94. *Absorption of Electrolyte by Alginate Gels without and with Cation Exchange.*

By I. L. Mongar and Albert Wassermann.

Various stoicheiometric relationships characterising the interaction of fully swollen fibrous alginates with simple electrolytes are established. It is shown that these gels are cation-exchange materials, and equilibrium concentration coefficients pertaining to one particular exchange reaction are determined.

It is known that the main valency chains of macromolecules can be induced to change their shape as the result of divers chemical reactions, and that alterations of molecular configuration can give rise to considerable changes of the physical properties of the materials containing the high polymers. In this series of papers experiments are reported which show that a curling up of stretched, chain-like, giant moleculcs, and the accompanying macroscopic effects, can be brought about by stoicheiometrically well-defined simple metatheses. The high polymers used for this work are alginates (polymeric D-mannuronic acid derivatives), and the reactions responsible for alterations of molecular shape are cation-exchange processes. This paper deals with the preparation of fully swollen, cylindrical alginic acid and alginate gels and with the absorption of simple electrolytes by these materials. The results provide the analytical background for effects discussed in a later paper.

EXPERIMENTAL

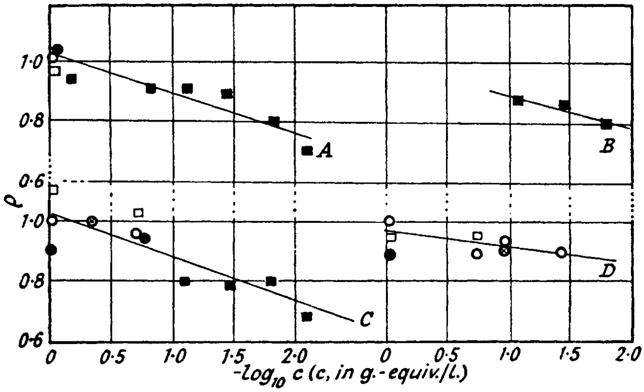
A 5% solution of sodium alginate (dry weight basis) of number average molecular weight 10^5 * was thoroughly freed from dust and air bubbles and extruded in 1N-hydrochloric acid. [The molecular weights of sodium alginate quoted in this series of papers were estimated with the help of equation (2), *J.*, 1952, 497.] A fibrous gel was thus precipitated which, before being fully coagulated, was immediately extended by hand to 5—10 times its initial length and

---

* The intrinsic viscosity of this alginate, dissolved in 0·1N-sodium chloride, is 870 ± 40 cm.^{3}/g., at 20°.

wound on rotating glass cylinders. In order to obtain fibres of sufficiently uniform diameter some practice is required, and the help of a collaborator who controls the speed of rotation of the supports. Similar methods of making alginate fibres have been described (cf. Speakman and Chamberlain, *J. Soc. Dyers Col.*, 1944, **60**, 264; Astbury, *Nature*, 1945, **155**, 667). The fibres were washed, placed in frequently renewed 0·1N-calcium acetate, until quantitative replacement of non-permeant sodium by calcium ions had taken place, washed again until free from permeant electrolyte,† and stored under water at 5°. Alginic acid and the various alginates were made shortly before use, by treating the fully-swollen calcium alginate gel with aqueous solutions of hydrochloric acid, the acetates or chlorides of magnesium, barium, sodium, or copper, silver nitrate, or aluminium sulphate. The treatment with the acid or the metal-salt solutions was frequently repeated until analytical tests showed that quantitative cation exchange had occurred. The gels were finally freed from permeant electrolytes by washing with water or with 25% ethyl alcohol. Before analysis, the surface of the fully-swollen gels was thoroughly dried by means of filter-paper strips; the accuracy of this method, for fibres 100 cm. long and weighing about 1 g., was ±1%. The diameter of these fully-swollen fibres, of known specific gravity, could be calculated from weight determinations, done with a torsion balance, and length determinations, carried out as indicated later (*J.*, 1952, 500). These measurements required less than 30 sec., so the error due to evaporation of gel water was negligible. In some cases the fibre diameter was also estimated with a microscope containing a calibrated eye-piece scale.

