
0.05	0.10	0.96	0.84	0.94	0.955
0.2	0.02	0.51	0.265	0.56	0.665
0.2	0.05	0.66	0.435	0.715	0.785
0.2	0.07	0.75	0.475	0.735	0.805
0.2	0.1	0.786	0.53	0.780	0.835

the amount of calcium bound to the alginate. This procedure is in order because the ionic strength or the Ca_g value in all cases tested was sufficiently high to make the Donnan effect negligible. Some results are given in Table 5, and compared with calculated values. Three different values of the selectivity coefficient are assumed. The observed results are in fair agreement with the calculation, assuming a selectivity coefficient of 7.

In Fig. 3, both the amount of calcium bound to the alginate (Ca_g) and the concentration of free cations vary when the concentration of calcium or sodium ions is changed. By calculating the Ca_g, using 7.5 as the value of the selectivity coefficient, it is possible to give the volume fraction of the gel for different, constant concentrations of free cations in the solution as a function of Ca_g. The results (given in Fig. 8) thus clearly demonstrate that the volume fraction in all cases decreases with increasing amounts of calcium bound to the alginate when the cation concentration is constant. For a constant value of Ca_g the volume fraction decreases markedly with increasing salt concentrations.

It is often of practical importance to know the conditions necessary for bringing the alginate to a certain stage of insolubility. McDowell observed the start of precipitation visually and found the minimum amount of calcium necessary to bring the alginate to this stage of insolubility. In our experiments we have used the viscosity maximum and the gel volume as a criterion of alginate insolubility. Fig. 9 shows the Ca_g value and cation concentration which give a certain volume fraction of gel. It is seen from the figure that the Ca_g value giving a certain volume fraction decreases when the concentration of free cations increases. Consequently, a low volume fraction of gel (as might be desired when alginate is isolated by precipitation with calcium) may be obtained either with a high Ca_g value or with a high concentration of salt in the solution. If, on the other hand, a loose, voluminous gel is required, the salt concentration must be low. In all cases a decrease in the Ca_g value requires a higher cation concentration if the same volume fraction of gel is to be obtained. It may be noted, that if the curves are extrapolated towards

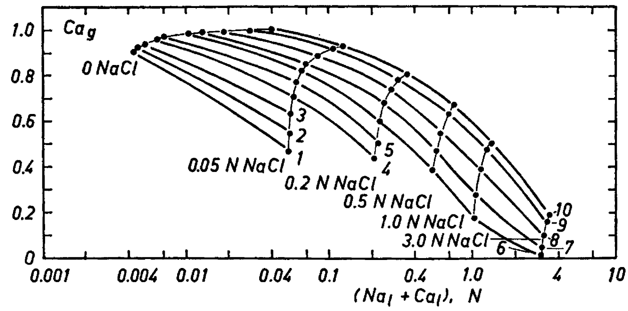

Fig. 9. Ca_g-values giving certain volume fractions of gel as a function of the concentration of free cations (calculated from Fig. 3). Gel volume: 1 = 80 %; 2 = 60 %; 3 = 40 %; 4 = 25 %; 5 = 15 %; 6 = 10 %; 7 = 7 %; 8 = 4 %; 9 = 2 %; 10 = 1.5 %.

$Ca_g = 0$, they approach sodium concentrations of 4—5 N, which are known to give fractional precipitation of alginate.

If Ca_g is calculated for the solutions giving viscosity maxima we find that $Ca_{g\ max}$ is steadily decreasing with increasing sodium chloride concentration (see Fig. 10). It is seen in this figure that at low concentration of free cations almost all the added calcium is bound to the alginate, and the curves for Ca_{max} and $Ca_{g\ max}$ follow each other. At higher sodium ion concentration the excess of calcium ions necessary to reach a certain Ca_g becomes higher, and the total amount of calcium in the mixture increases even though the amount of bound calcium steadily decreases.

The results thus demonstrate that sodium ions have two oppositely directed effects on the calcium-sodium alginates: 1. Displacement of the ion exchange equilibrium:

$$2\ NaAlg + Ca^{2+} \rightleftharpoons CaAlg_2 + 2\ Na^+ \quad (Alg = \text{uronic acid residues.})$$

The amount of calcium necessary to obtain a certain equivalent fraction of calcium in the sodium-calcium alginate increases when the amount of sodium ions in the solution increases.

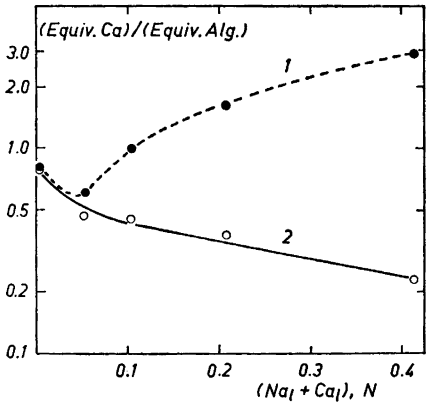

Fig. 10. Amounts of calcium giving viscosity maximum as a function of the concentration of free cations (calculated from Fig. 1).
- - - - = equiv. fraction added, Ca_{max}.
——— = » » bound to alginate, $Ca_{g\ max}$.

2. The "salting-out" effect. The solubility of a sodium-calcium alginate of a fixed composition decreases as the concentration of sodium ions in the solution increases.

It is known that the selectivity coefficient depends on the uronic acid composition of the alginates.[1] Thus the high selectivity coefficient (about 20) of the guluronic acid rich alginate from *L. hyperborea* stipes should, for a certain calcium concentration, lead to a higher $\mathrm{Ca_g}$ value for this alginate than for alginates from *A. nodosum* and *L. digitata* with selectivity coefficients of about 7. The result shown in Fig. 5 indicates that the alginate from *L. hyperborea* stipes needs less calcium to reach a certain volume fraction of gel than alginates from *L. digitata* and *A. nodosum.* This is in agreement with the difference in selectivity coefficient. Calculation of $\mathrm{Ca_g}$, however, shows that for volume fractions of 30 and 50 % the $\mathrm{Ca_g}$ values of the *L. hyperborea* alginate are 0.46 and 0.51 respectively, while the corresponding figures for the alginate from *L. digitata* were 0.58 and 0.71. Thus, the results indicate that even when compared at the same values of $\mathrm{Ca_g}$, the gel formation is different for guluronic- and mannuronic-rich alginates. A certain difference is also observed between alginate from *L. digitata* and *A. nodosum.* This is probably not due to the small difference in selectivity coefficients of the two alginates, but may be connected with the presence of small amounts of a sulphated polysaccharide, ascophyllan [15] in the *Ascophyllum* alginate.

The most marked difference between alginates from different species is observed when mixed sodium-calcium alginates with low calcium contents are dissolved in water. When the mannuronic acid content of the alginate is high, a loose gel is formed. This effect is much less pronounced for alginates with a high guluronic acid content. These observations clearly show, that for many practical purposes where sodium-calcium alginates are used, alginates prepared from different raw materials are not equally suitable.

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