519. *Molecular Size and Shape of the Ethylenediammonium Salt of a Polycarboxylic Acid.*

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The weight-average molecular weight, M_W, of an ethylenediammonium salt of alginic acid, prepared at relatively high concentration of alginate, is at least forty times larger than the M_W values of a sample made at lower concentration, or that of sodium and ammonium alginate. The intrinsic viscosities of both ethylenediammonium alginates are low, which indicates that the polyanion takes up a more compact molecular configuration if the univalent sodium or ammonium counterions are replaced by the bivalent ethylenediammonium ion. These changes in molecular size and shape are explained by the assumption that the ethylenediammonium alginate contains inter- and intra-molecular salt bridges, the former playing a more important role if the bivalent counterions are introduced at high polyelectrolyte concentration.

It has been shown [1] that the conversion of sodium or potassium alginate into the magnesium salt results in a marked alteration in the size and shape of the anions of the polyelectrolyte. Similar effects may play a role in biologically important mechanochemical systems,[2] and we were therefore interested to see what happens if a bivalent counterion other than magnesium combines with the alginate. Most bi- or multi-valent cations produce insoluble gels, but ethylenediammonium alginate is sufficiently soluble. We report here an investigation of dilute solutions of this polyelectrolyte by light-scattering and viscometric methods. For comparison, sodium and ammonium alginate were also tested.

EXPERIMENTAL

The starting material was a commercial sodium alginate (Messrs. Alginate Ltd.), the molecular weight and viscosity number of which are given in the first line of Table 1. The ratio sodium : carboxyl (equiv.) was 1·00 ± 0·05, and the value of $[\alpha]_D$ agreed with that given by Rose.[3] Solutions of ethylenediammonium alginate, type I, or ammonium alginate were made as follows. Sodium alginate (6×10^{-3} equiv.) was converted into alginic acid by treatment

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[1] Buchner, Cooper, and Wassermann, *J.*, 1961, **3947**.

[2] " Size and Shape of Contractile Polymers," ed. Wassermann, Pergamon Press, London, 1960.

[3] Rose, Ph.D. Thesis, London, 1937, Table H.

with 0·1N-hydrochloric acid; the fully swollen alginic acid gel, about 0·5M with respect to the repeating units, free from permeant electrolytes, was suspended in water (200 ml.), and 0·7M-ethylenediamine or ammonia was slowly added to the stirred suspension until the pH was 7·0. Ethylenediammonium alginate, type II, was made by dialysing $2{\cdot}5 \times 10^{-2}$N-sodium alginate against $1{\cdot}89 \times 10^{-2}$N-ethylenediammonium dichloride (pH 7·0) until the cation-exchange was complete. Both ethylenediammonium alginates were dialysed against water and centrifuged before use, precipitates being discarded. To establish the absence of significant quantities of permeant electrolytes in the sols, electrical conductance tests were carried out. Alginate concentrations were determined either interferometrically or by drying aliquot parts of the solution to constant weight *in vacuo* at 20° over phosphorus pentoxide. The dried residues were opaque brittle films. For some analyses of ethylenediammonium alginate, solutions were precipitated with ethanol or acetone, and the resulting white powders were washed with ether and dried. The analytical composition of films and powders agreed within the limits of experimental error.

The techniques and methods of evaluation of the refractive-index increment, light-scattering, and viscosity measurements have been described.[1] Most scattering tests were done with light of 436 and 546 mμ, but the refractive-index increments were determined with one wavelength only (546 mμ); as in the case of sodium, potassium, and magnesium alginate, there was no significant dispersion in the specified range.[1].

Most viscosities were measured in U-tube viscometers at rates of shear between 500 and 1500 sec.$^{-1}$. Solutions of ethylenediammonium alginate, type I, in water free from permeant electrolytes, were also investigated in a Couette instrument, at rates of shear below 20 sec.$^{-1}$. A significant dependence of the intrinsic viscosity on the rate of shear could not be detected.

RESULTS

Ten samples of ethylenediammonium alginate (films and powders) were analysed [Found (mean values): C, 35·0 ± 0·7; H, 6·4 ± 0·5; N, 6·5 ± 0·8. Calc. for $(C_7H_{16}NO_8)_n$: C, 34·7; H, 6·66; N, 5·79%], and four examples of ammonium alginate [Found (mean values): C, 32·3 ± 0·6; H, 6·1 ± 0·5; N, 6.2 ± 0·5. Calc. for $(C_6H_{15}NO_8)_n$: C, 31·4; H, 6·60; N, 6·11%]. The refractive-index increments of ethylenediammonium alginate, type I, in 0·0180M-ethylenediammonium dichloride or water, and of ammonium alginate in 0·0400 or 0·100M-ammonium chloride were respectively 0·198 * ± 0·005 and 0·168 ± 0·003 ml./g. These figures were determined at 25° in the concentration range 0·0336—0·146% (ethylenediammonium alginate) and 0·113—0·426% (ammonium alginate).

