95. *The Intrinsic Viscosity of Sodium Alginate.*

By M. L. R. HARKNESS and ALBERT WASSERMANN.

The viscosity of sodium alginate in solutions of simple electrolytes, $Na^+{}_yX^{y-}$, has been determined in order to estimate the average distance, $2R_s$, between the ends of the alginate chains. In 0·1N-electrolyte solutions the R_s values are not markedly influenced by the nature of X, but in more concentrated solutions a significant anion effect obtains. It is shown, moreover, that in these solutions the alginate chains are not fully extended.

THE viscosity of alginate solutions has been measured by Rose (Ph.D. Thesis, London, 1937), Lunde *et al.* (*Kolloid Z.*, 1938, **83**, 208), Pauli and Stenbach (ibid., **84**, 291), Saverbone (" A Contribution to the Knowledge of Acid Poly-uronides," Upsala, 1945), Deuel and Weber (*Helv. Chim. Acta*, 1945, **28**, 1096), and Donnan and Rose (*Canadian J. Res.*, 1950, **28**, *B*, 105). These experiments show that in the presence of simple electrolytes the dependence upon concentration of the ratio

$$\frac{\text{Specific viscosity * of sodium alginate solution}}{\text{Concentration of sodium alginate}} = \frac{\eta_{\text{sp.}}}{c} \quad . \quad . \quad . \quad . \quad (1)$$

is of a nature which permits a fairly reliable estimation of the intrinsic viscosity $[\eta] = \lim_{c \to 0} (\eta_{\text{sp.}}/c)$. Rose (*loc. cit.*) determined the number average molecular weight, M_n, of several sodium alginate samples and his results show that the intrinsic viscosity, relative to 0·1N-sodium chloride solution, can be represented by

$$[\eta] = AM^B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $A = 10^{-2\cdot5\pm1}$ cm.^{3}/g. and $B = 1\cdot0 \pm 0\cdot1$. No attempt has been made to estimate the intrinsic viscosity of sodium alginate dissolved in water, without added simple electrolytes, but measurements have been carried out (see, *e.g.*, Rose, *loc. cit.*) which showed that the ratio, defined by

$$\beta = \eta_{\text{sp.}} \text{ (without added electrolyte)}/\eta_{\text{sp.}} \text{ (in presence of simple electrolyte)} \quad (3)$$

is always larger than unity. These β values characterise the magnitude of the electroviscous effect.

In this paper the results of experiments are reported which enable a calculation to be made of the intrinsic viscosity of sodium alginate in solutions of sodium acetate, sulphate, phosphate, oxalate, fluoride, chloride, hydroxide, and carbonate. Experiments with the first five salts have not been previously published, but measurements with the last three electrolytes have already been described (*locc. cit.*). These previous tests were made with relatively dilute solutions of the simple electrolyte $Na^+{}_yX^{y-}$, and under these conditions a dependence of the intrinsic viscosity on the nature of X could not be established. We have now extended the concentration range of the simple electrolyte to 1N-solutions and could detect a specific anion influence, the occurrence of which is of relevance for a discussion of effects relating to the main topic of this series of papers (see following paper). Furthermore, the present measurements enable an estimate to be made of the average distance between the ends of the alginate chains. Similar calculations for this polyelectrolyte have not been reported elsewhere.

---

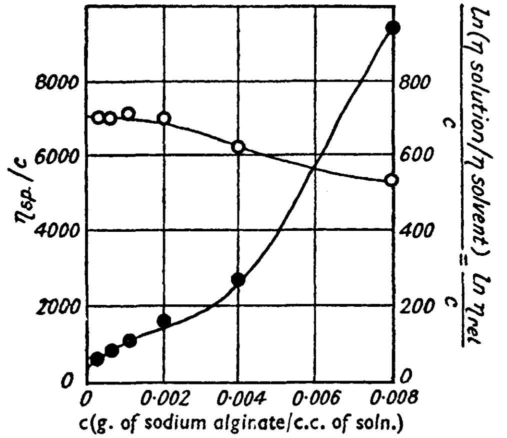
* The specific viscosity is defined by $\eta/\eta_0 - 1$ where η and η_0 are the viscosities of the solution and of the solvent, respectively.