Absorption of simple electrolytes by fully swollen alginate gels under conditions not conducive for cation exchange.



Ordinates : Distribution ratio ρ as defined by equation (1).
Abscissæ : Negative logarithm of equilibrium concentration, *c*, of electrolyte in aqueous phase (*c* in g.-equiv./l.).

Symbol *	Temp.	Surface/ volume ratio of fibres (cm.$^{-1}$)	Method of measurement	Symbol *	Temp.	Surface/ volume ratio of fibres (cm.$^{-1}$)	Method of measurement
□	40—60°	100	I	⊗	20	35	I
○	15—20		I	■	20	250	II
●	5—7		I				

* The size of the symbols in the figure indicates the error of these measurements.
(*A*) Alginic acid + HCl; (*B*) Silver alginate + $AgNO_3$; (*C*) Calcium alginate + $CaCl_2$; (*D*) Calcium alginate + NaCl (see p. 496).

Alginic acid was analysed by alkalimetric titration and by estimating the uronic acid carbon dioxide, an apparatus being used similar to that described by Whistler, Martin, and Harris (*Bur. Stand. J. Res.*, 1940, **24**, 13), the two methods giving results which agreed to within ±5%. The metal alginates were rinsed with 1N-hydrochloric or -nitric acid; the relevant cations were thereby dissolved and were estimated in the acid extract by standard methods, the remaining alginic acid gel being analysed as indicated above. Dry-weight was

---

† Here and below, the term " permeant electrolyte " refers to one which can be removed from the alginate gel by sufficiently long washing with water of pH 5. The counter ions, *e.g.*, calcium or sodium, which remain in the gel under such conditions, are termed " non-permeant."

found by drying at 80°/1 mm. Representative results of an analysis of calcium alginate were : Dry weight, 8·1 ± 0·2 g. per 100 g. of fully-swollen surface-dry fibre; Ca, $4{\cdot}84 \pm 0{\cdot}09 \times 10^{-3}$ g.-equiv./g. of dry gel; CO_2H, $4{\cdot}65 \pm 0{\cdot}15 \times 10^{-3}$ g.-equiv./g. of dry gel; Ca/CO_2H, 1·04 ± 0·06; equiv., 208 ± 8. The absence of sodium was established by digesting the calcium alginate with concentrated nitric acid and testing the residue in the usual way with magnesium uranyl acetate.

Absorption measurements of electrolytes, under conditions not conducive for cation exchange, were made as follows : *Method* I. The freely suspended alginate fibre was rinsed with water at a known temperature; at zero time the flow was discontinued and the fibre was rinsed with the solution of an electrolyte which had been kept at the same temperature. When equilibrium was established, the surface of the fibre was quickly dried, the weight was taken, and the permeant electrolyte was removed by rinsing with water, an analysis of this effluent enabling a computation to be made of the distribution ratio, ρ, where

$$\rho = \frac{\text{g.-equiv. of permeant electrolyte absorbed by 1 g. of fully swollen gel}}{\text{g.-equiv. of electrolyte in 1 g. of equilibrium solution}} \qquad (1)$$

Method II. In carrying out measurements according to this method, the surface of the fibres was freed from excess of liquid by centrifuging at about 500 r.p.m., the reaction vessel being an inverted centrifuge cup in which the gel was kept in position by means of a closely fitting perforated Perspex disc. The distance between the axis of rotation and the centrifuge cup was 12 cm. After about 10 mins.' centrifuging, the decrease of weight of the centrifuged gel was less than 0·1% per min. At this stage the fibre was rinsed with water until free from permeant electrolyte; analysis of the initial solution, of the centrifugate, and of the washings, and a determination of the weight of the centrifuged gel, enabled an estimation to be made of the ρ values. The results of the measurements are shown in the figure. In (*A*), (*C*), and (*D*), a number of variables (concentration of solution, temperature, and surface/volume ratio of the gel) were altered. This explains the relatively large deviations of some of the points from the straight lines, the significance of which is merely to indicate, roughly, the general trend of all the distribution ratios of each set. It is not suggested, of course, that there is a linear functional relation between ρ and $\log c$.

