

96. Influence of Ion Exchange on Optical Properties, Shape, and Elasticity of Fully-swollen Alginate Fibres.

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On treatment of fully-swollen, stretched, and optically anisotropic calcium alginate fibres with solutions containing sodium ions, a cation-exchange reaction occurs, which is accompanied by an increase of volume and transparency of the gel, by a loss of birefringence, by axial contraction, and by increase of elasticity. An investigation into the mechanism of elastic deformation of sodium alginate threads is carried out and it is shown that shortening of stretched test pieces involves an increase of entropy. The type of cation exchange is established which is conducive to axial contraction and simultaneous radial swelling of various alginate fibres. An attempt is made to explain the observations from the point of view of changes of shape of chain-like alginate molecules.

EXPERIMENTS already described (*J.*, 1952, 492) show that fully-swollen alginate fibres are cation-exchange materials. It is now established that some of these exchange reactions give rise to marked alterations in the macroscopic shape, optical behaviour, and elasticity of these gels. An attempt is made to show that ionic metatheses can be made responsible for a folding of initially straight segments of the chain-like alginate molecules, and that this, in turn, brings about the over-all alteration of the gel properties. The postulated internal flexibility of the macromolecules, here considered, and the influence of simple electrolytes on the degree of molecular folding, is in concordance with conclusions to be derived from the viscosity work described in the preceding paper.

EXPERIMENTAL

Materials.—In preparing sodium alginate fibres (see *J.*, 1952, 497) the volume and concentration conditions were adjusted in a manner to provide for complete removal of the calcium. The specific gravity of these gels was close to that of the suspension medium.

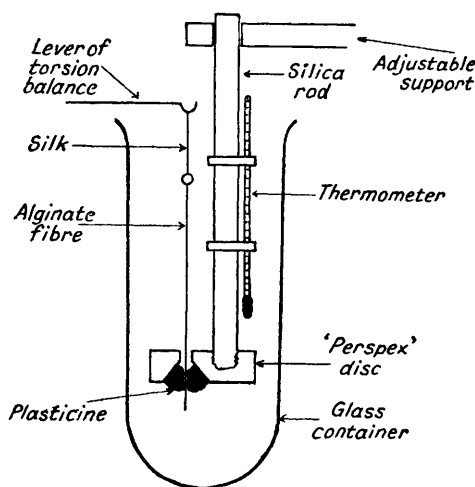
Viscosity of Magnesium Alginate.—The measurements were done as those described in the preceding paper.

Birefringence.—The relative retardation, or the distance by which the slow light wave lags behind the fast light wave in passing through an alginate gel, was measured with an optical system consisting of polarising and analysing nicols, compensator and accessory projection components, the light source being an electric lamp fitted with a daylight filter. The relative retardation could be calculated from the readings on the compensating disc, the tables for conversion being supplied with the instrument. In order to calculate the birefringence (relative retardation/unit thickness of fibre) the fibre diameter was determined either by focusing the microscope to the top and bottom of the fibre and measuring the change of position of the microscope tube, or else with a calibrated eye-piece scale in the ocular of the microscope. The measurements were done at room temperature (mostly 18–20°), the fibre being kept suspended in the relevant swelling medium.

Axial Contraction and Radial Swelling.—Fully swollen fibres were hung over a hook attached to the lever of a torsion balance, the length measurement being done with the help of a ruler, which was at a distance of 5–10 cm. from the fibre. Before being rinsed with the solution to be tested, the gel was treated with water until a single strand was formed. The length was 10 cm. in most experiments, and the accuracy of the length measurements of the fibre before ion exchange had taken place was ± 0.2 cm. Immediately after the initial rinsing with water, the electrolyte solution was passed over the fibre, at a rate of 2–5 cm.³/min.; after known time intervals the flow was discontinued and the weight of the gel was quickly determined after its surface had been dried. In other experiments the fibre was placed in a container, the bottom of which was covered with mercury or with a layer of Vaseline. Length measurements were done with the help of a ruler floating alongside the gel in the solution to be tested, or by means of a travelling microscope. The fibre was kept straight by pushing it against the edge of the ruler or against that of a glass plate.

Elasticity.—One end of a fully-swollen alginate fibre was fixed by a weaver's knot to a silk thread which was connected with the lever of a torsion balance. A little Vaseline was applied to make the silk into a single strand, which was inextensible compared with the swollen gel. The other end of the alginate thread was fitted into a Perspex disc, supported by a silica rod, as shown in Fig. 1. The rod was fitted into an adjustable support by means of which it could be placed into a vessel containing the required suspension medium. The alginate fibre was slightly stretched at the beginning of the tests, a load of 20–50 mg. being applied. The length of the fibre measured from the weaver's knot to the top of the Perspex disc was 10 cm. The

FIG. 1.



glass container could be quickly removed from the position, shown in Fig. 1, and be replaced by another similar vessel, the position of the test piece being unaltered during this operation. Length changes were observed with the help of a travelling microscope focused to a pointer on the lever of the torsion balance. In determining the coefficients of thermal expansion, two glass containers I and II, filled with water or the electrolyte solution, were kept in thermostats the temperatures of which were respectively t_I and t_{II} . The container I was fixed in the position shown in Fig. 1 and the length of the alginate fibre was measured; the container was then quickly exchanged for II and the length measurements were repeated, care being taken to ensure that both sets of determinations related to steady states.

