774. *Influence of Counter-ion Fixation on Molecular Weight and Shape of a Polyelectrolyte.*

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Weight-average molecular weights M_W, interaction constants B, radii of gyration ρ, and viscosity numbers of sodium, potassium, and magnesium alginates have been measured. On passing from the sodium to the magnesium salt, M_W and ρ increase, while B decreases. These changes occur if magnesium alginate is prepared in the gel phase, where the polyanions are close together. If the sodium–magnesium ion exchange is carried out in dilute solution, a different magnesium alginate, of lower molecular weight, is obtained. On conversion of sodium alginate gel into potassium alginate, M_W and B do not change significantly. Electrical conductance and transference measurements, made with sodium and magnesium alginate solutions, show that the fraction of free counter-ions in magnesium alginate is relatively small. These results, together with the influence of chemical and physical conditions on the viscosity numbers of these polyelectrolytes, show that magnesium alginate prepared under appropriate conditions is characterised by larger and more compact polymeric anions and by stronger counter-ion bonding than occur for sodium alginate. An attempt is made to explain these observations.

VISCOMETRIC investigation of solutions containing polyacids,[1] polybases,[2] or polyampholytes [3] has shown that the molecular shape of polyelectrolytes depends on the pH. It was established,[4] further, that the pH influences also the macroscopic properties of the fibres made from the polyacids, the solution behaviour of which had been investigated. Some of these effects are a confirmation of a hypothesis due to Meyer.[5]

Under biological conditions, polyelectrolytes are frequently in contact with buffered solutions. It is of interest, therefore, to find out whether stoicheiometrically defined, simple, and reversible reactions, which do not involve an alteration of pH, can change the shape of polyelectrolytes on a molecular and macroscopic level. For this reason solutions of sodium alginate [6] and fibres [7] made from various alginates have been studied, and it has been found that the replacement of multivalent by univalent counter-ions affects the molecular shape of the alginate, which in turn influences the small-angle X-ray scattering, macroscopic length, birefringence, and elastic properties of the fibres. The effects are interpreted as being due to the rupture of salt bridges formed between adjacent alginate chains by the multivalent counter-ions, thereby producing " melting " of ordered zones, an effect which also operates in the non-isothermal shrinkage of collagen [8] and in the contraction of oriented keratin, epidermis protein or fibrin,[9] fibrous natural rubber,[10] or Polythene.[11]

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[1] Kuhn, Kuenzle, and Katchalsky, *Bull. Soc. chim. belges*, 1948, **57**, 421; Hermans and Overbeek, *ibid.*, p. 154; *Rec. Trav. chim.*, 1948, **67**, 761; Katchalsky, Kuenzle, and Kuhn, *J. Polymer. Sci.*, 1950, **5**, 283; cf. Staudinger, " Die hochmolekularen organischen Verbindungen," Springer, Berlin, 1932, p. 363; Staudinger and Trommsdorff, *Annalen*, 1933, **502**, 201; Kern, *Z. phys. Chem.*, 1938, *A*, **181**, 283.

[2] Fuoss and Strauss, *J. Polymer Sci.*, 1948, **3**, 602; *Ann. New York Acad. Sci.*, 1948, **51**, 836; Fuoss, *J. Polymer Sci.*, 1948, **3**, 603; Fuoss and Cathers, *ibid.*, 1949, **4**, 112.

[3] Katchalsky, *J. Polymer Sci.*, 1951, **7**, 393.

[4] Kuhn, *Experientia*, 1949, **5**, 318; Katchalsky, *ibid.*, p. 319; Breitenbach and Karlinger, *Monatsh.*, 1949, **80**, 312; Kuhn, Hargitay, Katchalsky, and Eisenberg, *Nature*, 1950, **165**, 515; cf. Flory, " Principles of Polymer Chemistry," Cornell Univ. Press, 1953, p. 584.

[5] Meyer, *Biochem. Z.*, 1929, **214**, 272.

[6] Harkness and Wassermann, *J.*, 1952, 497.

[7] Mongar and Wassermann, *Nature*, 1947, **159**, 746; *Discuss. Faraday Soc.*, 1949, **7**, 118; *J.*, 1952, 500; MacArthur, Mongar, and Wassermann, *Nature*, 1949, **164**, 110.

[8] Gustavson, " The Chemistry and Reactivity of Collagens," Academic Press, New York, 1956, p. 211.

[9] Rudall, Symposium on Fibrous Proteins, *Soc. Dyers and Colourists*, 1946, **62**, 15.

[10] Oth and Flory, *J. Amer. Chem. Soc.*, 1958, **80**, 1297.

[11] Mandelkern, Roberts, Diorio, and Posner, *J. Amer. Chem. Soc.*, 1959, **81**, 4148.

