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THE DISSOCIATION AND SPECIFIC VISCOSITY OF POLYMETHACRYLIC ACID.

BY

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Solutions of polymethacrylic acid have been partially neutralized to different extents, and the pH values and viscosities of the resulting solutions determined. These measurements were carried out at several different potassium chloride concentrations, and on several polymer samples. The calculated dissociation constants of the polymer acid were substituted in the equation developed by J. Th. G. Overbeek, which expresses the change in dissociation constant of a polybasic acid as a function of the radius of the molecular coil and of the charge on the molecule. The derivation of this equation treats the polymer molecule as a sphere containing a continuous charge. The radii found are of the right order and change in the expected way with changing ionic strength and ionisation. Substitution of these radii in the *Debye* viscosity equation gives satisfactory agreement between observed and experimental viscosities at low degrees of ionisation. At higher degrees of dissociation it would seem that the treatment of the polymer coil as a sphere is no longer satisfactory, although a better approximation is obtained if the charge is considered to be entirely on the surface of the sphere.

The dissociation of polybasic acids has attracted considerable attention in recent years, and it is now well known that the dissociation "constants" of these substances depend both on the degree of ionisation of the acid and on the concentration of neutral salts in the solution. In a previous publication¹⁾, one of the present authors has presented a theory relating the change of dissociation constant of a macromolecular polybasic acid to the radius of the macromolecular coil. In the investigation described here, this theory has been subjected to experimental test.

1. Theory.

The underlying theory has been discussed in detail in earlier publications^{1) 2)}; only a short summary will be presented here.

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¹⁾ J. Th. G. Overbeek, Bull. soc. chim. Belges 57, 252 (1948).

²⁾ J. J. Hermans and J. Th. G. Overbeek, Rec. trav. chim. 67, 761 (1948); Bull. soc. chim. Belges 57, 154 (1948).

We consider a polybasic carboxylic acid such as polymethacrylic acid. The dissociation constant used is defined by the equation:

$$K = \frac{[\text{H}^+][-\text{COO}^-]}{[-\text{COOH}]} \quad \dots \quad (1)$$

where $[-\text{COO}^-]$ and $[-\text{COOH}]$ denote the total activities of ionised and unionised carboxyl groups respectively. In other words the molecular concentrations ordinarily used in the case of acids of low basicity are replaced by equivalent concentrations.

We denote by K_0 the value K would have if there were no interaction between the charged groups, i.e. the limiting value for a degree of dissociation zero. Then if, for a given degree of ionization, ΔF represents the change in electrical free energy of the molecule per ionised acid group, the dissociation constant at this stage of dissociation will be given by: $K = K_0 \exp(-\Delta F/kT)$, or taking negative logarithms:

$$pK - pK_0 = 0.434 \Delta F/kT \quad \dots \quad (2)$$

In calculating the required free energy term²⁾, the molecule was considered to have spherical symmetry, and the charge due to the ionised groups as continuous. Three distributions of this charge were considered: (I) a uniform distribution throughout the whole volume of a sphere of radius R ; (II) a Gaussian distribution, with the same mean square distance \bar{r}^2 of the charge from the centre as in (I); (III) a uniform distribution over the surface of a sphere of radius equal to this same mean square distance \bar{r}^2 .

Distributions (I) and (II) lead to two expressions for ΔF which are both represented quite accurately by the same approximation formula. Substitution of this latter formula in equation (2) gives the following result:

$$pK - pK_0 = 0.434 \cdot \frac{6 Ze^2}{5 \epsilon kT} \frac{1}{R(1 + 0.6 \kappa R + 0.4 \kappa^2 R^2)} \quad \dots \quad (3)$$

The assumption of a uniform surface charge leads to the equation:

$$pK - pK_0 = 0.434 \left(\frac{5}{3}\right)^{1/2} \frac{Ze^2}{\epsilon kT} \frac{1}{R(1 + \sqrt{3/5} \kappa R)} \quad \dots \quad (4)$$

In these equations: Z = number of charged (ionised) groups
 e = elementary charge
 ϵ = dielectric constant
 k = Boltzmann constant

κ = Debye reciprocal length

$$\kappa^2 = \frac{4\pi e^2 \sum n_i z_i^2}{\epsilon kT}, \text{ where } z_i \text{ and } n_i \text{ are the valency}$$

and number of ions per cm³.

In order to test the validity of these equations and the theoretical principles upon which they are based, measurements have been carried out of the effect of ionisation and ionic strength upon both the dissociation constant and the viscosity of solutions of polymethacrylic acid.

Experimental.