RESULTS

Elasticity.—Typical strain–stress curves of fully swollen calcium and sodium alginate fibres are shown in Figs. 2 and 3. In the former experiments 500 mg. were applied or removed every 10 sec.; and in the other tests, 100 mg. were applied or removed every 5 sec. These time scales were chosen for experimental convenience. A kinetic investigation of the elastic deformation has not been carried out, but it could be shown that the marked difference between the elastic properties of the two alginates cannot be due to the neglect of time effects. Fig. 2 shows that the first application of the load brings about a large amount of irreversible stretching, and the results of the second, third, and fourth cycles (the last is not shown in the figure) are reproducible, though not wholly reversible. These fibres become mechanically preconditioned, the effect being similar to that observed with other materials (see, e.g., Leadermann, *Text. Res.*, 1941, 11, 171). If the calcium alginate fibre is swollen in 5*N*-calcium chloride, instead of water, the first and subsequent cycles are similar. Mean elasticity moduli of "matured" fibres, estimated from the slope of such lines as those indicated by m , in the figures, are given in Table 1. The number average molecular weight of the sodium alginate, used for all the experiments, also for those described in the following sections, was 1.0×10^5 , unless otherwise specified. The fibre diameter (col. 1) relates to the unstretched fibres, and the moduli (E) in col. 5 were calculated with the help of these values. In view of the relatively large experimental errors of the moduli, the alteration of fibre diameter on stretching was not taken into account. The accuracy could be increased by carrying out tests with completely or partly dry gels; but such measurements

are of no relevance for the problems here considered. Attempts were made to measure the modulus of a sodium alginate fibre swollen in 1N-sodium chloride; under these conditions, the slipping was too large, however, to allow reproducible results to be obtained. In determining

FIG. 2. *The influence of load upon the elongation of fully-swollen calcium alginate fibres, of 0.2 mm. diameter and 10 cm. length, kept in water at 20°.*

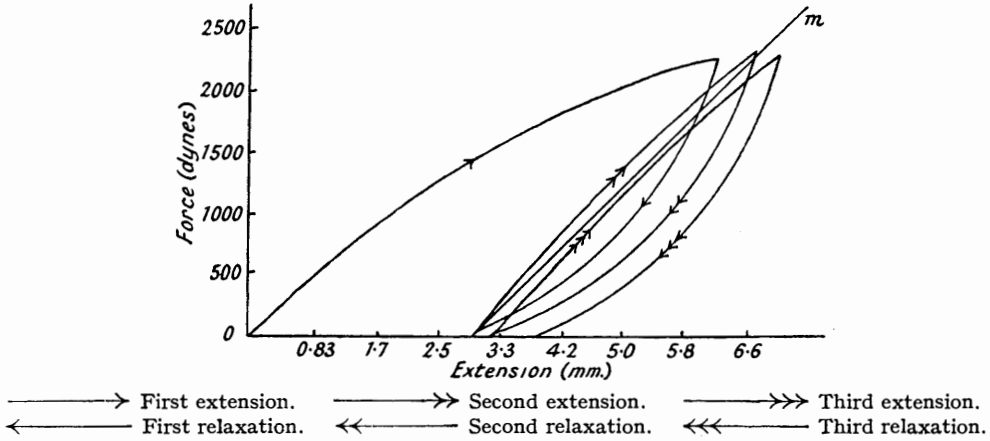
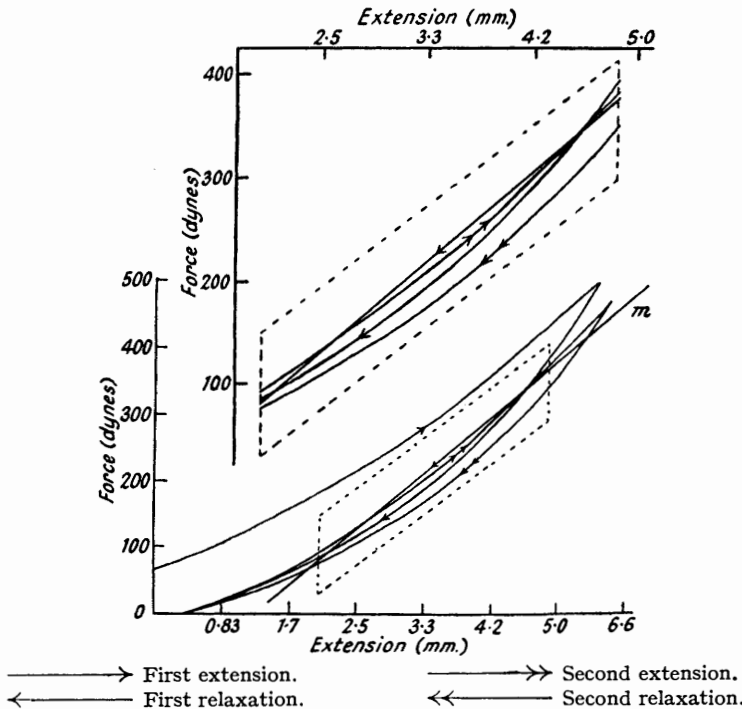


FIG. 3. *The influence of load upon the elongation of fully-swollen sodium alginate fibres, of 0.2 mm. diameter and 10 cm. length, kept in 5N-sodium chloride solution at 20°.*



(Only two cycles are shown; the load-elongation relationships in further cycles are similar to those represented by the graphs.)

the temperature-elongation relationships, at constant load, experiments such as those shown in Fig. 4 were carried out. A summary of these measurements is in the last column of Table 1. A negative sign of α indicates that the fibres shorten on increase of temperature. For a theo-

retical interpretation of these results it is of importance that the volume of sodium alginate gels does not significantly change, on deformation, if the temperature is constant. In the following two sections the results of further elasticity tests are mentioned. In these experiments the initial slope of the strain-stress curve was determined, elongations being usually up to about 1%.