These experiments are mentioned because they show that the solution properties of polyacids fully neutralised by uni- and bi-valent counter-ions are of interest. It is important to compare the counter-ion association in such systems, and to find out whether the nature of the counter-ion influences the size and shape of the polyanion. Such an investigation is now described. As in the earlier work,[6,7] the polyelectrolyte was an alginate, the repeating units of which are D-mannuronic and L-guluronic acid residues.[12] The counter-ions were sodium, potassium, and magnesium. The last was chosen because magnesium alginate is soluble in water, while most alginates containing multivalent counter-ions are insoluble gels. Similar precipitates are formed if other polyacids are completely neutralised with bivalent cations.[13]

EXPERIMENTAL

Commercial sodium alginate was freed from heavy-metal impurities by treatment with ion-exchange resins in the sodium form or with a dilute solution of the sodium salt of ethylenediaminetetra-acetic acid. Some samples were dissolved in 0·1M-sodium chloride, centrifuged, and fractionally precipitated by gradual addition of ethanol or of 4M-sodium chloride. The gels were centrifuged off, washed free from permeant electrolytes with aqueous ethanol or acetone, and dried *in vacuo*. Four types of magnesium alginate were prepared. (1) Fully swollen alginic acid, obtained from commercial sodium alginate and N-hydrochloric acid, was treated with an equivalent quantity of moist magnesium carbonate. (2) Solid commercial sodium alginate was treated with 2M-magnesium acetate, the alginate concentration during the cation exchange being about 7 equiv. per l. of gel. When the sodium was completely replaced, permeant electrolytes were removed by dialysis against aqueous acetone; the magnesium alginate was precipitated with acetone, centrifuged off, and dried as described above. (3) 0·2—0·4% Solutions of magnesium alginate, of type (2), either in water or in 0·01—0·04M-magnesium chloride, were centrifuged for 4 hr. at 2×10^4 *g* and 20°, then a small quantity of precipitate that separated was discarded; analyses and other tests showed that this precipitate was a magnesium alginate of relatively high molecular weight, not an impurity. (4) Solutions (0·1—0·3%) of commercial sodium alginate in water or in 0·1N-sodium chloride were dialysed against 0·01—0·04M-magnesium chloride until complete cation exchange had occurred. Potassium alginate was prepared as magnesium alginate, type (2), except that 2M-potassium acetate was used. In experiments in which alginate solutions free from permeant electrolytes were used, dialysis was continued until the specific electrical conductance of the outside solution was below $10^{-5}\Omega^{-1}$ cm.$^{-1}$. In some of these dialyses the stirred outside solution contained a mixed ion-exchange resin of the type used for the simultaneous removal of cationic and anionic impurities.

Analysis of the alginate showed that 1·00 equivalent of permeant sodium, potassium, and magnesium was combined with 1·00 equivalent of alginate.* In carrying out the transference tests, sodium was determined flame-photometrically, after alginic acid had been removed by precipitation with 2N-hydrochloric acid, the excess of which was evaporated from silica beakers. Magnesium was titrated with disodium dihydrogen ethylenediaminetetra-acetate at pH 10 (ammonium chloride–ammonia buffer), with Eriochrome Black T as indicator. Alginate concentrations were determined as follows. The solution was added, with stirring, to an excess of a nearly saturated calcium chloride solution, thereby precipitating calcium alginate; this was washed free from soluble electrolytes and dissolved in an excess of EDTA, the pH being adjusted to 10 with the buffer mentioned above. The EDTA which was not consumed in the reaction with calcium alginate was back-titrated with magnesium chloride. All these analyses were made on a weight basis. The accuracy of the sodium determinations was ±1% and that of the magnesium and alginate analyses ±0·2—0·5%.

For light-scattering tests, 0·2—0·4%, solutions of sodium, potassium, or magnesium alginate, of type (1) or (3), in 0·1M-sodium or -potassium chloride or 0·01—0·04M-magnesium chloride were

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* Equivalents of alginate or alginate normalities (see below) were deduced from titrations; a knowledge of the equivalent weight of alginic acid is not required.

[12] Hirst, Jones, and Jones, *J.*, 1939, 1880; Astbury, *Nature*, 1945, **155**, 667; Fischer and Doerfel, *Z. physiol. Chem.*, 1955, **302**, 186.

[13] Deuel and Solms, *Kolloid Z.*, 1951, **124**, 65; Wall and Drenan, *J. Polymer. Sci.*, 1951, **7**, 83.

centrifuged as specified above. The middle portion of the centrifuged solution was removed by a pipette, which operated without disturbing a precipitate. In some tests the centrifuged solution was filtered, under slight over pressure, through sintered glass (porosity 3 or 4). Solutions of magnesium alginate of types 2 and 4 were not in all cases centrifuged, but were then either filtered through sintered glass or prepared from dust-free starting materials. Magnesium alginate of type 4, for instance, was made by dialysing a dust-free centrifuged sodium alginate solution from a dust-free semipermeable container. Pipettes, filters, and light-scattering cells were rinsed with dust-free acetone and dried under conditions preventing contamination. Solutions were checked for purity by observations at low angles, relative to a light beam focused on the centre of the light-scattering cell.

Calibration of the Brice–Phoenix light-scattering instrument has been described.[14] The Cabannes correction factors were determined but were found to be not significant. Direct transmission measurements were carried out with cells of optical path-lengths between 1·0 and 10 cm. and a Unicam S.P. 500 instrument, the precautions mentioned by Doty and Steiner [15] being observed. Refractive-index increments were determined in a Rayleigh interferometer modified for measurements with monochromatic light. Viscosities were measured in a Flory viscometer [16] in which the rate of shear, $G_{\text{max.}}$, could be varied from 2000 to 200 sec.$^{-1}$, or in a Couette instrument, covering shear rates from 20 to 0·5 sec.$^{-1}$. Rates of shear, designated below by G, were either measured in the Couette viscometer or they were $G_{\text{max.}}$ values multiplied by 2/3.