The results of experiments pertaining to cation exchange are in Table 1. The runs marked with an asterisk were done in a static system, while in all other tests the conditions were as in method I, the rate of flow of the electrolyte solution varying between 1 and 10 cm.^{3}/min., and the number of g.-equiv. of electrolyte in the solution passed over the fibre being at least twice as large as the number of g.-equiv. of alginate. The replacement ratio in the last column of the table is defined by

$$\alpha = \frac{\text{g.-equiv. of cation removed from original fibre}}{\text{g.-equiv. of cation transferred from solution into gel and combined with alginate}} \qquad (2)$$

The reactions can be classified into four groups from the point of view of analytical procedure. Group 1 comprises Nos. 1, 2, 5—12, 14, 15, 19, 20, 22, 24, and 26—28; in these runs no detectable amount of alginate dissolved (this being checked by total alginate estimation before and after reaction); and it was possible to wash out the low-molecular products of the ion exchange. In run No. 15, for instance, the gel, after being treated with the sodium chloride solution, was washed with water or aqueous ethyl alcohol until it was free from permeant electrolytes. The washing, e_2, was mixed with the effluent, e_1, obtained during the treatment with the sodium chloride solution, the replacement ratio being deduced from calcium determinations in $e_1 + e_2$ and from sodium estimations in the washed gel. Group 2 comprises the reactions Nos. 13, 16—18, 21, and 25 in which some of the alginate formed during the cation exchange dissolved, while a sparingly soluble salt was formed which remained in the gel. In the interaction between calcium alginate and sodium carbonate solution, for instance, the initial operations were as in run No. 15; it was necessary, however, to acidify the joint solutions $e_1 + e_2$, thereby precipitating free alginic acid which was determined as follows. The gel was centrifuged, and the precipitate transferred to a glass filter and converted into copper alginate by treating it with 0·5N-copper acetate. After removal of the permeant electrolyte, the copper alginate was decomposed with N-hydrochloric acid, the alginic acid being estimated by titrating the dissolved cupric ions. The washed calcium sodium alginate gel, contaminated with the calcium carbonate formed during the ion exchange, was introduced into an apparatus suitable for the determination of carbonate carbon dioxide, this being determined after addition of 1N-hydrochloric acid. (For an alternative method of analysis, see Mongar and Wassermann, *Nature*, 1947, **159**, 746.)

The figures in the last two columns of No. 16 of Table 1 could be calculated by taking into account the results of four sets of analyses, namely, the determination of calcium in the solution $e_1 + e_2$, alginic acid, carbonate carbon dioxide, and sodium, the last determination being done in the acid extract of the washed calcium sodium alginate gel. Group 3 comprises reactions 4 and 23, in which a sparingly soluble salt of non-stoicheiometric composition is formed. In No. 23, for instance, the basic copper carbonate, precipitated in the gel, had to be determined by estimating the carbon dioxide evolved on addition of 1N-hydrochloric acid and by analysing a washed precipitate obtained by mixing 0·4N-copper acetate with an excess of 2N-sodium carbonate. It was furthermore necessary to analyse the sodium in the acid extract of the washed copper sodium alginate. Group 4 is represented by the reaction between alginic acid and sodium hydroxide, the replacement value being obtained in this case from the results of alkalimetric titrations. A mixed calcium sodium alginate, on being fully recalcified with 0·1N-calcium acetate, does not release a detectable quantity of hydrogen ions.

TABLE 1. *Absorption of simple electrolytes by fully-swollen alginate gels under conditions conducive to cation exchange* (Temp. ~20°).