TABLE 1. *Elasticity moduli, E, and linear coefficients of thermal expansion, α , of fully-swollen alginate fibres.*

Diam. (mm.)	No. of cycles	Temp. range	Load (mg.)	$10^{-8}E$ (dynes/cm. ²)	$10^5\alpha$ (degrees ⁻¹)
Calcium alginate fibre in water.					
0.18—0.23	4	20°		2.0 ± 0.5	
	22	9—33	500		$+0.0 \pm 0.1$
	5	11—37	100		$+0.2 \pm 0.1$
	3	10—44	100		$+0.2 \pm 0.2$
	3	10—40	50		$+0.5 \pm 0.3$
Calcium alginate fibre in 5N-CaCl ₂ .					
	4	-7—22		4.0 ± 0.5	
	6	11—43	100		$+0.5 \pm 0.3$
	6	10—46	500		$+0.5 \pm 0.3$
	4	-15—15	500		0.0 ± 0.3
	3	-10—15	200		0.0 ± 0.3
Sodium alginate fibre in 5N-NaCl.					
0.16—0.23	4	-7—22		0.25 ± 0.05	
0.41	6	20		0.15 ± 0.05	
0.18—0.23	27	5—45	50		-4.0 ± 0.5
	3	5—45	80		-4.2 ± 0.8
	24	5—45	100		-3.4 ± 0.5
	2	5—45	130		-2.7 ± 0.8
	14	5—45	150		-3.0 ± 0.6
	12	5—45	200		-2.4 ± 0.4
	14	5—45	250		-1.6 ± 0.4
	4	5—45	300		-1.2 ± 0.4
	5	-7—21	100		-8.6 ± 1
	7	-7—21	250		-4.2 ± 0.5
	Sodium alginate fibre in 2N-NaCl.				
0.2	4	20		0.10 ± 0.05	

Birefringence tests ; effects accompanying the conversion of calcium alginate into the sodium salt. Fully-swollen, sufficiently stretched calcium alginate fibres are birefringent, the refractive index, n_1 , in the direction of the length axis of the fibre being larger than that, n_2 , perpendicular to this direction. Fig. 5 shows that the birefringence is approximately proportional to the reciprocal fibre diameter. The considerable deviations of some of the results from the straight line, shown in Fig. 5, are probably due, *inter alia*, to the fact that the birefringence of different sections of one and the same fibre is not always identical, and that the surface area of most gels is more birefringent than the core. In a test with a fully-swollen calcium alginate fibre, 0.4 mm. in diameter, the birefringence increased, on removal of gel water, from $1.0 \pm 0.1 \times 10^{-4}$ to $6.0 \pm 0.5 \times 10^{-4}$. Other tests showed that the birefringence of dried sodium and calcium alginate threads is similar, while fully swollen sodium alginate is optically isotropic. The graphs *A* and *E* in Fig. 6 show, moreover, that a replacement of the non-permeant calcium by sodium ions gives rise to a gradual disappearance of the optical anisotropy. These experiments were done with sodium chloride solution, but similar observations were made with other electrolytes. Calcium alginate fibres are opaque, but on conversion into mixed calcium sodium alginate, the gel becomes gradually transparent. If the permanent anion is chloride or acetate, the change of birefringence and transparency at the outside of the fibres is similar to the corresponding alterations near the core. If, however, solutions of sodium carbonate, sulphate, or phosphate are used, the birefringence near the outside of the fibre disappears before the whole fibre becomes optically isotropic. The outside portion becomes transparent while the birefringent interior remains opaque, the boundary being sufficiently sharp to measure the gradual increase of the depth of the non-birefringent layer with an accuracy of about 5%. The relationship between this depth and the degree of axial contraction is shown in Fig. 7, which relates to tests done with 1N-sodium carbonate.

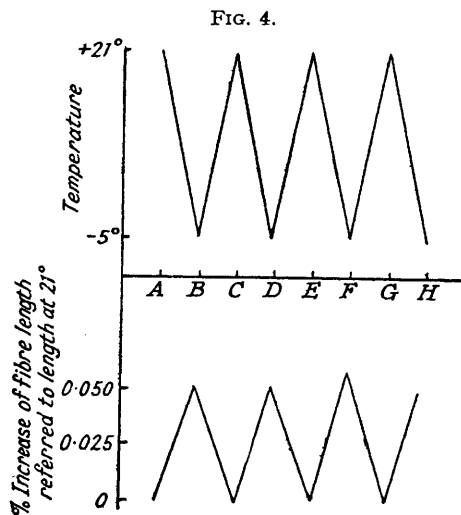


FIG. 4. Change of length of a fully-swollen sodium alginate fibre, of 0.18 mm. diameter and 10.0 cm. length, suspended in 5N-sodium chloride solution and stretched with a load of 100 mg. A, B, C, etc., indicate various heating and cooling cycles between the temperatures indicated in the ordinate of the upper part of the figure. The ordinate of the lower part of the figure indicates the % increase of fibre lengths, on cooling from 21° to -5°, referred to the initial lengths of the test piece.