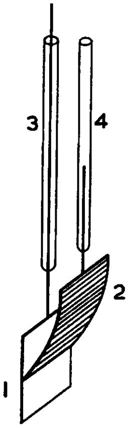

FIG. 1. *Anode used for transference measurements with alginate solutions.* (1) *Platinum sheet* 1 × 1 *cm.*, *connected to battery*; (2) *platinum scraper not connected to battery. The glass tubing* (3) *and* (4), *held together by a rubber band, dipped loosely into a circular opening of the anode compartment of the transference cell. Contamination by dust was avoided by a paper shield over the apparatus.*

The transference cell was of the horizontal type; [17,18] the two compartments were separated by a sintered-glass disc of 3·0 cm. diameter and the distance between the electrodes was 13·5 cm. The transference cell was mounted on a frame which could be removed from a water-thermostat bath without much vibration. The total quantity of electricity which passed through the transference cell was calculated from current–time observations and frequently checked with a calibrated gas-coulometer. The potential across the electrodes was measured with a voltmeter. The current was kept constant by adjusting a rheostat in series with the transference cell. The anode is shown in Fig. 1. Precipitation of alginic acid during the electrolysis occurred on the scraper rather than on the electrode. If the anode becomes coated with alginic acid (which occurred in tests without the scraper) adjustment of the current, as mentioned above, is not possible. The cathode was a square platinum sheet (1 × 1 cm.); in experiments with magnesium alginate it was not significantly coated with hydroxide, which was precipitated at the bottom of the cell. At the end of the transference measurements precipitates in the anode and the cathode compartment were dissolved by adding known

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[14] French, Roubinek, and Wassermann, *J.*, 1961, 1953.

[15] Doty and Steiner, *J. Chem. Phys.*, 1950, **18**, 1214.

[16] Fox, Fox, and Flory, *J. Amer. Chem. Soc.*, 1953, **75**, 1901.

[17] Huizenga, Grieger, and Wall, *J. Amer. Chem. Soc.*, 1950, **72**, 2636; Wall, Ondrejcin, and Pikramenou, *ibid.*, 1951, **73**, 2821; see also Martin and van Winkle, *J. Phys. Chem.*, 1959, **63**, 1539.

[18] Wall, Terayama, and Techakumpuch, *J. Polymer Sci.*, 1956, **20**, 477.

quantities of standard alkali or acid; back-titration after complete dissolution (which sometimes required several hours, although the solution was stirred) indicated the pH changes. Weighed portions of the neutral solutions were used to determine the sodium, magnesium, and alginate content. The results, together with a knowledge of the concentration of the original solution and of the weight of the solution in the anode and the cathode compartment, enabled a calculation to be made of the net change of sodium, magnesium, and alginate. The specific electrical conductances of the alginate solutions were measured by means of a conventional A.C. bridge, operating at 10^3 cycles sec.$^{-1}$.

Calculations.—If the solution contained water (component 1), alginate (component 2), and permeant chloride (component 3), the weight average molecular weight M_W of the alginate was calculated from

$$\frac{Kc_2}{R_\theta} = \frac{1}{(1 - D)^2}(A + 2Bc_2), \tag{1}$$

$$D = \frac{\partial n/\partial c_3}{\partial n/\partial c_2}\frac{M_3}{M_W}\frac{a_{23}}{a_{33}} \tag{2}$$

and

$$M_W = \frac{1}{A}\frac{1}{P_{(\theta)}}, \tag{3}$$

where K is a constant, depending on the wave length, λ, of the incident light and on the refractive indices n_0 and n of solvent and solution, R_θ is the Rayleigh ratio at angle θ, corrected for light scattered by the solvent, c_j is the concentration of component, j, M_3 is the molecular weight of the permeant chloride, and a_{jk} is given by $(1/\boldsymbol{R}T)(\partial\mu_j/\partial m_k)$, μ_j and m_k being the chemical potential and molarity of the component indicated by the subscript; $\partial n/\partial c_j$ and a_{jk} were calculated from refractive indices previously [19] determined and from those listed below and from membrane equilibria of sodium, potassium, or magnesium alginate in solutions of sodium, potassium, or magnesium chloride.* The correction factor $(D - 1)^{-2}$ is 1·3 ± 0·1 for sodium or potassium alginate in 0·100M-sodium or -potassium chloride, 1·1 ± 0·1 for sodium alginate in 0·500M- or 1·00M-sodium chloride, and for magnesium alginate in 0·02—0·04M-magnesium chloride. The particle scattering factor, $P(\theta)$, was calculated from the intrinsic dissymmetry, $[Z']$, if it was below 1·6. The alginates were taken to be polydisperse coils, the difference between linear and branched structure not being significant [21] in this range of $[Z']$ values. If the intrinsic dissymmetries were larger than 1·5, the M_W and B values were calculated without estimation of $P(\theta)$, by extrapolation of R_θ to zero angle. If the molecular weight of magnesium alginate was sufficiently large it was also computed from

$$\frac{Hc_2}{\tau} = \frac{1}{M_W Q} + 2Bc_2, \tag{4}$$

where H is $(16\pi/3)K$, τ is the turbidity of the solute, determined by direct transmission measurements, and Q is the particle dissipation factor.[15] If $(Hc_2/\tau)_{c_2 \to 0}$ is plotted [22] against $(n_0/\lambda)^2$, the intercept of the resulting graph gives $1/M_W$. The interaction constant, B, is given by

$$2B = [\partial\,(Kc_2/R_\theta)/\partial c_2]_{c_2 = \text{small}}^{\theta = 90^\circ\ (\text{or} \to 0)};\quad 2B = [\partial\,(Hc_2/\tau)/\partial c_2]_{c_2 = \text{small}}^{\lambda \to \infty} \tag{5}$$

The Z average radius of gyration, ρ, was calculated either from dissymmetries [21] or from

$$\rho = (\lambda'/4\pi)\{3M[\partial\,(Kc_2/R_\theta)/\partial \sin^2\theta/2]\}^{\frac{1}{2}}_{c_2 \to 0}, \tag{6}$$

where λ' is the wave length of the light in solution.

