717. *The Electrophoretic Mobility and Viscosity of Poly(acrylic Acid) and Poly(methacrylic Acid).*

By A. R. Mathieson and J. V. McLaren.

The electrophoretic mobility of poly(acrylic acid) of molecular weight $2{\cdot}5 \times 10^6$ has been measured at different concentrations of polyacid and at four different ionic strengths over a pH range of 3—12, the boundaries used being those between polyacid solutions and solvent dialysed to osmotic equilibrium. Corresponding measurements of the solution viscosity have been made. The boundaries were sharp and the ascending boundary moved more rapidly. Polyacid concentration has little influence on the mobility, but this increases with ionic strength at constant pH to a maximum at ionic strength 0·07—0·08 and then falls. At constant ionic strengths of 0·11 and 0·20, the mobility increases with increased pH to a limiting value for complete ionisation, but at lower ionic strengths the mobility has a maximum value around pH 7 and falls gradually for higher pH values. Mobility experiments at constant conductivity are also reported. From the viscosity experiments the Huggins constant was found to have a minimum at an ionic strength of 0·11. Molecular dimensions calculated from the Flory–Fox theory indicate that the maximum molecular extension is 3-fold. Potentiometric titrations at constant ionic strength showed agreement with Katchalsky's theory, but the dissociation constants decreased slightly with increased ionic strength. For poly(methacrylic acid) of molecular weight $2{\cdot}71 \times 10^5$, the mobility decreases with increased concentration and ionic strength and increases with increased pH.

Few detailed experimental studies of the electrophoretic mobilities (μ) of polyelectrolytes have been reported, although several theoretical treatments have been given. Qualitative measurements of the reversal of charge were made by Bungenberg de Jong [1] and his collaborators in 1934—1939 on a number of polysaccharides, and viscosity has been correlated with mobility for sodium carrageenate,[2] poly-(*N*-ethyleneglycine),[3] and other polyampholytes,[4] showing that there is a minimum in the reduced viscosity (η_{sp}/c) at the isoelectric point. Fitzgerald and Fuoss [5] found very complicated behaviour for poly-(1-n-butyl-4-vinylpyridinium bromide) but they were able to identify the true mobility. Theories of polyelectrolyte solutions have been based either on the Debye–Hückel approximation [6] or the Donnan approximation,[7,8] or numerical [9] and analytical [10] solutions of the Poisson–Boltzmann equation, and they have been applied to the calculation of the molecular extension [7,11-13] and the electrophoretic mobility.[14-16] No agreement with the

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[1] Holleman and Bungenberg de Jong, *Kolloid Beih.*, 1937, **46**, 113; Teunissen and Bungenberg de Jong, *ibid.*, 1939, **48**, 37; Bungenberg de Jong and Dekker, *ibid.*, 1935, **43**, 185, 190; Teunissen van Zyp, Thesis, Leyden, 1938; Bungenberg de Jong and Hartkamp, *Rec. Trav. chim.*, 1934, **53**, 622.

[2] Goring, *J. Colloid Sci.*, 1954, **9**, 141.

[3] Gregor, Gold, and Haeschele, *J. Amer. Chem. Soc.*, 1955, **77**, 4743.

[4] Alfrey, Morawetz, Fitzgerald, and Fuoss, *J. Amer. Chem. Soc.*, 1950, **72**, 1864; Alfrey, Fuoss, Morawetz, and Pinner, *ibid.*, 1952, **74**, 438.

[5] Fitzgerald and Fuoss, *J. Polymer Sci.*, 1954, **14**, 329.

[6] Hermans and Overbeek, *Rec. Trav. chim.*, 1948, **67**, 761.

[7] Kimball, Cutler, and Samelson, *J. Phys. Chem.*, 1952, **56**, 57.

[8] Osawa, Imai, and Kagawa, *J. Polymer Sci.*, 1954, **13**, 93.

[9] Wall and Berkowitz, *J. Chem. Phys.*, 1957, **26**, 114.

[10] Lifson, *J. Chem. Phys.*, 1957, **27**, 700.

[11] Flory, *J. Chem. Phys.*, 1953, **21**, 162.