Ref. No.	Gel	Fibre diam. (mm.)	Soln.	Concn. (g.-equiv./l.)	Time of absorption (sec.)	Non-permeant cation replaced (%)	Replacement ratio (a)
1	Alginic acid	0·5	$Ca(OAc)_2$	1·0	100—200	100	1·0 ± 0·05
2		0·7	NaCl	1·0	30	16	1·0 ± 0·05
3		0·8	NaOH	1·0	100—200	100	1·0 ± 0·05
4	Aluminium alginate	0·4	Na_2CO_3	0·2	30	49	1·3 ± 0·2
5	Barium alginate	0·5	HCl	1·0	600—800	100	1·0 ± 0·05
6	Calcium alginate	0·4	$AgNO_3$	1·0	25	85	0·95 ± 0·05
7		0·5	$Al_2(SO_4)_3$	2·6	30	71	2·0 ± 0·3
8		0·5	$Ba(OH)_2$	1·0	100—200	100	1·0 ± 0·5
9		0·4	$Cu(OAc)_2$	0·6	30	84	1·0 ± 0·05
10		0·5	HCl	1·0	600—800	100	1·0 ± 0·05
11		0·4	KCl	4	30	52	1·1 ± 0·2
12		0·4	$Mg(OAc)_2$	2·0	25	28	0·9 ± 0·1
13		0·5	Na_4ATP ‡	0·9	30	40	0·8 ± 0·2
14		0·4	NaOAc	2·0	20	44	0·9 ± 0·1
15		0·4	NaCl	1·0	30	31	0·9 ± 0·1
16		0·5	Na_2CO_3	2·0	20	20	1·1 ± 0·1
17		0·4	$Na_2C_2O_4$	0·33	20	30	1·1 ± 0·1
18		0·5	NaF	0·25	10	52	$\leqslant 1$
19		0·5	$NaHCO_3$	1·0	30	12	1·0 ± 0·1
20		0·5	NaOH	1·0	30	10	1·9 ± 0·2
21		0·5	Na_3PO_4	1·0	30	66	1·1 ± 0·1
22		0·5	Na_2SO_4	2·0	30	47	0·8 ± 0·2
23	Copper alginate	0·4	Na_2CO_3	2·0	30	71	0·8 ± 0·2
24 *	Magnesium alginate	0·5	NaOAc	2·0	100—200	100	1·0 ± 0·1
25	Silver alginate	0·5	NaCl	0·1	15	52	1·0 ± 0·1
26 *	Sodium alginate	0·8	HCl	1·0	600—800	100	1·0 ± 0·05
27	Sodium calcium † alginate	0·5	$Ca(OAc)_2$	1·0	200—400	100	1·0 ± 0·1
28	Sodium copper † alginate	0·5	$Cu(OAc)_2$	1·0	200—400	100	1·0 ± 0·1

† These gels were prepared by treating calcium or copper alginate with 1N-sodium chloride until about 50% replacement had taken place; the gels so obtained were washed with 25% ethyl alcohol–water.

‡ This symbol is an abbreviation for the sodium salt of adenosine triphosphate.

The reversible metathesis, calcium alginate + sodium chloride $\rightleftarrows$ mixed calcium sodium alginate + calcium chloride, is of particular importance for some of the experiments described in the following papers. This ion exchange is schematically represented as follows :

$$\mathrm{Ca_g}^{\bullet\bullet} + 2\mathrm{Na}^{\bullet} \rightleftarrows 2\mathrm{Na_g}^{\bullet} + \mathrm{Ca}^{\bullet\bullet} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\mathrm{Ca_g}^{\bullet\bullet}$ and $\mathrm{Na_g}^{\bullet}$ are symbols for the non-permeant ions combined with the alginate residue. An equilibrium coefficient, characterising (3), can be defined by the expression

$$K = [\mathrm{Ca_g}^{\bullet\bullet}][\mathrm{Na_s}^{\bullet}]^2/[\mathrm{Na_g}]^2[\mathrm{Ca_s}^{\bullet\bullet}] \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the subscripts indicating that the relevant concentrations refer respectively to the gel phase and to the aqueous solution.

The equilibrium coefficients were determined by two methods : (*a*) Surface-dry, fully-swollen calcium alginate fibres, of known weight, were placed in a known volume of a sodium chloride solution, the concentration of which had been determined. After equilibrium, the calcium chloride concentration in the supernatant liquid was estimated. (*b*) The supernatant liquid was almost completely removed by centrifuging; the remaining gel was extracted with hydrochloric acid, calcium estimations being done in the centrifugate and in the acid extract. The results of these measurements are in Table 2. Tests under comparable concentration and volume conditions, done at 6·5°, 24°, 49°, and 65°, showed that K decreases with increasing temperature.