Preparation of polymethacrylic acid. Methacrylic acid *) was redistilled at low pressure under nitrogen, a few copper turnings being placed in the distilling flask to inhibit polymerisation. Polymerisation was carried out at 25° C in 10% aqueous solution, using the Fe⁺⁺-H₂O₂ system as initiator. It was assumed that the reaction has the same mechanism as that found for the polymerisation of methyl methacrylate with this catalysing system by *Baxendale, M. G. Evans and Kilham* ³⁾, that is, that every two molecules of hydrogen peroxide used up give rise ultimately to one polymer molecule. An average molecular weight of about 150,000 was aimed at. It was found that addition of initiator in the proportions required to give an average molecular weight of this order gave rise to about 10% polymerisation, reaction ceasing within 10–15 minutes. The reaction was therefore carried out as follows: To the monomer solution was added a slight excess of ferrous sulphate (dissolved in 1 N H₂SO₄), and after expulsion of air with nitrogen, successive small quantities of dilute hydrogen peroxide solution saturated with nitrogen were added. From time to time the monomer concentration was determined; from the percentage polymerisation occurring and the concentration of monomer remaining the quantity of hydrogen peroxide required for further polymerisation was calculated. The process was continued until a total polymerisation of about 80% had been attained.

To determine the monomer concentration samples of the reaction mixture were added to cold potassium bromide-hydrochloric acid solutions; a known excess of potassium bromate was then added, and the excess bromine determined iodimetrically after about five minutes.

Fractionation and purification. Fractionation was carried out by addition of methyl ethyl ketone, the products being separated into five fractions.

Samples IA and IB referred to under "Results" were two fractions of a polymer sample which was only purified by fractionation, reprecipitation of the separate fractions being resorted to where necessary to bring about freedom from monomer.

Samples IIA, IIB and IIC were obtained from a product which was first electro-dialysed by the method of *de Bruyn and Troelstra* ⁴⁾ until free of monomer.

*) The authors are indebted to the Kunststoffen Instituut, Delft, for the sample of methacrylic acid.

³⁾ *J. H. Baxendale, M. G. Evans and J. K. Kilman*, *Trans. Faraday Soc.* **42**, 668 (1946).

⁴⁾ *H. de Bruyn and S. A. Troelstra*, *Kolloid-Z.* **84**, 192 (1938).

Attempts to fractionate this purified sample gave rise to stable emulsions however, which required the addition of a trace of hydrochloric acid to bring about separation of the phases. Consequently the separate fractions were further electro-dialysed to ensure freedom from foreign electrolytes.

The polymer solutions were stored under nitrogen in a refrigerator; exposure to air was found to result in a continual fall of viscosity⁵⁾.

Determination of polymer concentration. The concentration of polymethacrylic acid in solution was determined by titration with carbonate-free alkali using as indicator alizarin yellow R, (transition interval 9—10). This indicator gives a sharp end-point, and gives results agreeing to within 1% with both conductimetric and potentiometric titrations.

Measurements of pH and viscosity. All measurements were carried out at 25° C. For the pH determinations a cell consisting of a hydrogen electrode and a silver—silver chloride electrode was used, both electrodes dipping directly into the solution investigated. (Solutions containing known concentrations of potassium chloride were used throughout). In this way the use of a salt-bridge, which would probably have disturbing effects on the E.M.F. in a system of this type, was eliminated. For the measurements a vacuum-tube potentiometer was used^{*}).

Viscosity measurements were carried out with an Ostwald viscometer having an outflow time for water of 118.3 seconds at 25° C. According to *Staudinger*⁶⁾ solutions of polyacrylic acid show considerable structural viscosity, even in 0.02% solution. This however does not appear to be the case with polymethacrylic acid. Thus it was found by means of a *Bungenberg de Jong* three-bulb viscometer⁷⁾ that the viscosities of 0.1% solutions both of the free acid and of the partially (70%) neutralized acid are independent of the rate of shear.

In each of the potentiometric titrations a series of solutions was prepared, each of equal polymer and potassium chloride concentration, but neutralized to different extents with carbonate-free sodium hydroxide solutions. On each such solution a measurement of both pH and viscosity was carried out.

Results.

Degree of polymerisation of the samples. As yet no absolute determinations of the molecular weight of the polymethacrylic acid have been carried out. The mean molecular weights of the samples used have therefore been estimated from viscosity measurements. For this purpose solutions of the polymer were neutralized with sodium hydroxide, and the viscosity then determined in 2 N NaNO₃ solution. The degrees of polymerisation were then calculated by the equation given by *Baxendale, Bywater and Evans*⁸⁾ for polymethyl methacrylate in benzene, i.e.

$$\overline{D.P.} = 2.81 \cdot 10^3 [\eta]^{1.32}; c = \text{concentration in g per 100 cm}^3.$$

^{*}) Radiometer, Copenhagen.