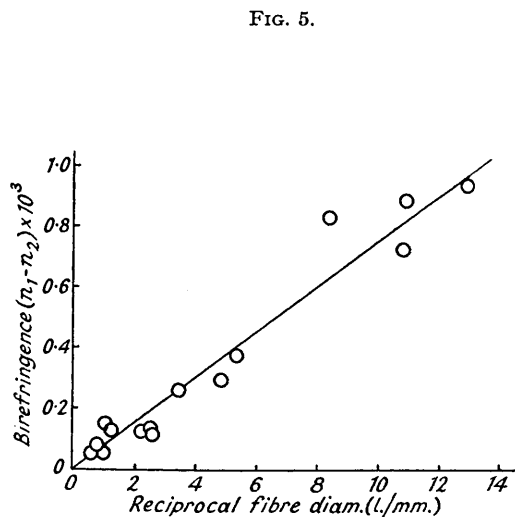


FIG. 5. Birefringence of fully-swollen calcium alginate fibres. The refractive indices n_1 and n_2 relate to daylight. The experimental error is indicated by the diameter of the circles.

FIG. 6. Influence of ion exchange on various properties of alginate fibres.

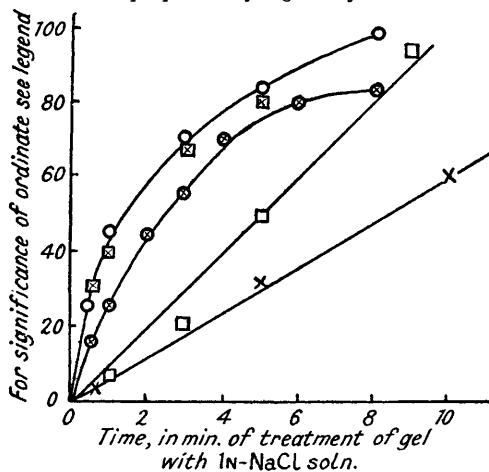


FIG. 6. The graphs relate to tests in which fully-swollen calcium alginate fibres, of 0.4—0.5 mm. diameter, were rinsed at 20° with 1N-sodium chloride solution.

- = (A) = % Non-permeant calcium replaced by sodium ions.
- ⊗ = (B) = % Decrease of length of fibre.
- = (D) = Increase of elasticity defined by $\frac{\text{Elasticity modulus of fully calcified fibre}}{\text{Elasticity modulus of mixed Ca-Na alginate}}$.
- = (E) = % Decrease of birefringence.
- × = (C) = % Increase of volume of gel.

FIG. 7. Loss of birefringence on contraction of calcium alginate fibres brought about by treatment with 1N-sodium carbonate.

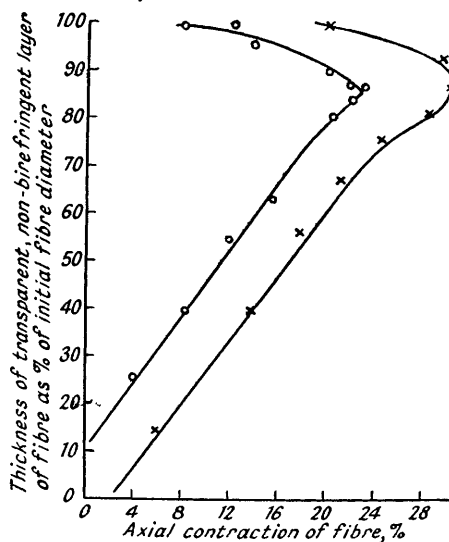


FIG. 7. Diameter of fully-swollen calcium alginate fibre: O = 0.8 mm.; X = 1.1 mm.

On treatment of a calcium alginate thread, fully swollen with water, with 1N-calcium chloride no length or volume change could be detected. If, on the other hand, solutions containing sodium ions are used, the calcium-sodium ion exchange gives rise to marked axial contraction and simultaneous swelling, typical results being represented by the graphs *A*, *B*, and *C*, in Fig. 6. Graph *D* shows that the ion exchange is also accompanied by a considerable increase of elasticity. The error of these measurements is indicated by the size of the various symbols. Table 2 shows that the shape changes depend, under the specified concentration conditions, on the nature of the permeant anion, *e.g.*, chloride or carbonate. It has also been observed that the elasticity increases much more markedly on treatment with 1N-sodium carbonate than with 1N-sodium chloride, the degree of calcium-sodium ion exchange being similar in the two sets of experiments. In 0.1N-solutions, on the other hand, such specific anion effects could not be detected. Table 2 shows, furthermore, that relatively thin fibres, which had been stretched to a considerable extent during their preparation, alter their shape more markedly than thick fibres.