[12] Katchalsky and Lifson, *J. Polymer Sci.*, 1953, **11**, 409.

[13] Trap and Hermans, *J. Phys. Chem.*, 1954, **58**, 957.

[14] Hermans, *J. Polymer Sci.*, 1955, **18**, 527.

[15] Longworth and Hermans, *J. Polymer Sci.*, 1957, **26**, 47.

[16] Napjus, Thesis, Leyden, 1958.

molecular-extension theories was found for chitosan[17] or sodium carboxymethylcellulose.[13,18] Measurements of polyelectrolyte mobility correlated with viscosity and titration are required to establish regularities of behaviour and to test the theories further. As a sequel to the work on deoxyribonucleic acid,[19] results for poly(acrylic acid) and poly(methacrylic acid) will be reported here, and for alginic acid in a further communication.

EXPERIMENTAL

Materials.—Poly(acrylic acid) was prepared by irradiating an aqueous solution of the monomer, outgassed and under nitrogen, with ultraviolet light from a 250 w mercury arc for 50 hr. The molecular weight, determined by the method of Katchalsky and Eisenberg[20] using diazomethane, was $2\cdot5 \times 10^6$. Poly(methacrylic acid) was prepared by the method of Arnold and Overbeek,[21] the Fe^{2+}–H_2O_2 system being used as catalyst.[22] The molecular weight was determined viscometrically by using 2N-aqueous sodium nitrate and the expression for poly(methylmethacrylate):[23] $M = 2\cdot42 \times 10^5[\eta]^{1\cdot32}$, which has been shown to be valid for ionised poly(methacrylic acid) in an excess of salt.[24,25] Salts were of " AnalaR " grade, and water was doubly distilled in a nitrogen atmosphere, Stuart and Wormwell's apparatus[26] being used.

Electrophoresis.—The modified Tiselius electrophoresis apparatus manufactured by Adam Hilger Ltd. was used. The electrodes were 18-gauge silver spirals, prepared by dipping them in concentrated nitric acid, washing, and making the anode in aqueous hydrochloric acid with 50 mA passed for 48 hr. They were kept in water and never allowed to dry. Ilford orthotone plates, speed group E, were used to record the boundaries with an exposure of 5 sec., and they were developed with a high-contrast quinol developer above 60°. For the solutions, the series of buffers recommended by Miller and Golder[27] were used, with added sodium chloride contributing most of the ionic strength. For pH 3·0 and 3·5 glycine–hydrochloric acid buffers were used, for pH 4·0—5·5 acetate, pH 6·0—7·5 phosphate, pH 8·0—9·0 sodium veronal, and pH 9·0—12·0 glycine–sodium hydroxide. For electrophoresis, solutions of polyelectrolyte of twice the desired concentration were mixed with equal volumes of buffer and sodium chloride of twice the desired ionic strength. The solutions were then dialysed in Cellophane tubes against the appropriate buffer–sodium chloride solution for at least 7 hr. No precipitation occurred during dialysis. The temperature of electrophoresis was $4° \pm 0\cdot01°$.

For poly(acrylic acid) both boundaries were single and extremely sharp, the ascending boundaries remaining so throughout electrophoresis, but the descending boundaries became somewhat more diffuse though maintaining a single peak. The ascending boundary always moved more quickly and it seems likely that this boundary gives the true mobility. Large δ and ε boundaries were observed. For poly(methacrylic acid) both boundaries remained single and sharp throughout electrophoresis, the ascending boundary moving more quickly. No δ or ε boundaries were observed.

Potentiometric Titration.—The cell consisted of hydrogen and silver–silver chloride electrodes separated by a saturated potassium chloride–agar salt bridge, and the E.M.F.'s were measured on a Tinsley potentiometer accurate to $\pm 0\cdot01$ unit of pH. Acid and alkali were added from a micrometer syringe. Katchalsky, Shavit, and Eisenberg's method[28] was used, the solution of polyacid of known concentration being neutralised with sodium hydroxide, and sodium chloride being added to bring the solution to the desired ionic strength, the polymer ions being taken into account. Polyacid was then brought to the same ionic strength with aqueous sodium chloride and titrated with the neutralised polyacid. The polysalt was also titrated with the

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[17] van Duin, Thesis, Leyden, 1957.