⁵⁾ Cf. *H. Staudinger and E. Trommsdorff*, *Ann.* **502**, 201 (1933).

⁶⁾ *H. Staudinger*, "Makromolekulare Chemie und Biologie", Basle 1947, p. 85.

⁷⁾ *H. G. Bungenberg de Jong*, "First Report on viscosity and plasticity", Amsterdam 1939, p. 124.

⁸⁾ *J. H. Baxendale, S. Bywater and M. H. Evans*, *J. Polymer Sci.* **1**, 237 (1946).

An indication that this procedure is not entirely unjustified is given by *Staudinger* and *Trommsdorff*⁵⁾. These authors compared the viscosities of polyethyl acrylate solutions in butyl acetate with those of the sodium salt formed by saponification, the viscosities of the latter being measured in 2 N sodium hydroxide. They found the viscosity of the sodium salt to be consistently 1.5 times that of the ester.

It seems probable therefore that the procedure adopted here leads to fairly accurate relative values of the mean molecular weights, and to absolute values of the right order. In table I are given the results of these measurements.

Table I.

Sample	$[\eta]$ (25° C)	Mean molecular weight
IA	0.85	195000
IB	0.52	99000
IIA	1.075	266000
IIB	0.658	139000
IIC	0.25	40000

Dissociation constants and pH. From the E.M.F. values of the hydrogen—silver—silver chloride cell the pH values were calculated by means of the equation:

$$\text{pH} = \frac{E - 0.2224 + 0.05916 \log a_{\text{Cl}^-} + 0.0004}{0.05916}$$

Here 0.2224 is the standard potential of the silver—silver chloride electrode at 25° C, and the factor 0.0004 is the correction to the hydrogen pressure for the water vapour pressure.

We have further:

$$\text{pK} = -\log C_{\text{H}^+} \cdot \frac{\alpha}{1-\alpha} - 2 \log f_{\pm} ;$$

$$-\log C_{\text{H}^+} = \text{pH} + \log f_{\pm}$$

$$\alpha = (C_{\text{H}^+} + C_{\text{Na}^+})/C$$

C = concentration of polymer in equivalents/litre.

The activity coefficients for potassium chloride of the relevant concentration were first used. This procedure led however to extremely low values of pK and pK₀ in the experiments where 1.0 and 0.5 normal potassium chloride were used. Use of the activity coefficients for hydrochloric acid of the same concentration as the potassium chloride led however to values of pK₀ which agreed well with those obtained

from the experiments with lower salt concentrations. The activity coefficients for hydrochloric acid have therefore been used throughout⁹⁾. With 0.1 and 0.01 normal potassium chloride this makes no appreciable difference. For the solutions 10^{-3} and 10^{-4} normal with respect to potassium chloride, activity coefficients were calculated by means of the *Debye-Hückel* equation.

The contribution of the sodium ions of the polymer salt to the ionic strength is difficult to assess, and has not been taken into consideration. It is to be expected that the sodium ions will be immobilised to large extent by attraction to the charged polymer coil, and that consequently their activity will be low. This expectation is confirmed by the work of Kern¹⁰⁾ on sodium polyacrylate.

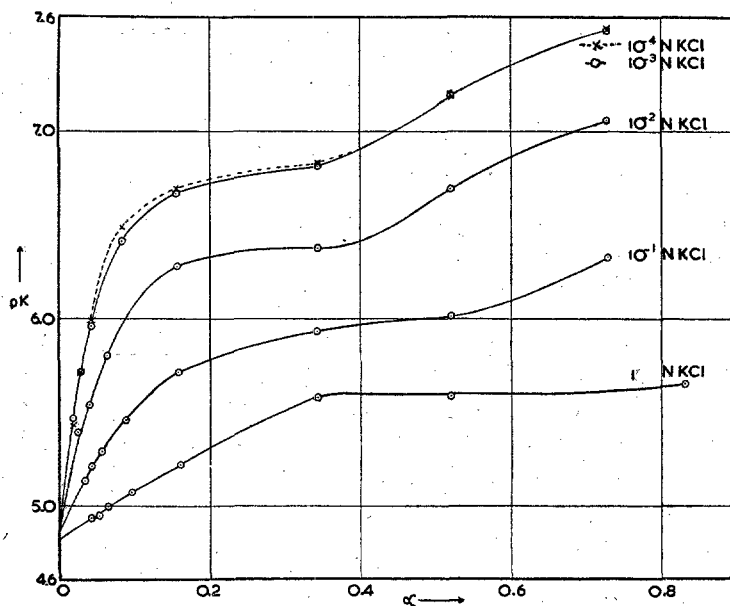


Fig. 1. Potentiometric titrations of polymethacrylic acid. Sample IIB. Polymer concentration = 0.01 equiv./litre.