The rate of solution of sodium alginate, formed in these ion-exchange processes, is very small if the reaction mixture is 1N. with respect to sodium chloride, hydroxide, or acetate. In

TABLE 2. *Axial contraction and radial swelling of calcium alginate fibres, on treatment with solutions containing sodium ions.*

Ref. No.	Diam. of fibre before reaction (mm.)	Solution and concn. (g.-equiv./l.)	Increase of vol. of gel on maximum contraction, %	Increase of fibre radius on maximum contraction, %	Maximum axial contraction, %	Non-permeant Ca replaced, %
1		1N-NaCl	30 ± 3	20 ± 0.3	7.0 ± 0.5	100
2		1N-NaOH	40 ± 3	20 ± 0.3	5.0 ± 0.5	
3		1N-NaOAc	6 ± 1	10 ± 0.2	5.0 ± 0.5	
4	0.45	1N-Na ₂ CO ₃	30 ± 3	30 ± 3	20 ± 1	12—15
5		1N-Na ₂ SO ₄	5 ± 1	10 ± 0.2	6.0 ± 0.5	
6		1N-Na ₃ PO ₄	35 ± 3	25 ± 0.3	16 ± 1	
7		0.5N-Na ₂ C ₂ O ₄	40 ± 3	20 ± 0.2	4 ± 0.5	
8		0.5N-NaF	24 ± 2	20 ± 0.2	10 ± 1	
9	0.96	1N-NaCl	5 ± 1	3 ± 0.5	4.0 ± 0.5	100
10	0.28	1N-NaCl	90 ± 6	110 ± 10	10 ± 1	100
11	0.45	0.1N-NaCl	200	—	3 ± 0.5	90

the presence of the other sodium salts, listed in Table 2, and under the same concentration conditions, the sodium alginate dissolves within a few minutes. In runs Nos. 1—3 the axially contracted fibres remained mechanically coherent and the length did not alter for many hours; in Nos. 4—8, on the other hand, the final dissolution of the gel was preceded by a gradual lengthening of the shortened test piece (*cf.* also Fig. 7).

In order to find out whether the axial contraction is reversible, calcium alginate fibres, of 0.2 mm. diameter, were treated as follows. (1) The gel was saturated with 1N-calcium acetate; (2) the permanent electrolyte was washed out with water and the threads were placed in 2N-sodium chloride until maximum axial contraction was reached; (3) the non-birefringent gel was recalcified by bringing it into contact with 1N-calcium acetate. At the end of stage (3) some parts of the thread were slightly birefringent; the fibre was at this stage 7 ± 1% shorter than at the end of stage (1), but 3 ± 1% longer than at the end of stage (2).

Shape changes of various alginate fibres. These are indicated in Table 3; in these experiments the nature of both the non-permeant cation in the gel and the permeant ions in solution was varied. The pH of the solution was 12—13 in the runs with carbonates, tertiary phosphates, and hydroxides; 8.5—9 in tests with bicarbonates, secondary phosphates, citrate, or succinate; and 6—8 in the other experiments. A run with an oxalic acid-ammonium oxalate buffer of pH 5 was also done, a result similar to that at higher pH values being obtained. The fully swollen fibres (diameter 0.3—0.6 mm. in most tests), free from permeant electrolytes, were brought into contact with solutions of electrolytes, the concentration of which was 1N. unless otherwise specified. In run No. 9 the sodium carbonate was dissolved in 25% ethyl alcohol, and in No. 11 the calcium alginate fibres had been made from sodium alginate samples, the number average molecular weight of which was 4 × 10⁴, 6 × 10⁴, 8 × 10⁴, and 1 × 10⁵. Na₄ATP (in No. 10) is an abbreviation for the sodium salt of adenosine triphosphate.

Experiments 1—9. Axial contraction and simultaneous radial swelling of the alginate fibres could not be observed, this being indicated by the negative signs in lines 4 and 8 of the table.

If, for instance, a calcium alginate fibre is rinsed with 1*N*-hydrochloric acid (Expt. No. 1) until the calcium-hydrogen ion exchange is practically complete, the gel remains opaque, the extensibility does not alter to any marked extent, and the decrease in length and radius is respectively 4% and 18%. Similar observations were made on rinsing alginic acid fibres with 4*N*-calcium acetate, or calcium alginate fibres with 5*N*-aluminium sulphate. No shape changes occurred in runs Nos. 5, 6, and 7.

TABLE 3. *Influence of ion exchange reactions on the shape of various alginate fibres.*