If the direct transmission technique was used, ρ could be estimated from the slopes and intercepts [22] of graphs of the type shown in Fig. 2.

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* These measurements will be described elsewhere; for the theory of, and application to, light-scattering measurements see Strauss and his collaborators.[20]

[19] Heydweiller, *Ann. Phys.*, 1913, **41**, 505; Kruis, *Z. phys. Chem.*, 1936, *B*, **34**, 13.

[20] Strauss and Ander, *J. Amer. Chem. Soc.*, 1958, **80**, 6494; Strauss and Wineman, *ibid.*, p. 2366.

[21] Beattie and Booth, *J. Polymer Sci.*, 1960, **44**, 81.

[22] Cashin and Debye, *Phys. Rev.*, 1949, **75**, 1307.

The viscosity number, $[\eta]$, at a rate of shear G, is defined by

$$[\eta] = [\{(\eta/\eta_0) - 1\}/c_2]_{c_2 \to 0} = Z_{c_2 \to 0}, \tag{7}$$

where η and η_0 are viscosities of solution and solvent. If the solution contained a permeant electrolyte, the extrapolations to zero alginate concentration could be carried out by plotting the reduced viscosity, Z, against c_2. If, on the other hand, the alginates were dissolved in water free from permeant electrolytes, the Z values increased rapidly with decreasing concentration down to the lowest c_2 values at which reliable measurements could be made. No definite evidence for a maximum of Z could be observed, but the existence of a maximum at lower concentrations than those specified in the heading of Table 4 is not excluded. In attempting to estimate $[\eta]$ in water we followed Fuoss and his collaborators [2] in representing Z by

$$Z = [A'/(1 + B'c_2^{\frac{1}{2}})] + D'. \tag{8}$$

The sum of D' and A' is taken to be $[\eta]$, D' and A' being calculated from plots of Z against $c_2^{-\frac{1}{2}}$ and of $(Z - D')^{-1}$ against $c_2^{\frac{1}{2}}$. The latter graphs, however, are not linear for the systems here considered, so that extrapolation to zero concentration is uncertain (see errors specified in Table 4).

The fraction, f_x, of counter-ions not associated with alginate is given by [17, 18]

$$f_x = 1/c\left[\frac{1}{N_e}\cdot\frac{Q_{\text{Alg}}}{c} + \frac{\Lambda'_x}{\kappa}\right] \tag{9}$$

where c is the stoicheiometric sodium or magnesium alginate concentration, Q_{Alg} is the number of equivalents of alginate transferred by N_e equivalents of electricity from the anode to the cathode compartment, Λ'_x is the equivalent conductivity of the counter-ion, and κ is the specific conductance of the alginate. A more complicated expression for f_x is obtained [17,18] if the equivalent concentrations of counter-ions and polymeric anions are not identical, but this case does not occur here. Λ'_x was calculated by a convergent approximation method; [17] this is based on the assumption that Kohlrausch's rule of the independent migration of ions is valid and makes use of the known conductances of sodium and magnesium chloride of concentrations equal to those of the " free " counter-ions in the alginate solution.

Results.—The refractive-index increments required for calculation of K, $\partial n/\partial c_2$ and H in eqns. (1), (2), and (4) are listed in Table 1. Typical experiments showing the application of the dissymmetry method, extrapolation to zero angle, and results of direct transmission measurements are in Table 2 and Figs. 2 and 3; and a summary of the light scattering tests is in Table 3, which also shows some viscosity numbers of these alginates. The M_W, B, and ρ values of

TABLE 1. *Refractive-index increment of alginates in solutions of permeant chlorides at* 20—25°.

Alginate	Permeant chloride (P)	Molarity of (P)	Alginate concn. ($100c_2$) (c_2 in g./cm.^{3})	No. of tests	Refractive-index increment (cm.^{3}/g.) 4360 Å	5460 Å
Na	NaCl	0·100	0·119—0·371	7	0·165 ± 0·004	0·163 ± 0·004
	NaCl	0·500	0·0950—0·344	5	0·166 ± 0·004	0·163 ± 0·004
K	KCl	0·100	0·0548—0·263	7	0·160 ± 0·004	0·159 ± 0·004
Mg	$MgCl_2$	0·0200	0·0324—0·289	6	0·158 ± 0·005	0·157 ± 0·005
		0·0300	0·0621—0·240	6	0·156 ± 0·005	0·154 ± 0·005