TABLE 2. *Concentration equilibrium coefficients,* K, *characterising the reaction between fully swollen calcium alginate gels and sodium chloride solution* (Temp. ~20°).

Method	No. of runs	Fully-swollen, surface-dry calcium alginate fibres (g.)	Diam. of fibre (mm.)	Vol. of soln. (cm.^{3})	Equil. concn. of solution : NaCl	$CaCl_2$	K *
a & *b*	10	0·16—1·0	0·2—0·8	5—11	0·8—1·0	0·002—0·015	60 ± 10
b	2	1·0	0·3	4—10	0·7—0·8	0·01—0·016	48 ± 6
a	5	0·16—1·0	0·2—1·0	10—50	0·4—0·6	0·006—0·0017	30 ± 10
b	6	0·48—1·2	0·3—0·9	10—50	0·06—0·19	0·0016—0·0024	10 ± 3
b	2	1·0	0·31	50	0·02—0·05	0·0004—0·0009	10 ± 3

* These K values are dimensionless because the concentration units of the various factors occurring in equation (4) are identical.

DISCUSSION

There is no marked difference between the distribution ratios, ρ, relating to the interaction of alginic and hydrochloric acid and those relating to the electrolyte absorption by the alginates (see figure), although the ionisation of the free acid is strongly repressed at pH values below 2 (Saris and Schofield, *Proc. Roy. Soc.*, 1946, *A*, **185**, 431). In three of the systems characterised by the graphs in the figure the permeant and the non-permeant cations are identical, while in system (*D*) the absorption of sodium chloride by the gel is followed by an ion-exchange reaction. It has been found (Mongar and Wassermann, *Discuss. Faraday Soc.*, 1949, **7**, 118) that the attainment of a stationary sodium chloride concentration in the gel is faster than the replacement of the non-permeant calcium by sodium ions and, therefore, the distribution ratios relating to this particular system could also be estimated. The distribution ratios vary between 0·68 and 1·04, although the electrolyte concentration in the outside solution varies over 100-fold. In the whole range, the stationary concentration of the permeant electrolytes in the gel is not markedly smaller than the electrolyte concentration in the outside solution.

The figures in Table 1 show that fully-swollen alginate gels are cation-exchange materials. In those runs in which the replacement ratio, α, is unity, within the limits of the experimental errors, a membrane hydrolysis could hardly play a predominant rôle. This view is consistent with observations mentioned on p. 495 which pertain to the recalcification of a mixed sodium calcium alginate gel; for, if the replacement of calcium by sodium ions, leading to the mixed alginate, had been accompanied by an uptake of hydrogen ions, the latter species would probably be released during the final recalcification. No such effect, however, could be detected. Membrane hydrolysis could operate, on the other hand, in reactions in which the replacement ratio differs markedly from 1, *e.g.*, in run No. 7 of Table 1. Other effects, however, could also play a rôle.

Turning now to the equilibrium measurements, the results of which are in Table 2, it should be noted that concentrations, not activities, are used in (4), and, therefore, it is not surprising that K depends on the electrolyte concentration. Equation (4) can be written in the form

$$X^3 + WV[\mathrm{NaCl_s}]^2X/4K - yWV[\mathrm{NaCl_s}]^2/4K = 0 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where X is the number of g.-mol. of permeant calcium in the equilibrium solution, y is the number of g.-mol. of calcium in the original gel, W is the volume of the gel, and V is that of the solution. The expression, in conjunction with the knowledge of K, can be utilised in order to adjust the experimental conditions prevailing during the conversion of calcium alginate in such a manner as to introduce a specified quantity of sodium ions into the gel.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES; and THE BIOPHYSICS RESEARCH UNIT,
UNIVERSITY COLLEGE, GOWER STREET, LONDON, W.C.1. [*Received, May* 10*th*, 1951.]