In fig. 1 graphs of pK against the degree of dissociation α are reproduced for sample II B with different potassium chloride concentrations. Titration of other samples in the presence of 0.1 N and 0.01 N KCl led to almost identical pK — α curves, whereas with

⁹⁾ Values taken from S. Glasstone "Introduction to Electrochemistry", Nostrand (1942), p. 139.

¹⁰⁾ W. Kern, Die makromol. Chem. 2, 279 (1948).

0.001 N KCl the pK values found for sample II A ($[\eta] = 1.075$) were correspondingly higher than these for sample II B ($[\eta] = 0.658$). The complete results are to be found in tables II—VI, columns 1—5.

Table II.

Potentiometric titrations and viscosity of polymethacrylic acid solutions.
Sample IA ($M = 195000$); polymer concentration = 0.0114 equiv./litre.

Conc. KCl mols/litre	C_{Na^+} Milliequiv./l	pH	α	pK	$R(\text{\AA})$	η_{sp} Calculated	η_{sp} Observed
0.1	0.00	3.55	0.031	5.14	53.0	0.015	0.019
0.1	0.251	3.74	0.042	5.19	55.9	0.017	0.019
0.1	0.502	3.96	0.057	5.28	57.4	0.018	0.020
0.1	1.00	4.36	0.093	5.47	60.2	0.020	0.021
0.1	2.01	4.97	0.177	5.75	66.3	0.024	0.030
0.1	4.02	5.55	0.351	5.94	80.1	0.035	0.102
0.1	7.03	6.24	0.614	6.15	91.5	0.046	0.192
0.1	10.0	7.36	0.878	6.61	93.5	0.048	0.206
0.02	0.00	3.61	0.025	5.26	69.2	0.026	0.027
0.02	0.251	3.88	0.032	5.21	83.0	0.038	0.029
0.02	0.502	4.21	0.050	5.55	75.0	0.031	0.032
0.02	1.00	4.75	0.090	5.79	88.4	0.043	0.036
0.02	2.01	5.36	0.175	6.09	98.0	0.053	0.046
0.02	4.02	5.91	0.350	6.24	122	0.079	0.231
0.02	7.03	6.84	0.614	6.69	136	0.101	—
0.02	10.0	7.83	0.878	7.03	145	0.115	0.452

Table III.

Potentiometric titrations and viscosity of polymethacrylic acid solutions.
Sample IB ($M = 99000$); polymer concentration = 0.0117 equiv./litre.

Conc. KCl mols/litre	C_{Na^+} Milliequiv./l	pH	α	pK	$R(\text{\AA})$	η_{sp} Calculated	η_{sp} Observed
0.02	0.00	3.60	0.025	5.26	52.3	0.015	0.014
0.02	0.509	4.20	0.050	5.52	55.0	0.017	0.016
0.02	1.12	4.82	0.097	5.85	63.5	0.022	0.020
0.02	2.24	5.46	0.192	6.14	77.1	0.033	0.039
0.02	4.58	6.01	0.392	6.26	98.2	0.053	0.153
0.02	5.90	6.42	0.505	6.48	102	0.058	0.169
0.02	8.14	7.12	0.697	6.82	110	0.067	0.197

An experiment in which polymer concentrations of 0.02, 0.01 and 0.005 N were used showed that the pK values obtained are independent (within the experimental error) of the concentration in this region. In all other cases, solutions 0.01 N with respect to the polymeric acid were used.

Table IV.

Potentiometric titrations and viscosity of polymethacrylic acid solutions. Sample II A ($M = 266000$); polymer concentration = 0.0101 equiv./litre.

Conc. KCl mols/litre	C_{Na^+} Milliequiv./l.	pH	α	pK	$R(\text{\AA})$	η_{sp} Calculated	η_{sp} Observed
0.1	0.00	3.61	0.031	5.20	55.0	0.014	0.025
0.1	0.205	3.80	0.040	5.27	57.5	0.016	0.022
0.1	0.410	3.99	0.054	5.34	60.2	0.017	0.023
0.1	0.821	4.38	0.087	5.50	64.6	0.020	0.022
0.1	1.54	4.88	0.154	5.72	72.2	0.025	0.029
0.01	0.00	3.67	0.023	5.34	89.0	0.038	0.034
0.01	0.205	3.97	0.032	5.49	91.5	0.040	0.040
0.01	0.410	4.28	0.046	5.63	96.7	0.044	0.047
0.01	0.821	4.85	0.083	5.94	107	0.054	0.068
0.01	1.54	5.50	0.153	6.28	123	0.072	0.105
0.01	3.39	6.07	0.336	6.41	161	0.123	0.536
0.01	5.13	6.68	0.509	6.71	176	0.148	0.739
0.01	7.18	7.42	0.714	7.07	187	0.166	0.821
0.001	0.00	3.81	0.016	5.61	109	0.056	0.051
0.001	0.205	4.22	0.027	5.80	128	0.078	0.084
0.001	0.410	4.81	0.042	6.18	137	0.089	0.155
0.001	0.821	5.47	0.082	6.54	164	0.129	0.278
0.001	1.54	5.93	0.153	6.69	217	0.224	0.589