Ref. No. Alginate	1 Ca	2 H	3 Ba	4 Ca	5 Ca
Solution	HCl	Ca(OAc) ₂ (4 <i>N</i>)	HCl	Al ₃ (SO ₄) ₃ (5 <i>N</i>)	Cu(OAc) ₂
Axial contraction and radial swelling	—	—	—	—	—
Ref. No. Alginate	6 Ca	7 Ca	8 Na	9 Mg	10 Ca
Solution	AgNO ₃	Ba(OH) ₂	HCl	Na ₂ CO ₃	Na ₄ ATP (S); NaHCO ₃ Na ₄ P ₂ O ₇ (S); sodium citrate (S)
Axial contraction and radial swelling	—	—	—	—	+
Ref. No. Alginate	11 Ca	12 Ca	13 Ca	14 Ca	15 Ca
Solution	K ₂ CO ₃ (S); K ₃ PO ₄ (S); KCl (3 <i>N</i>)	KHCO ₃ ; KH ₂ PO ₄	(NH ₄) ₂ C ₂ O ₄ (S)	Li ₂ CO ₃ (S) (0.3 <i>N</i>)	RbOAc; CsCl
Axial contraction and radial swelling	+	+	+	+	+
Ref. No. Alginate	16 Ca	17 Ca + Mg	18 Ca + Mg	19 Ca	20 H
Solution	Guanidinium carbonate (S)	Na ₂ CO ₃ (S)	Na ₂ CO ₃ (S)	Mg(OAc) ₂	Na ₂ CO ₃ (S); Na ₂ HPO ₄ NaOH (S); NaF (S) Na ₃ PO ₄ (S)
Axial contraction and radial swelling	+	+	+	+	+
Ref. No. Alginate	21 H	22 Ag	23 Ag	24 Al	25 Al
Solution	K ₂ CO ₃ (S); K ₂ HPO ₄ KOH (S); KH ₂ PO ₂	NaCl	K ₂ CO ₃ (S); KCl	Na ₂ CO ₃ (S)	K ₂ CO ₃ (S)
Axial contraction and radial swelling	+	+	+	+	+
Ref. No. Alginate	26 Ba	27 Cu ⁺⁺	28 Cu ⁺⁺	29 Cu ⁺⁺	
Solution	K ₂ CO ₃ (S); K ₂ SO ₄ (S)	K ₂ CO ₃ (S); K ₃ PO ₄ (S) KOH	Na ₂ CO ₃ (S)	NH ₃ (S)	
Axial contraction and radial swelling	+	+	+	+	

Experiments 10—29. These cation-exchange reactions led to simultaneous axial contraction and radial swelling, as indicated by the positive sign in the relevant lines of the table. The axial contraction was at least 3% (in many runs up to 20%), while the gel volume increased at least by 10%. In the tests with solutions containing the salts marked (S), the axially-contracted gel dissolved, the effect being similar to that mentioned in the preceding section. With the other salt solutions, however, the axially-contracted and radially-swollen gels remained coherent. In most runs the initially opaque gels became transparent and the elasticity modulus as well as the mechanical coherence decreased considerably, while the extensibility increased. When a copper alginate fibre was rinsed with 10*N*-potassium carbonate, the resulting gel could be elongated to twice its initial length, and after release the fibre returned to its original length to within $\pm 20\%$.

Experiments 9 and 19. These reactions involve magnesium alginate; for an interpretation of the results the following observations are of relevance. The viscosities of 0.1% aqueous solutions of magnesium and sodium alginate are similar; the elasticity modulus, ϵ , of a magnesium alginate fibre, fully swollen with 25% ethyl alcohol, is respectively 100, 50, and 6 times smaller than the E values of copper alginate, calcium alginate, and alginic acid threads; and on conversion of calcium alginate into the magnesium salt, the birefringence decreases to about 0.05 of its initial value.

DISCUSSION

Calcium-Sodium Ion Exchange.—It can be assumed that the main valency chains in stretched calcium alginate fibres are attached to each other, in broadside-on positions, by salt bridges, *s*, operating between the bivalent calcium and the carboxylate groups of the polyanion. The formation of cross links implies that segments of adjacent alginate chains are relatively straight and approximately parallel to each other, and to the macroscopic fibre axis, this regular arrangement being responsible for the birefringence of the gels. The graphs in Fig. 6 and the results listed in Table 2 show that a replacement of calcium by sodium ions gives rise to the following effects: (1) Increase of fibre diameter, volume, and transparency of the gel; (2) loss of birefringence; (3) axial fibre contraction; (4) increase of elasticity. These observations are consistent with the model for calcium alginate specified above. The cation exchange will remove the lateral bonds, *s*, the univalent sodium not being capable of acting as cross-linking unit; and the devulcanisation can be made responsible for an increase of the distance between segments of adjacent main valency chains. The space thus made available will be filled with the outside solution * which, in

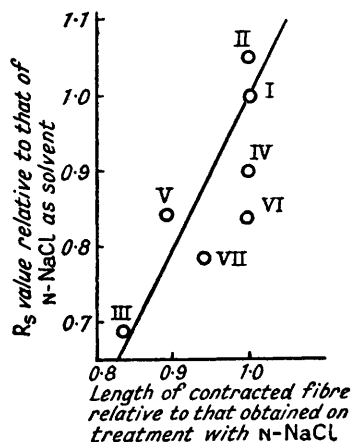


FIG. 8. *Functional relationship between the parameter R_s , as deduced from the intrinsic viscosity of sodium alginate, and the axial contraction of alginate fibres.* (The R_s values are those listed in cols. 3 and 7 of the table in the preceding paper; a similar functional relationship is obtained if the figures in cols. 4 and 8 are taken.)

I = 1N-NaCl; II = 1N-NaOH and 1N-NaOAc; III = 1N-Na₂CO₃; IV = 1N-Na₂SO₄; V = 1N-Na₃PO₄; VI = 0.5N-Na₂C₂O₄; VII = 0.5N-NaF.

turn, explains the effects (1). Further, the breaking of cross links will bring about a removal of geometrical restrictions imposed on the main valency chains, and it is reasonable to assume that the liberated chain segments will take up statistically more probable, folded configurations, and that these alterations of the molecular shape are responsible for the effects (2)—(4).