EXPERIMENTAL

The sodium alginate, freed from traces of calcium by addition of sodium oxalate, was dialysed against 25% acetone–water and aliquots were dried as indicated on p. 494 of the preceding paper. Representative results of analyses, relating to a sample of number average molecular weight = $1{\cdot}2 \times 10^5$, were as follows: Na, $(4{\cdot}90 \pm 0{\cdot}10) \times 10^{-3}$; CO_2H, $(4{\cdot}71 \pm 0{\cdot}10) \times 10^{-3}$ g.-equiv./g. of dry gel. The absence of calcium was established by digesting the sodium alginate with concentrated nitric acid and testing the residue with ammonium oxalate.

At least one hour was allowed to lapse between preparation of the solution and measurement of the viscosity; control tests several hours later showed that the viscosity did not change to any detectable extent. Filtration of the sol through a glass filter was without influence on $[\eta]$. The sodium alginate was in the first instance dissolved in water, the required amount of the simple electrolyte, also dissolved in water, being added to the solution. A sufficiently accurate extrapolation of the ratio (1) to $c = 0$ could be done for all the alginate samples and simple electrolytes that have been tested by us, typical result being in the figure.[†] The various intrinsic viscosities are in the table. The results were obtained by using different sets of standard Ostwald viscometers, and Rose's observation (*loc. cit.*), that the viscosity depends on the rate of shear, was confirmed. The effect decreases with decreasing concentration and, in calculating the $[\eta]$ values listed in the table, an influence of the rate of shear, exceeding the specified experimental errors, could not be detected. The intrinsic viscosity of sodium alginate of number average molecular weight $7{\cdot}6 \times 10^4$ and $9{\cdot}8 \times 10^4$ was also determined, these measurements being done with solutions of the electrolytes indicated by an asterisk in the table. It could thus be established that the intrinsic viscosities could be represented by (2) with a B value which agreed within the limits of the experimental errors ($\pm 0{\cdot}15$) with that given on p. 497.

Estimation of intrinsic viscosity.



Solvent: $1N$-Na_2SO_4 of pH6; solute: sodium alginate of number average molecular weight $1{\cdot}2 \times 10^5$. The black circles relate to the left ordinate, the open circles to the right ordinate. [For the method of plotting ln $\eta_{rel.}$ against c, see, *e.g.*, Kraemer and van Natta, *J. Phys. Chem.*, 1932, **36**, 3175.] The $[\eta]$ values estimated from these two graphs are respectively 650 ± 100, and 690 ± 50 cm.³/g.; $t = 20°$. It should be noted that, by definition, the intrinsic viscosity is the value relating to the left-hand ordinates.

Intrinsic viscosities $[\eta]$ *of sodium alginate* (*of number average molecular weight* $1{\cdot}2 \times 10^5$) ($t = 20°$), *and approximate distance between the chain ends of sodium alginate* (*of number average molecular weight* $9{\cdot}6 \times 10^4$) *in solutions of various simple electrolytes.*

Electrolyte and normality	$[\eta]$ (cm.³/g.)	$2R_e \times 10^1$ (cm.) Eqn. (4)	Eqn. (5)	Electrolyte and normality	$[\eta]$ (cm.³/g.)	$2R_e \times 10^5$ (cm.) Eqn. (4)	Eqn. (5)
N-NaCl *	870 ± 20	3·6	7·6	0·5N-$Na_2C_2O_4$ ...	620 ± 30	3·1	6·8
N-NaOH *	920 ± 100	3·7	7·8	0·6N-NaF	500 ± 40	2·7	6·3
N-NaOAc *	940 ± 50	3·8	7·8	0·1N-NaCl *	870 ± 40	3·6	7·6
N-Na_2CO_3 *	410 ± 50	2·5	5·9	0·1N-NaOH * ...	850 ± 50	3·6	7·6
N-Na_2SO_4	690 ± 50	3·2	7·0	0·1N-NaOAc * ...	870 ± 50	3·6	7·6
N-Na_3PO_4	620 ± 40	3·1	6·8	0·1N-Na_2CO_3 ...	690 ± 50	3·2	7·0

Measurements with all eight simple electrolytes listed in the table showed that the β values, defined by (3), are substantially larger than unity, as in the earlier experiments referred to above. With a sodium alginate sample of number average molecular weight $1{\cdot}2 \times 10^5$, for instance, and with 0·5—1N-solutions of the eight simple electrolytes listed in the table, we found that β was in the range 4·6—9·7 (20°).

[†] If the solutions are 1N. with respect to the permanent electrolytes, the slope of the $\eta_{sp.}/c$ versus c graphs depends markedly on the nature of the electrolyte.