Viscosity. The effect of dissociation on the specific viscosity is shown by fig. 2, which refers to sample II B. Changes of the same type were observed for the other samples; see tables II—VI, column 8.

The value of K_0 . In order to make use of equations (3) and (4), the value of pK_0 is required, i.e. the value of pK for $\alpha = 0$. The

monomer unit of polymethacrylic acid has the structure $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}-\text{CH}_2- \\ | \\ \text{COOH} \end{array}$

and is thus very similar to isobutyric acid. The value of pK for the latter is 4.84 at 25° C¹¹).

Extrapolation of the pK— α curves for solutions containing 0.01, 0.02, 0.1 and 1.0 N KCl, and for a more concentrated (0.06 N) polymer solution in 0.5 N KCl, gave values for pK_0 ranging from 4.81 to 4.87. The value actually used in the calculations was $pK_0 = 4.85$.

Interpretation of the results.

From the results obtained values of the radius R of the polymer coil have been calculated by means of equation (3). The number of

¹¹ See for e.g. E. Larsson and B. Adell, Z. physik. Chem. A 156, 386 (1931); P. E. Verkade, Rec. trav. chim. 35, 79 (1915).

Table V.

Potentiometric titrations and viscosity of polymethacrylic acid solutions.
Sample IIB ($M = 139000$); polymer concentration = 0.0099 equiv./litre.

Conc. KCl mols/litre	C_{Na^+} Milliequiv./l	pH	α	pK	$R(\text{\AA})$	η_{sp} Calculated	η_{sp} Observed
1.0	0.00	3.48	0.041	4.94	38.1	0.007	0.007
1.0	0.205	3.60	0.052	4.95	40.0	0.007	0.010
1.0	0.410	3.74	0.064	4.99	38.1	0.007	0.010
1.0	0.821	4.00	0.095	5.07	37.4	0.006	0.004
1.0	1.54	4.41	0.160	5.22	37.5	0.007	0.005
1.0	3.39	5.21	0.343	5.58	38.5	0.007	0.011
1.0	5.13	5.53	0.520	5.58	44.4	0.009	0.032
1.0	8.19	6.26	0.831	5.65	51.0	0.012	0.062
0.1	0.00	3.58	0.033	5.14	48.8	0.011	0.015
0.1	0.205	3.76	0.043	5.21	49.2	0.011	0.013
0.1	0.410	3.96	0.055	5.29	50.0	0.012	0.013
0.1	0.821	4.35	0.088	5.46	52.6	0.013	0.014
0.1	1.54	4.88	0.157	5.71	57.0	0.015	0.018
0.1	3.39	5.55	0.343	5.93	70.1	0.023	0.057
0.1	5.13	5.95	0.520	6.01	79.8	0.030	0.110
0.1	7.18	6.66	0.728	6.33	82.6	0.032	0.121
0.01	0.00	3.65	0.025	5.39	65.5	0.020	0.016
0.01	0.308	4.12	0.040	5.54	73.1	0.025	0.018
0.01	0.616	4.60	0.065	5.80	79.0	0.029	0.023
0.01	1.54	5.45	0.156	6.28	95.8	0.043	0.046
0.01	3.39	6.05	0.343	6.38	129	0.077	0.221
0.01	5.13	6.68	0.520	6.70	141	0.093	0.299
0.01	7.18	7.44	0.728	7.06	148	0.102	0.334
0.001	0.00	3.74	0.019	5.46	94.5	0.042	0.021
0.001	0.205	4.16	0.028	5.71	96.7	0.044	0.030
0.001	0.410	4.60	0.044	5.96	108	0.054	0.046
0.001	0.821	5.35	0.083	6.41	127	0.075	0.093
0.001	1.54	5.91	0.155	6.66	162	0.124	0.200
0.001	3.39	6.52	0.343	6.82	227	0.241	0.727
0.001	5.13	7.21	0.520	7.19	252	0.296	0.891
0.001	7.18	7.95	0.728	7.54	273	0.348	0.980
0.0001	0.00	3.72	0.020	5.42	148	0.101	0.031
0.0001	0.205	4.16	0.028	5.71	142	0.094	0.055
0.0001	0.410	4.65	0.044	5.99	160	0.120	0.086
0.0001	0.821	5.44	0.083	6.49	195	0.177	0.186
0.0001	1.54	5.95	0.155	6.69	272	0.346	0.403
0.0001	3.39	6.54	0.343	6.83	409	0.732	1.119
0.0001	5.13	7.22	0.520	7.19	470	1.030	1.339
0.0001	7.18	7.96	0.728	7.54	560	1.463	1.453