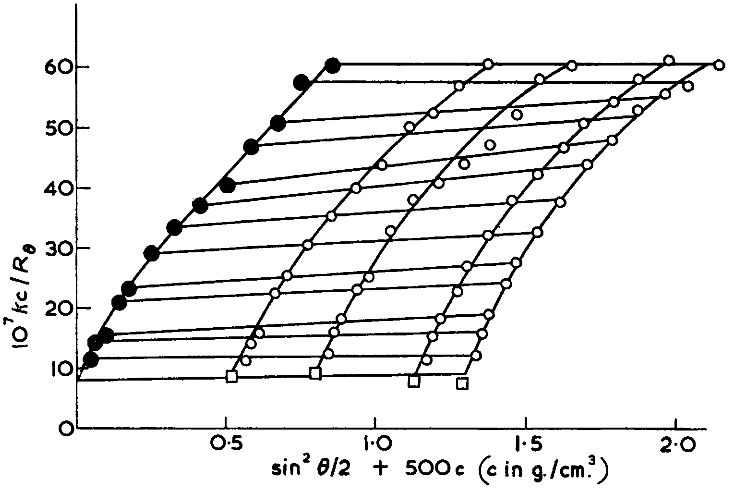
TABLE 2. *Weight average molecular weight,* M_W, *interaction constant,* B, *and radius of gyration,* ρ, *of sodium alginate in* 0·100M-*sodium chloride at* 25°; 4360 Å.

$[Kc_2/R_{90}]_{c_2 \to 0} = (80 \pm 7) \times 10^{-7}$ mole/g.; $Z' = 1·4 \pm 0·1$; $(1 - D)^2 = 0·78 \pm 0·10$; $M_W = (2·1 \pm 0·3) \times 10^5$; $B = (6 \pm 1) \times 10^{-4}$ mole cm.^{3}/g.^{2}; $\rho = 400 \pm 100$ Å.

Concn. of Na alginate ($100c_2$) (g./100 cm.^{3}) ...	0·160	0·119	0·0930	0·0650	0·0560	0·0310
10^7 (Kc_2/R_{90}) (mole/g.)	98·3	87·2	94·2	80·5	90·7	85·4
Z' (45°/135°)	1·67	1·47	1·59	1·61	1·56	—
Z' (60°/120°)	1·42	1·37	1·35	1·41	1·46	1·38

magnesium alginate of type 3 were computed by light-scattering and direct transmission measurements and it was found that the results agreed within the limits of the experimental errors. Magnesium alginate of type 1 was prepared from sodium alginate of molecular weight $(1\cdot3 \pm 0\cdot6) \times 10^5$; potassium alginate and the other magnesium alginates were obtained from a sodium alginate characterised by the figures in the first line of Table 3. Magnesium alginate of type 2 was dialysed against 0·100M-sodium chloride, thereby producing a sodium alginate whose M_W, B, and ρ values agreed with those of the sodium alginate used as a starting material for making the magnesium alginate. The molecular weights of sodium alginate in 0·500M- and 1·00M-sodium chloride and of magnesium alginates of types 2 and 3 in 0·0100M-, 0·0300M-, and 0·0400M-magnesium chloride agreed with the M_W values relating respectively to 0·100M-sodium chloride and 0·0200M-magnesium chloride. The M_W values of magnesium alginates of types 2 and 4 were determined shortly after preparation and after the solutions had been kept for 5 days at 25° (there was no difference).

FIG. 2. *Angular light-scattering dependence of magnesium alginate* (*type* 3) *in* 0·0200M-*magnesium chloride at* 24°; 4360 Å: $M_W = (12 \pm 2) \times 10^5$, $B = (2\cdot0 \pm 0\cdot5) \times 10^{-4}$ mole cm.^{3}/g.^{2}; $\rho = (1600 \pm 300)$ Å.



○ *Experimental points.* ● *Extrapolated to zero concentration.* ☐ *Extrapolated to zero angle.*

TABLE 3. *Weight average molecular weights,* M_W, *interaction constants,* B, *viscosity numbers,* $[\eta]$, *and radii of gyration,* ρ, *of sodium, potassium, and magnesium alginates.*

Alginate	Solvent = aq. soln. of	Molarity of permeant chloride	$10^5 M_W$ (25—28°)	$10^3 B$ (mole cm.^{3}/g.^{2}) (25—28°)	$[\eta]$ (*dl*/g.) (25·0°)	$10^{-3}\rho$ (Å) (25—28°)
Na	NaCl	0·100	1·9 ± 0·5	>0·5	9·4 ± 0·2	0·4 ± 0·1
K	KCl		1·0 ± 0·4		8·9 ± 0·2	
Mg, type 1	$MgCl_2$	0·0200	12 ± 2	<0·2	6·6 ± 0·2	1·2 ± 0·2
Mg, type 2			400 ± 100		7·5 ± 0·2	1·6 ± 0·3
Mg, type 3			12 ± 2		7·3 ± 0·2	1·2 ± 0·2
Mg, type 4			2·2 ± 0·5		7·6 ± 0·2	0·8 ± 0·2

Fig. 4 shows the influence of the molecular weight on the viscosity number of sodium alginates. The relation can be represented by:

$$[\eta] = 10^{-4\cdot8 \pm 1\cdot0} M_W^{1\cdot1 \pm 0\cdot3} \qquad (10)$$

The $[\eta]$ values of magnesium alginate, on the other hand, are practically independent of the molecular weight, as shown in the last four lines of columns 4 and 6 of Table 3, indicating that

$$[\eta] = (7\cdot0 \pm 0\cdot6) \times M_W^{0\cdot0 \pm 0\cdot2} \qquad (11)$$

A typical concentration-dependence of the reduced viscosity in a solvent containing a permeant electrolyte is shown in Fig. 5. The relation [23]

$$\text{Reduced viscosity} = \{[\eta] + k'[\eta]^2 c_2\}_{c_2 = \text{small}} \qquad (12)$$

with k' between 0·4 and 0·6 holds in most cases. The influence of the ionic strength of the solvent on the viscosity number is shown in Fig. 6, this mode of representation facilating comparison with other polyelectrolytes.[2] The smallest ionic strengths of the solvent were 0·00643 (sodium alginate) and 0·00965 (magnesium alginate). Under these conditions, or at higher

FIG. 3.