Some of the results in Table 2 show, however, that on treatment of calcium alginate threads with 0.1N-sodium chloride a substantial shortening in the direction of the length axis does not occur, although about 90% cation exchange had taken place. These observations indicate that a removal of lateral cross links is not a sufficient condition for conversion of stretched calcium alginate fibres into a self-curling system. It appears that a marked folding of the devulcanised segments takes place if an ionic atmosphere around the polyanion is created, which is capable of reducing the intramolecular electrostatic repulsion operating between the carboxylate groupings; and that this is brought about if the electrolyte concentration of the outside solution and of the gel phase is sufficiently high. In this connection it should be noted that some of the results, represented by the figure in the first paper of this series (p. 493), show that the relevant ratios characterising the distribution of sodium ions between the outside solution and calcium alginate are of the order of unity; and that the penetration of permeant sodium ions into the calcium alginate gel is much faster than the replacement of the non-permeant calcium (cf. Mongar and Wassermann,

* In the early stage of the interaction between calcium alginate and a relatively concentrated electrolyte solution, osmotic-pressure gradients must be operative, which could, in principle, give rise to a shrinking of the gel. As this has not been observed it is concluded that the diffusion of the electrolytes from the outside solution into the gel is fast, compared to the migration of gel water.

Discuss. Faraday Soc., 1949, 7, 118). The influence of simple electrolytes on the overall length of partly or completely devulcanised alginate fibres can be compared with that responsible for the electro-viscous effect. The axial fibre contraction and the change of viscosity of sodium alginate, as shown by the numerical values of R_s given in the preceding paper, appear to be due to an interaction between simple electrolytes and the polyanion, which gives rise to a compression of hydrodynamic units of the main valency chains. This hypothesis is supported by the relationship represented in Fig. 8 which shows, on the whole, that those electrolytes which are capable of reducing the numerical value of the parameter R_s are also conducive to marked axial contraction of the alginate fibres. It is not surprising, of course, that the points in Fig. 8 do not fall on a smooth curve, or on a straight line. The R_s values were deduced from the results of tests done with dilute alginate sols, while the figures plotted on the abscissa of Fig. 8 relate to experiments in which the alginate concentration was considerably higher.

It can be regarded as further confirmation of the present hypothesis that those solutions, e.g., 1N-sodium carbonate, which are conducive to strong axial contraction, also give rise to a marked increase of the elasticity; and that in tests with 0.1N-solutions of permeant electrolytes, neither the intrinsic viscosity nor the degree of axial contraction depends to any marked extent on the nature of the permeant anion.

Tests have been described which relate to the question of reversibility of contraction. During the recalcification of sodium alginate threads, under the specified experimental conditions, the formation of intramolecular salt bridges is more probable than during the first preparation of the calcium alginate threads, these materials having been stretched during the sol-gel transformation. Any intramolecular salt bridges which may be formed during the recalcification process will stabilise loops of folded main valency chains and, therefore, a full return to the original length and birefringence, without application of an external force, could hardly be expected.

Quantitative Interpretations of Some of the Elasticity Measurements.—This is done with the help of the following formulæ (cf., e.g., Meyer and Picken, *Proc. Roy. Soc.*, 1937–38, [B], 124, 29):

$$(\partial k / \partial T)_l = - (\partial \Delta S / \partial l)_T \quad \dots \quad (1)$$

in which the temperature coefficient of a force, k , exerted by a deformed material in equilibrium, and at constant length, l , is related to the change of entropy, ΔS , accompanying the mechanical deformation. Over a small temperature range k may be taken to be a linear function of the absolute temperature, T , the curve $k = f(T)$ being replaced by its tangent, the equation of the resulting straight line being

$$k = a + bT \quad \dots \quad (2)$$

The slope b is given by

$$b = (\partial k / \partial T)_l = - (\Delta l / \Delta T)_k / (\Delta l / \Delta k)_T \quad \dots \quad (3)$$

where the two ratios on the right-hand side are obtained from some of the results listed in Table 1. The free energy change, ΔF , and the heat change, ΔH , characterising the mechanical deformation can be estimated from

$$(\partial \Delta F / \partial l)_T = k \text{ and } \Delta F = - \Delta H + T \cdot \Delta S \quad \dots \quad (4)$$

In order to relate these thermodynamic quantities to one number average g.-mol. of the sodium alginate, the number of g.-equiv. in the test piece must be known. This quantity can be calculated from $dr^2 \pi h / M_s$, where ρ is the specific gravity of the fully swollen fibre, r and h are respectively the fibre radius and length, both measured in cm., and M_s is the equivalent weight of sodium alginate. The signs of the α values in the first two sections of Table 1 indicate that calcium alginate fibres lengthen with increasing temperature, which implies a decrease of entropy on contraction of the stretched gels. The experimental errors of these measurements are so large, however, that numerical values of ΔS have not been calculated. The coefficients of thermal expansion of sodium alginate are listed in the last sections of Table 1; the values decrease with increasing load and temperature, the accuracy of each set of figures being between 15 and 30%. It should be noted that all the coefficients