charged groups, Z , is given by: $Z = \overline{DP} \cdot \alpha$, where \overline{DP} is the degree of polymerisation. The radii thus found are recorded in the sixth columns of tables II—VI.

Table VI.

Potentiometric titrations and viscosity of polymethacrylic acid solutions. Sample IIC ($M = 40000^*$); polymer concentration = 0.00993 equiv./litre.

Conc. KCl mols/litre	C_{Na^+} Milliequiv./l	pH	α	pK	$R(\text{\AA})$	η_{sp} Calculated	η_{sp} Observed
0.01	0.00	3.55	0.031	5.09	59.0	0.016	0.004
0.01	0.205	3.78	0.039	5.22	53.0	0.013	0.008
0.01	0.410	4.06	0.051	5.37	51.2	0.012	0.009
0.01	0.821	4.60	0.086	5.68	52.3	0.013	0.007
0.01	1.54	5.28	0.156	6.06	58.0	0.016	0.009
0.01	3.39	6.02	0.341	6.35	76.5	0.027	0.042
0.01	5.13	6.63	0.516	6.64	84.2	0.033	0.059
0.01	7.18	7.38	0.724	7.01	89.8	0.038	0.067

*) Sample IIC, to which the above table refers, consisted of that portion of the dialysed polymerisation product which could not be precipitated by methyl ethyl ketone. It was therefore probably rather heterogeneous, and the value assigned to M is not very certain.

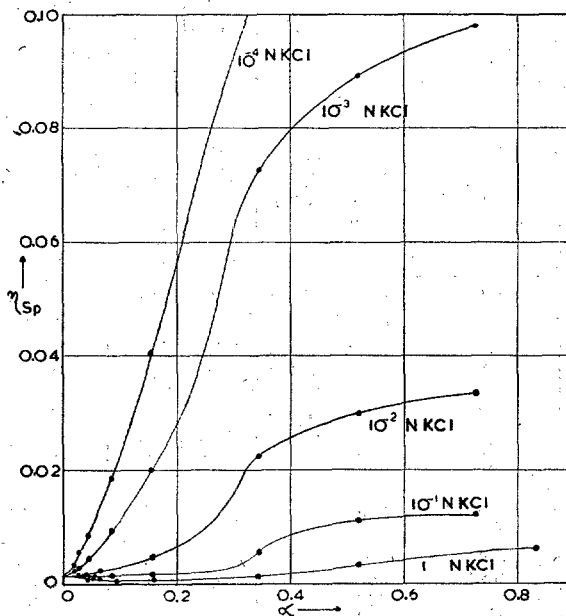


Fig. 2. Effect of dissociation on the viscosity of polymethacrylic acid solutions. Sample IIB; polymer concentration = 0.0099 equiv./litre (0.085 %).

In order to relate these values to the experimentally found viscosities, use has been made of the equation of *Debije*¹²⁾. This equation, which

¹²⁾ P. Debije, J. Chem. Phys. 14, 636 (1946).

assumes unhindered flow through the polymer coil, is as follows:

$$\eta - \eta_0 = (1/6)nf\bar{\Sigma r^2} \dots \dots \dots (5)$$

Here n is the number of molecules per cm^3 , f the frictional coefficient of each "bead" or segment of the polymer chain, and $\bar{\Sigma r^2}$ is the sum of the mean square distances of the separate beads from the centre of gravity. The viscosities η and η_0 refer to solution and solvent respectively.

If we consider the polymer segments as being uniformly distributed over a sphere of radius R , then

$$\bar{r^2} = \frac{\int_0^R r^2 \cdot 4\pi r^2 dr}{\int_0^R 4\pi r^2 dr} = \frac{3}{5} R^2$$

Assuming further that f is given by Stokes' law we have that $f = 6\pi\eta_0 b$, where b is the radius of the bead.

Substituting these results in equation (5), we obtain:

$$\frac{\eta - \eta_0}{\eta_0} = \eta_{sp} = n\pi b N_s \cdot 3/5 R^2,$$

where N_s is the number of beads per molecule. Expressing n in terms of the concentration c in g per 100 cm^3 , we obtain finally:

$$\eta_{sp} = \frac{3}{5} \frac{\pi c b R^2}{100 m} \dots \dots \dots (6)$$

Here m represents the mass of each segment.