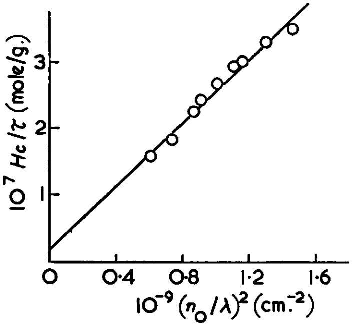


FIG. 4.

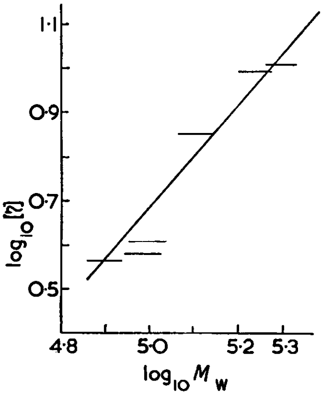


FIG. 3. *Wave-length dependence of turbidity of magnesium alginate (type* 2) *in* 0·0200M-*magnesium chloride at* 24°. *The results relate to* $c_2 = 0{\cdot}00142$ g./cm.^{3}; $(Hc_2/\tau)^{\lambda \rightarrow \infty}_{c_2 = 0\cdot00142} = (0{\cdot}20 \pm 0{\cdot}07) \times 10^{-7}$ mole/g. *Similar experiments were carried out with* $c_2 = 0{\cdot}00103$, 0·000736, 0·000466 *and* 0·000322 g./cm.^{3}. *Extrapolating the relevant intercepts, one obtains* $(Hc_2/\tau)^{\lambda \rightarrow \infty}_{c_2 = 0} = (0{\cdot}30 \pm 0{\cdot}10) \times 10^{-7}$ mole/g.; $M_W = (3{\cdot}3 \pm 1{\cdot}0) \times 10^7$, $B < 10^{-5}$ mole cm.^{3}/g.^{2}. *On plotting* $(Hc_2/\tau)_{c_2 = 0}$ *against* $(n_0/\lambda)^2$, *the slope and intercept of the resulting graph is* $1{\cdot}5 \times 10^{-16}$ mole cm.^{2}/g. *and* 3×10^{-8} mole/g.; *from this it follows* [22] *that* $\rho = (1400 \pm 700)$ Å.

FIG. 4. *Functional relation between logarithm of viscosity number,* $[\eta]$, *of sodium alginates and logarithm of weight-average molecular weight,* M_W, *in* 0·100M-*sodium chloride. The approximate experimental error of* $\log_{10} M_W$ *is indicated by the length of the horizontal lines.* $[\eta]$ *is expressed in dl/g. and relates to* 0·1M-*sodium chloride at* 25·0°.

TABLE 4. *Viscosity numbers,* $[\eta]$, *of sodium and magnesium alginates at different rates of shear at* 25·0°.

The weight average molecular weights of the sodium and the magnesium alginate (type 3) were, respectively, $(1{\cdot}2 \pm 0{\cdot}2) \times 10^5$ and $(8 \pm 2) \times 10^5$. The $[\eta]$ values listed under V relate to a solvent containing a sodium veronal buffer of ionic strength $\mu' = 0{\cdot}00643$ and to a magnesium veronal buffer of $\mu' = 0{\cdot}00965$, the pH of both buffers being 7·50. The $[\eta]$ values listed under W relate to water free from permeant electrolytes. Concn. range (g./100 cm.^{3}) of sodium alginate = 0·0141—0·0840 in buffer and 0·00230—0·0493 in water; concn. range of magnesium alginate = 0·0133—0·0933 in buffer and 0·004150—0·0922 in water. At each rate of shear, 4—7 concentrations, in the specified range, were tested.

Rate of shear (G) (sec.$^{-1}$)	$[\eta]$ (*dl*/g.)			
	Sodium alginate		Magnesium alginate	
	V	W	V	W
0·5—20 *	18·2 ± 0·9	160 ± 30	9·6 ± 0·9	180 ± 30
200	18·0 ± 0·9	160 ± 30	9·4 ± 0·9	100 ± 20
400	17·5 ± 0·8	160 ± 30	9·4 ± 0·9	60 ± 10
600	17·0 ± 0·8	160 ± 30	9·0 ± 0·9	50 ± 10
1000	16·0 ± 0·8	135 ± 40	8·9 ± 0·9	40 ± 10
1400	16·0 ± 0·8	125 ± 30	9·0 ± 0·9	30 ± 10

* In this range, 4—5 different rates of shear were tested; neither in buffer nor in water solution was a change of $[\eta]$ detected.