The results of most of the light-scattering and viscosity measurements are in Table 1. The experiments were carried out in the concentration range 0·0157—0·205%, each M_W or $[\eta]$ value being derived from tests with at least four solutions of different concentration. The molecular weights in the first, second, and fourth lines were calculated with the help of the dissymmetry method, intrinsic dissymmetries being computed for 60—120° and 45—135°. For an estimate of the M_w value in the third line, the angular dependence of the scattered light was measured at ten angles in the range 135°—25°, extrapolation to zero angle being carried out. Interaction constants, B, and radii of gyration, ρ, were calculated from these measurements, and it was found that B was in all cases below 3×10^{-4} mole cm.^{3} g.$^{-2}$ and ρ was between 300 and 500 Å for sodium, ammonium, and ethylenediammonium alginate, type II, and 1800 ± 300 Å for ethylenediammonium alginate, type I. Dialysis of this polyelectrolyte solution or of the precipitate formed during its preparation (see above) against 0·1N-sodium chloride produces sodium alginate the properties of which will be discussed elsewhere.

The intrinsic viscosities of the ethylenediammonium alginate in water free from permeant electrolytes, in the second column of Table 2, were obtained from measurements in the concentration range 0·0400—0·235%. By using the appropriate values in Table 1, the ratios, r, in the last column of Table 2 were calculated. In all experiments with ethylenediammonium alginate, with and without permeant electrolytes, and with sodium or ammonium alginate, in the solvents specified in Table 1, the dependence on concentration of the reduced viscosities can be approximately represented by Huggins's relation,[4] the constant k' being between 0·20 and 3·0.

* The same value was used for the computation of the molecular weight of ethylenediammonium alginate, type II.

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

DISCUSSION

Table 1 shows that the molecular weight, M_W, of ethylenediammonium alginate, type I, prepared at relatively high alginate concentration is at least forty times larger than M_W of ethylenediammonium alginate, type II, prepared at lower concentration, and of sodium or ammonium alginate. The intrinsic viscosities, $[\eta]$, of both ethylenediammonium alginates are lower than those of sodium or ammonium alginate. To explain this and the solubility of ethylenediammonium alginate we postulate two types of ethylenediammonium counterions: (*a*) those which are firmly bound to ionic sites of the polyanion and produce relatively stable inter- and intra-molecular salt bridges, and (*b*) those in which site-binding plays a role. It is assumed that intermolecular ethylenediammonium salt bridges give rise to an increase in the molecular weight, while intramolecular links produce loops in the backbone structure of the polyanion and a more compact configuration of small intrinsic viscosity. Salt bridges of these types cannot occur in alginates containing only univalent counterions. The high molecular weight and the low intrinsic viscosity in the third line of Table 1 are correlated with inter- and intra-molecular salt bridges, the latter, together with counterions of type (*b*) being responsible for the fact that the gel point [5] is not reached and that this alginate is soluble. The probability that intermolecular salt bridges will be formed decreases with decreasing alginate concentration, and it appears that, under the conditions of formation of ethylenediammonium alginate, type II, a significant number of cross-links are not formed because the molecular weights in the last line of Table 1 are not substantially larger than those of the alginates containing the univalent counter-ions. Intramolecular salt bridges, however, seem to play a role, for the value of intrinsic viscosity in the last line is smaller than those in the first two lines of Table 1.

TABLE 1.

Weight-average molecular weights, M_W, and intrinsic viscosities, $[\eta]$, of sodium, ammonium, and ethylenediammonium alginates.

Alginate	Solvent	Molarity of permeant chloride	$10^{-5} M_W$ (25—27°)	$[\eta]$ (dl./g.) 25·0°	30·0°
Na	aq. NaCl	0·100	0·9 ± 0·3	2·5 ± 0·2	
NH_4	aq. NH_4Cl	0·0400	1·6 ± 0·4	2·4 ± 0·2	
$[CH_2NH_3]_2$, type I *	aq. $[CH_2{\cdot}NH_3Cl]_2$	0·0180	100 ± 20	1·5 ± 0·2	1·1 ± 0·1
$[CH_2NH_3]_2$, type II †			1·7 ± 0·3	1·3 ± 0·2	

* Alginate concentration during preparation ~0·5N.

† Alginate concentration during preparation 0·025N.

The previously investigated magnesium alginate, also a soluble polycarboxylic acid fully neutralised with bivalent counter-ions, shows similar effects, except that the ratio, *r*, is greater than 10, rather than 2·3 ± 0·4 (first line of Table 2). It has been found [6] that the fractions of osmotically free counterions in magnesium and ethylenediammonium alginate are respectively 0·15 ± 0·02 and less than 0·02, and it follows, therefore, that in the former polyelectrolyte there is a less effective screening by counterions of the

TABLE 2.

Intrinsic viscosities of ethylenediammonium alginate.

	$[\chi]_{(H_2O)}$ (dl./g.)	$\dfrac{[\eta]_{(H_2O)}}{[\eta]_{\text{(solvent containing permeat electrolyte)}}} = r$
Type I	2·5 ± 0·2 (30·0°)	2·3 ± 0·4 (30·0°)
Type II	2·1 ± 0·2 (25·0°)	1·6 ± 0·4 (25·0°)

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

[6] Katchalsky, Cooper, Upadhyay, and Wassermann, *J.*, 1962, 5198.

negatively charged carboxylate groupings. This in turn will give rise to a more powerful electrostatic repulsion of the repeating units in magnesium alginate, which will take up a more elongated configuration characterised by larger values of $[\eta]_{H_2O}$ and r.

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[*Received, November* **14*th*, 1961.**]