The absolute value of the radius b is uncertain; the value was therefore chosen by comparison with the observed viscosities. Regarding the individual monomer residues as the units of the chain, the value of b was taken as 0.42 Å. The mass m then becomes $86/N$ g, where N is Avogadro's number. (It would be more in keeping with the statistics of the polymer coil to consider, say, ten monomer groups as constituting the unit of the chain, but this would not affect the ratio b/m).

It may be noted that *Debye* gives an example of the application of his equation to a polymer having individual groups of molecular weight 50. The value of b found in this case was 0.33 Å, which compares favourably with the value used here.

The specific viscosities calculated by means of equation (6) are compared with the experimental values in columns 7 and 8 of tables

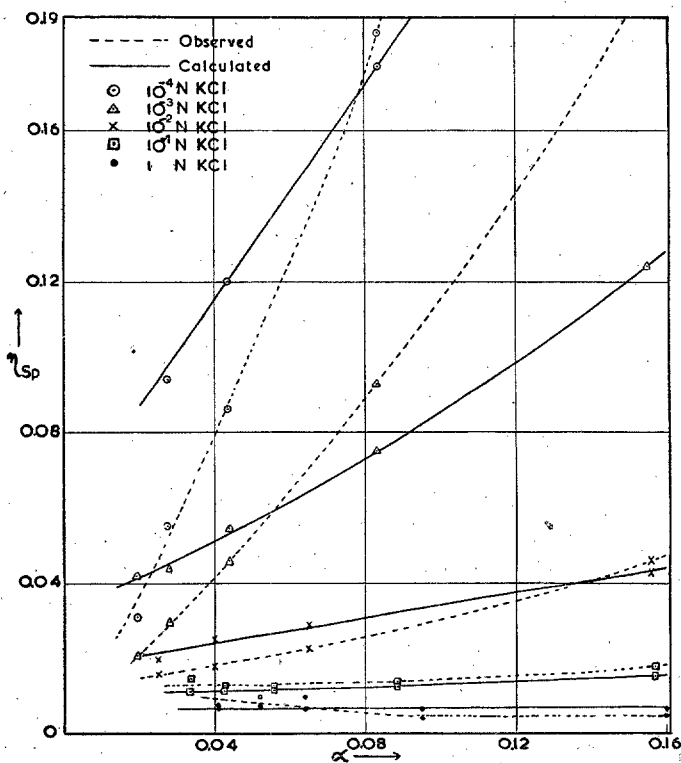


Fig. 3. Comparison of observed and calculated values of the specific viscosity of polymethacrylic acid solutions. Sample IIB; polymer concentration = 0.0099 equiv./litre (0.085 %).

II—VI, and graphically, for values of α up to 0.16, in figure 3. Some results obtained by treating the data of table V by means of equation (4) (which assumes a uniform surface charge) are given in table VII.

Discussion.

It will be seen from the tables that the values of R obtained are of the right order, and are in keeping with theory in that they increase with increasing degree of dissociation but decrease with salt concentration, for a given degree of dissociation. Furthermore, inserting these radii into the *Debye* equation, specific viscosities are obtained which are not only of the right order of magnitude, but which, up to a degree

Table VII.

Radii of the polymer coil calculated on the assumption of a uniform surface charge (Equation (4)). Treatment of data from Table V (Sample II B).

Conc. KCl mols/litre	α	R (Å) Eqn. (4)	η_{sp} calculated	η_{sp} observed	η_{sp} calculated R from Eqn. (3) *
1.0	0.041	105	0.052	0.007	0.007
1.0	0.160	103	0.049	0.005	0.007
1.0	0.343	107	0.054	0.011	0.007
1.0	0.831	160	0.120	0.062	0.012
0.1	0.043	90.2	0.038	0.013	0.011
0.1	0.157	114	0.061	0.018	0.015
0.1	0.343	154	0.111	0.057	0.023
0.1	0.728	192	0.172	0.121	0.032
0.01	0.040	104	0.049	0.018	0.025
0.01	0.156	150	0.105	0.046	0.043
0.01	0.343	219	0.224	0.221	0.077
0.01	0.728	268	0.336	0.334	0.102
0.001	0.028	110	0.057	0.030	0.044
0.001	0.155	210	0.206	0.200	0.124
0.001	0.343	320	0.479	0.727	0.241
0.001	0.728	417	0.810	0.980	0.348
0.0001	0.028	146	0.100	0.055	0.094
0.0001	0.155	307	0.441	0.403	0.346
0.0001	0.343	496	1.15	1.119	0.732
0.0001	0.728	657	2.02	1.453	1.463

*) For purposes of comparison the corresponding values of the η_{sp} are here given, calculated from the radii derived from equation (3).

of dissociation of about 0.2, follow consistently the changes in degree of ionisation and in salt concentration in the same way as do the experimental values.