of thermal expansion are negative; these gels, like rubber, shorten on increase of temperature. The measurements enable an approximate estimate to be made of the thermodynamic quantities ΔS , ΔF , and ΔH , which relate, however, only to sodium alginate fibres of 0.2-mm. diameter, fully-swollen with 5*N*-sodium chloride solution, under the specified load and temperature conditions; for instance, the modulus and the coefficient of thermal expansion being taken respectively as $0.25(\pm 0.05) \times 10^8$ dyne/cm.² and $4.0(\pm 0.5) \times 10^{-5}$ degree⁻¹, it can be shown with the help of the above equations that the entropy increase accompanying an axial contraction of 5% of the length of the stretched fibre, amounts to 1.5 ± 0.4 cal./degree-g.-mol., *i.e.*, the term $T\Delta S$ of eqn. (4) equals 0.4 ± 0.11 kcal./g.-mol. at 20°. This value is smaller than the free-energy change, ΔF , which equals 2.0 ± 1.0 kcal./g.-mol. It appears, therefore, that the shortening of these stretched sodium alginate fibres involves an increase both of entropy and of heat content, ΔH being at least 0.45 kcal./g.-mol. For other load and temperature conditions the parameter b , estimated from eqn. (3), will be somewhat different; it can easily be verified, however, that in the whole range that has been tested, the increase of free energy, on contraction, is numerically larger than the term $T\Delta S$. The main conclusion to be derived from these measurements relates to the sign of the coefficient of thermal expansion of these gels. The relevant deductions are independent of the numerical accuracy of ΔH or $T\Delta S$.

The sign of the ΔS value, relating to sodium alginate fibres, can be explained as follows. In the stretched gel the main valency chains are extended, owing to an application of external force; on shortening, the macromolecules will curl, thereby giving rise to an entropy increase. The effect is comparable to that playing a rôle in the axial fibre contraction brought about by calcium-sodium ion exchange. In the calcium alginate thread the main valency chains are kept straight by lateral cross links, the removal of which will give rise to a statistically more probable configuration.

Other Cation-exchange Reactions.—It is of interest to find out whether axial fibre contraction, comparable to that accompanying the calcium-sodium ion exchange, occurs also in the cases of metatheses involving other cations, and the results of the relevant experiments are given in Table 3. The gels can be divided into class (1), which includes magnesium, ammonium, sodium, and potassium alginates, and class (2), which includes calcium, barium, copper, aluminium, and silver alginates and alginic acid. In the salts of the first class the intermolecular forces appear to be great enough to prevent a gel-sol transition in organic solvents, alcohol-water mixtures, or in aqueous solutions of certain electrolytes; if water is used, on the other hand, dissolution occurs. The undegraded gels of class (2) are different in that they swell only to a limited extent in water, or in all other solvents that have been tested, and it is concluded that this is due to salt bridges and oxygen-silver* or hydrogen bonds. Magnesium appears to act as a "unifunctional" ion in the gels here considered, as indicated by the solubility, viscosity, and low birefringence of magnesium alginate.

If fibres containing alginates of class (2) are suspended in solutions of bifunctional cations an ion exchange occurs, but the results of runs Nos. 1—7 of Table 3 indicate that this is not accompanied by axial contraction and simultaneous radial swelling. Another type of cation exchange, not conducive for such shape changes, occurs in runs Nos. 8 and 9, in which alginates of class (1) are suspended in solutions of bi- or uni-functional cations. If, however, solutions of unifunctional cations are brought in contact with fibres made from alginates of class (2), as in runs No. 10—29, a shortening of the test pieces without loss of gel water takes place. These effects can be explained with reference to a mechanism similar to that specified in the preceding sections, if one assumes that the rôle ascribed to the bi- and uni-valent calcium and sodium ions can be fulfilled by the other ions listed in Table 3.

In run No. 1 an exchange involving hydrogen ions occurs. The electrolytic dissociation of the alginic acid is repressed, under the conditions of this experiment, and thus the intramolecular electrostatic repulsion between the carboxylate groupings of the polyanion should decrease very markedly as a result of this ion exchange; it follows therefore, from

* Other compounds containing "bifunctional" silver are silver cyanide or oxalate. The terms "uni" and "bi-functional" are used in the sense defined by Flory (*J. Amer. Chem. Soc.* 1941, **63**, 3091, 3296).

considerations mentioned above, that conditions ought to be particularly favourable for the curling of initially stretched chain segments. Axial contraction with simultaneous radial swelling and increase of transparency and extensibility could not be observed either in run No. 1 or in experiment No. 3, and it appears that the formation of lateral hydrogen bonds between adjacent chains prevents the expected alteration of the molecular shape. The relatively small axial contraction in run No. 1 can be accounted for by a loss of gel water, similar effects having been observed in reactions involving the interchange of bi- or ter-valent ions. This de-swelling is regarded as a salting-out effect which, in turn, may be due to alterations in the heat of swelling, caused by a dissolution of permeant electrolytes in the gel water. Such energy changes are similar to those described in the following paper. As a result of the partial collapse of the gel structure, a relatively large number of segments of adjacent chains may be situated in juxtaposition, thereby being prevented, for stereochemical reasons, from taking up positions of relatively high statistical probability. The increase of birefringence on de-swelling of alginates is perhaps also compatible with the assumption that the removal of gel water involves an increase of molecular orientation. These possibilities are pointed out in order to make it clear why the main deductions referred to in this section are based on the results of experiments in which the axial fibre contraction is accompanied by uptake of water from the outside solution.

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