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[23] Huggins, *J. Amer. Chem. Soc.*, 1942, **64**, 2716.

concentrations of the permeant salts, the viscosity numbers were practically independent of the rate of shear, as shown for the low ionic strengths in columns 2 and 4 of Table 4. If water, free from permeant electrolytes was used, the viscosity numbers, $[\eta]$, increased considerably.* The $[\eta]$ values of sodium alginate were not sufficiently accurate to prove an influence of the rate of shear on them although there is no doubt that reduced viscosities depend on the rate of shear. On the other hand, for magnesium alginate, $[\eta]$ decreases with increasing G values, as shown in the last column of Table 4. These results are qualitatively compatible with the assumption that the magnesium alginate in water, free from permeant electrolyte, behaves hydrodynamically as a prolate ellipsoid of rotation,† the axial ratios, p, and rotary diffusion constants, δ, of which can be calculated [25] from the molecular weights and the viscosity numbers given in Table 4 and a partial specific volume [26] of 0·605 cm.^{3} g.$^{-1}$. The p and δ values obtained in this manner are 4000 ± 900 and 26 ± 8 sec.$^{-1}$. By using Scheraga's [27] computations in the manner indicated by Eisenberg,[28] $[\eta]_{G=0}/[\eta]_G$ was calculated and found to agree, within the limits of the experimental errors, with the experimental values derived from the figures in the last column of Table 4.

FIG. 5. *Reduced viscosity of magnesium alginate* (*type* 2; M_W ~10^7) *in magnesium veronal buffer of ionic strength* 0·00965 *at* pH 7·50 *and* 25·0°, *with a rate of shear* = 10 sec.$^{-1}$

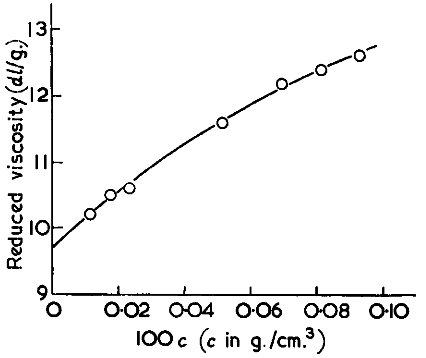
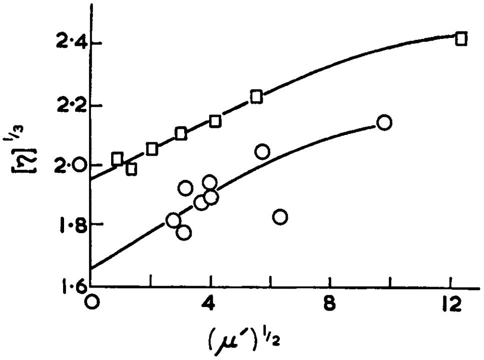


FIG. 6. *Influence of ionic strength,* μ', *on viscosity number* $[\eta]$ (*dl*/g.) *at* 25·0°.



□, *Sodium alginate,* M_W ~8 × 10^4, μ' 0·00643—1·00, *sodium veronal buffer* (pH 7·50) *and* NaCl. ○, *Magnesium alginate* (*type* 3), M_W ~10^6, μ' 0·00965—0·0400, *magnesium veronal buffer* (pH 7·50) *and* $MgCl_2$.

The results of transference and conductance measurements are in Table 5. The sodium alginate was the sample characterised in the first line of Table 3 and the magnesium alginate was of type (2). A few conductance measurements with magnesium alginate of type (4) were also made; there was no detectable difference. If Λ_x and Q_{Alg} are correctly estimated, and if proper account is taken of the pH changes during the transference,[18] the equivalents of electricity, N_e, calculated from ionic transport, should agree with N_e values computed from current and time measurements. This was found to be the case within about ±5%. The influence of variation of N_e at constant current and field strength was investigated for 0·0115N-sodium alginate and 0·0105N-magnesium alginate solutions. Six tests were done with each solution, the time varying respectively from 13 to 67 and from 29 to 120 mins. There was no detectable variation of the fraction f_x of free counter-ions. It is known from previous work [17] that f_x depends on the field strength if this is low; at sufficiently high field strengths, such as those in column 4 of Table 5, the variation of f_x is not significant.[18]

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* This effect is well known for sodium alginate [24] and for other polyelectrolytes.[1,2,3]

† It is, of course, not proved that other hydrodynamic models are less suitable.

[24] See, *e.g.*, Rose, Ph.D. Thesis, London, 1937.

[25] Kuhn, Kuhn, and Buchner, *Ergebn. exakt. Naturwiss.*, 1951, **25**, 39; Sadron, Progress Biophysics Chem., Pergamon Press, London, 1953, Vol. III, 287.

[26] Saverbone, Thesis, " A contribution to the knowledge of acid polyuronides," Upsala, 1945.

[27] Scheraga, *J. Chem. Phys.*, 1955, **23**, 1526.

[28] Eisenberg, *J. Polymer. Sci.*, 1957, **25**, 266.

TABLE 5. *Results of transference and electrical-conductance measurements at 25·0°. Counter-ion fixation in aqueous solutions of sodium and magnesium alginates. For significance of the symbols in the heading of this Table see p.* 3978.