That the agreement between observed and experimental values is not better is not necessarily to be attributed entirely to the approximation on which the calculation of the radii is based, since the accuracy and applicability of the *Debye* viscosity equation is also involved in the comparison. The latter equation assumes unhindered flow of liquid through the polymer coil. This condition probably applies, in the case considered here, at high degrees of dissociation and low salt concentrations, where the coil is extended. With decreasing values of α and increasing salt concentration the molecule becomes more and more compact, and will probably give rise to increasing resistance to internal flow. The case of partially hindered flow has been considered by *Brinkman*¹³⁾, *Debye* and *Bueche*¹⁴⁾, and *Kirkwood* and *Riseman*¹⁵⁾,

¹³⁾ *H. C. Brinkman*, Proc. Koninkl. Nederland. Akad. Wetenschap. 50, 618 (1947).

¹⁴⁾ *P. Debye* and *A. M. Bueche*, J. Chem. Phys. 16, 573 (1948).

¹⁵⁾ *J. G. Kirkwood* and *J. Riseman*, J. Chem. Phys. 16, 565 (1948).

and it would be more correct to make use of the results of these authors. This was not done however, as the use of these more complex formulae did not seem justified for our purposes.

It will be noticed however that when the degree of dissociation rises above about 0.2, the observed viscosity rises steeply. This rise is not reflected in the calculated viscosities, nor do the radii themselves show any such sudden rise. This points to the conclusion that the theory underlying the equation used here is applicable only at low degrees of dissociation, that is to say, when the coil is not very highly charged. At higher charges it appears to break down. This is not entirely unexpected, since when the polymer molecule becomes highly charged it will tend to be stretched out by electrostatic repulsion between the charged groups, approaching thus a rod-like rather than a sphere-like form. That this does occur at fairly low values of α has recently been established by *W. Kuhn, Künzle and Katchalsky*¹⁶⁾. Consequently the assumption of a spherical distribution of charge will no longer be applicable.

Use of equation (4), based on a uniform surface distribution of charge on the spheres, leads to values of R which are both higher and which increase more rapidly with α . Consequently this equation (using the same value of b/m in the *Debye* expression) leads to results which are less in agreement with experiment at low values of α , but which agree somewhat better at higher α -values especially at low concentrations of potassium chloride (cf. table VII). This would seem to indicate that the more extended polymer molecule approximates to a superficially charged sphere, the charged groups being driven outwards towards the surface by mutual electrostatic repulsion.

The shape of the α -pK curves is also of interest. It will be seen that, except in the case where 1.0 N KCl was used, they are characterised by a rather sharp rise in pK as α exceeds a value of about 0.4. For lower values of α however, the pK— α curves are of the same form as those predicted theoretically by correcting the statistics of the polymer coil with the free energy term used in the theory outlined in this paper¹⁷⁾. The fact that an anomaly appears at high values of the charge on the coil may perhaps again be due to the uncoiling of the molecule. The derivation of the above-mentioned theoretical α —pK curves is based on a statistical treatment which assumes the radius of the coil to be small compared with the length of the extended chain.

¹⁶⁾ *W. Kuhn, O. Künzle and A. Katchalsky, Helv. Chim. Acta 31, 2037 (1948).*

¹⁷⁾ Refs. 1) and 2), esp. fig. 1 of ref. 1).

From the data of Kern¹⁸⁾ for polyacrylic acid a $pK-\alpha$ curve of totally different form from those found here may be derived. Some of the results of Katchalsky and Spitnik¹⁴⁾ for polymethacrylic acid seem to lead to curves of the same type as those found here, but comparison is difficult, since their data do not extend to low values of α . It should be mentioned, however, that the values of pK calculated from the results of Katchalsky and Spitnik are considerably lower than those found here. It is assumed that these authors used a salt-bridge in their measurements (although they do not explicitly say so), and herein may perhaps lie the cause of the discrepancy between our results and theirs. It has been shown²⁰⁾ that the use of a salt-bridge in conjunction with colloidal systems gives rise to faulty E.M.F. values, leading to pH values which are too low.

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¹⁸⁾ W. Kern, Z. physik. Chem. A 181, 249 (1938).

¹⁹⁾ A. Katchalsky and P. Spitnik, J. Polymer Sci. 2, 432 (1947).

²⁰⁾ See e.g. R. Loosjes, Thesis, Utrecht (1942); H. Pallmann, Kolloid-Beihefte 30, 334 (1930).