DISCUSSION

Debye and Bueche (*J. Chem. Physics*, 1946, **14**, 636; 1948, **16**, 573) deduced formulæ which can be written as follows :

$$[\eta] = 6\pi r_s R_s^2/10m \ \text{[if } B \text{ in eqn. (2)} = 1] \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$[\eta] = 4\pi R_s^3\,\phi(\sigma)/3M \ \text{[if } B \text{ in eqn. (2)} < 1] \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Here $[\eta]$ is the intrinsic viscosity, r_s is the radius of a spherical volume substituted for the base molecule, m is the mass of the base molecule, $2R_s$ is a distance which is approximately equal to the square-root of the average square of the distance between the chain ends,* M is the mass of the whole polymer, and $\phi(\sigma)$ is a quantity the value of which depends on that of the parameter B. (Similar correlations were deduced by a number of other authors, notably by W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, 1943, **26**, 1442; 1947, **30**, 1234.)

The figures in cols. 4 and 8 of the table were calculated from (4), r_s being taken to be $4{\cdot}4 \times 10^{-8}$ cm. (cf. Astbury, *Nature*, 1945, **155**, 667). In order to show the influence of a variation of B on R_s, the values in cols. 4 and 8 were calculated by using (5), with $M = 1{\cdot}5 \times 10^{-19}$g and $B = 0{\cdot}84$ $[\phi(\sigma) = 0{\cdot}6]$.

Equations (4) and (5) relate primarily to uncharged polymers. In the case of polyelectrolytes it has to be taken into account that the intrinsic viscosity depends also, to a certain extent, on the size of the counter-ion and on the thickness of the double layer formed by the simple electrolyte in conjunction with the poly-ion. It appears, however (cf. Kuhn, Kuenzle, and Katschalsky, *Helv. Chim. Acta*, 1948, **31**, 1994), that the contribution of the counter-ions to the intrinsic viscosity is small. If the correction is taken into account, the average distance between the ends of the alginate chains would be somewhat smaller than the figures given in cols. **3**, **4**, **7**, and **8** of the table. If an alginate chain of molecular weight 10^5 were fully extended, the distance between the chain ends would be more than 5 times larger than the largest value in cols. 4 and **8**. It can be concluded, therefore, that these poly-anions are curled, to a certain extent; *i.e.*, the main valency chains composed of repeating D-mannuronic acid residues are characterised by some internal flexibility.

Results of viscosity measurements (Pauli and Stenbach, *loc. cit.*; Fuoss and Strauss, *J. Polymer Sci.*, 1948, **3**, 216, 602, 603) and theoretical considerations (*e.g.*, Kuhn, Kuenzle, and Katschalsky, *loc. cit.*) make it probable that the shape of chain-like flexible macromolecules is dependent on the intramolecular electrostatic interaction between charged groups attached to the repeating units.† It appears probable, therefore, that sodium alginate, dissolved in water which is free from other electrolytes, is relatively extended, owing to the electrostatic repulsion of the carboxylate groupings. On addition of simple sodium salts, the tendency to form pairs between sodium and alginate ions will be enhanced, thereby decreasing the net charge of the poly-anion. This, in turn, appears to give rise to the formation of a self-curling system of greatly reduced viscosity, as shown by the numerical values of the ratio defined by (**3**). The electroviscous effect plays a rôle in solutions of sodium alginate which are 0·1—1N with respect to added electrolyte $\text{Na}^+_y\text{X}^{y-}$. The intrinsic viscosities, relating to the 0·1N-solutions, are not detectably dependent on the nature of X, but in 1N-solutions an influence of the anion obtains. One possible explanation involves the assumption that in 1N-solutions of $\text{Na}^+_y\text{X}^{y-}$ the dielectric constant of the reaction mixtures is so strongly modified by the nature of X as to bring about an alteration in the concentration of pairs between sodium and alginate ions to an extent sufficient to give rise to the actually observed viscosity changes.

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

---

* H. Kuhn (*Experientia*, 1945, **1**, 28) showed that the shape of flexible chain-like molecules can be characterised by the average distance between the chain ends, $\bar{h}$, and by the " effective " length, $\bar{H}$, which equals $1{\cdot}5\bar{h}$. It follows, therefore, that $\bar{H} \approx 3Rs$. This is mentioned in view of relationships to be discussed in the following paper.

† Meyer (*Biochem. Z.*, 1929, **214**, 253) was the first to discuss possible relationships between intramolecular electrostatic effects and the shape of chain-like polyelectrolytes.