Alginate	Concn. (g.-equiv./l.)	Current (10^{-3} amp.)	Field strength (v/cm.)	$10^5 N_e$	$10^5 Q_{\mathrm{Alg}}$	$10^4 \kappa$ (ohm^{-1} cm.$^{-1}$)	Λ'_x (ohm^{-1} × g.-equiv.$^{-1}$ × cm.$^{-1}$)	f_x
Sodium ...	0·02305	12·45	3·5	56·0	43 ± 2·5	11·95	46·7	0·60 ± 0·02
	0·0115	7·1	3·6	26·3	23 ± 1	6·21	47·5	0·57 ± 0·02
	0·00576	3·33	3·3	28·8	21 ± 1	3·36	48·0	0·64 ± 0·03
	0·00243	1·485	3·6	5·35	4·6 ± 0·4	1·39	47	0·58 ± 0·04
Magnesium	0·0105	2·625	3·5	20·6	21 ± 1	2·52	47·4	0·33 ± 0·02
	0·00525	1·265	3·4	8·40	8·5 ± 1·5	1·23	48·3	0·32 ± 0·02
	0·00210	0·589	4·0	4·53	4·3 ± 1	0·49	49·2	0·31 ± 0·03

DISCUSSION

The viscosity–molecular weight relation (10) with an exponent of about unity indicates that these sodium alginates in 0·1M-sodium chloride behave like linear, coiling polymers in which the solvent drainage is enhanced by a degree of stiffness and by the movement of the counter-ions in the polymer coil.[29] On conversion into magnesium alginate polymerisation can occur, as shown by the molecular weights in Table 3. It is assumed that magnesium ions combine with carboxylate groups of the polymeric anions, thereby producing inter- and intra-molecular cross-links. The intramolecular combination of adjacent carboxylate groups with one magnesium ion is prevented by stereochemical requirements, but more distant carboxyl groups can react. In this manner loops are formed that pull the alginate chain together and produce a more compact configuration. This explains why the viscosity numbers of the magnesium alginate listed in Table 3 are somewhat smaller than those of sodium and potassium alginate, although the molecular weights of the magnesium alginates are larger.

In preparing magnesium alginates of types 1—3, the replacement of sodium by magnesium was carried out in the gel phase where the alginate molecules are close together, thereby favouring the formation of intermolecular magnesium–carboxylate bonds. Magnesium alginate of type 4, on the other hand, was obtained in dilute solution, where intramolecular salt bridges are more probable. So the molecular weight of this magnesium alginate should be relatively low, and this has been observed. The molecular weights of these magnesium alginates showed no significant change with time at 25°. It is concluded that an equilibrium mixture is not formed, under the specified conditions. This indicates localised counter-ion fixation, possibly assisted by complex formation with some hydroxyl groups of the mannuronic or guluronic acid residues; the magnesium carboxylate hydroxy-complexes appear to be more stable than ordinary salt bridges, yet not stable enough to prevent the exchange of magnesium for other cations. The suggested complex formation is possibly a co-operative effect and need not have a counterpart in reactions between magnesium ions and sugar acids of low molecular weight. The formation of intermolecular magnesium–carboxylate links should make certain properties of magnesium alginate comparable with those of non-linear, coiling polymers which are characterised[30] by relatively small interaction constants, B, small exponents, γ, in the relation $[\eta] = \text{Constant} \times M_{\mathrm{W}}^{\gamma}$, and small ratios $[\eta]_{\text{non-linear species}}/[\eta]_{\text{linear species}}$ (provided the $[\eta]$ values relate to polymers of the same weight-average molecular weight, M_{W}). The figures in Table 3 and relationships (10) and (11) show that the B and γ values of the magnesium alginates are, in fact, relatively small and that the ratio $[\eta]_{\text{Mg alginate}}/[\eta]_{\text{Na alginate}}$ is about 0·08 if M_{W} is 10^6.

In other experiments magnesium alginate behaves like sodium or potassium alginate

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[29] Overbeek and van Geelen, *Trans. Faraday Soc.*, 1959, **55**, 363.

[30] Zimm and Stockmayer, *J. Chem. Phys.*, 1949, **17**, 1301; Stockmayer and Fixman, *Ann. New York Acad. Sci.*, 1953, **57**, 334; Zimm and Kilb, *J. Polymer Sci.*, 1959, **37**, 19; Kilb, *ibid.*, 1959, **38**, 403.

for which localised counter-ion fixation is not postulated. The curves in Fig. 6 and corresponding relations of linear flexible polyelectrolytes,[2] neutralised by univalent counter-ions, are similar in form, and on passing from solutions of permeant electrolytes to water as solvent the intrinsic viscosities of both sodium and magnesium alginate increase considerably. It is suggested that magnesium alginate contains counter-ions of two types: (*a*) those which are firmly bound to ionic sites of the polymeric anion and give rise to relatively stable inter- and intra-molecular bonds, and (*b*) those in which site-binding plays no role. Counter-ions of type (*b*) and those of type (*a*) which form intramolecular bonds are then responsible for the solubility of magnesium alginate. If all the magnesium ions required to neutralise the polymeric anions were of type (*a*) and formed stable intermolecular links, the critical gel point [31] would be reached and magnesium alginate would be insoluble.

The transference results show that there is a considerable difference between the fraction of free sodium and magnesium ions in sodium and magnesium alginate solutions, the means of the two sets of f_x values in the last column of Table 5 being $0{\cdot}60 \pm 0{\cdot}03$ and $0{\cdot}32 \pm 0{\cdot}03$. Thus, magnesium alginates prepared under appropriate conditions are characterised by larger and more compact polymeric anions and by stronger counter-ion association. It is possible that the difference between the counter-ion fixation of sodium and magnesium alginate is mainly due to magnesium ions of type (*a*). It cannot be excluded, however, that magnesium ions of type (*b*) also migrate to the anode, because they are trapped in the region occupied by the alginate or because they are held outside this region by strong coulombic attraction.

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[31] Flory, *J. Amer. Chem. Soc.*, 1941, **63**, 3083, 3091, 3096.