[18] Schneider and Doty, *J. Phys. Chem.*, 1954, **58**, 762.

[19] Mathieson and McLaren, *J.*, 1956, 303.

[20] Katchalsky and Eisenberg, *J. Polymer Sci.*, 1951, **6**, 145.

[21] Arnold and Overbeek, Proc. Internat. Coll. Macromol., Amsterdam, 1949, p. 314.

[22] Baxendale, Evans, and Park, *Trans. Faraday Soc.*, 1946, **42**, 155; Baxendale, Evans, and Kilham, *Trans. Faraday Soc.*, 1946, **42**, 668.

[23] Baxendale, Bywater, and Evans, *J. Polymer Sci.*, 1946, **1**, 237.

[24] Oth and Doty, *J. Phys. Chem.*, 1952, **56**, 43.

[25] Flory and Osterheld, *J. Phys. Chem.*, 1954, **58**, 653.

[26] Stuart and Wormwell, *J.*, 1930, 85.

[27] Miller and Golder, *Arch. Biochem.*, 1950, **29**, 420.

[28] Katchalsky, Shavit, and Eisenberg, *J. Polymer Sci.*, 1954, **13**, 69.

polyacid to the same point so that a complete titration curve was obtained. pH measurements for electrophoresis were made with the same apparatus. The titration cells were kept at 25° ± 0·01°.

Viscosity.—Ostwald dilution viscometers of 30 ml. capacity were used having a minimum content of 3 ml., and with a high rate of shear. The viscosities were measured in the same buffer solutions as used for electrophoresis, at 25° ± 0·01°. It was shown that the effect of shear was negligible for the solutions containing salt by comparing the results with determinations at very low shear gradients in the Couette viscometer described by Jordan, Mathieson, and Porter.[29] Table 1 shows this comparison for aqueous solutions and for 0·02M-sodium chloride solutions, the most dilute salt solutions used. The results at zero shear were obtained by a short, almost linear extrapolation of the Couette results. The effect of shear is very great for the aqueous solutions as is to be expected, but is negligible for the 0·02M-sodium chloride solutions. In a more detailed study [30] of the effect of shear it has been shown that, for deoxyribonucleic acid of high molecular weight, 0·004M-salt was sufficient to suppress the shear dependence of the viscosity at low concentrations. The viscosities and mobilities reported here, which all refer to solutions of polyacid in salt solutions at least 0·02M, may therefore be interpreted on the basis of Newtanian flow.

TABLE 1. *Effect of shear on reduced viscosity of poly(acrylic acid).*

	Reduced viscosities (η_{sp}/c)					Reduced viscosities (η_{sp}/c)			
10^3c	Aqueous soltn. of free acid		0·02M-NaCl soltn. at pH 10		10^3c	Aqueous soltn. of free acid		0·02M-NaCl soltn. at pH 10	
(c in g./100 ml.)	Zero shear	High shear	Zero shear	High shear	(c in g./100 ml.)	Zero shear	High shear	Zero shear	High shear
1·00	80	—	—	—	5·00	544	128	54	53
1·10	320	78	—	—	7·20	512	128	56	56
1·70	416	80	—	—	10·00	672	131	61	60
3·40	496	112	51	51	21·60	—	—	77	76

RESULTS FOR POLY(ACRYLIC ACID)

Effect of pH, *Ionic Strength, and Concentration on Mobility.*—Two series of experiments were carried out in which the mobilities from the ascending and descending boundaries (μ_a and μ_d respectively) were measured at different pH values and ionic strengths (I) at a single polyacid concentration of 0·17 g./100 ml. The agreement between the two series of experiments was within ±0·2 × 10^{-4} in the values of μ obtained (Table 2). For a given pH, μ always increases with ionic strength to a maximum and then falls, the maximum value of μ occurring at ionic strengths of 0·07—0·08. For a given ionic strength of 0·02 or 0·06, μ rises with pH to a maximum at pH 7—9, then falls. For ionic strengths of 0·11 and 0·20, increase of pH causes only a slow rise in μ. For this high-molecular-weight polyelectrolyte then, more complex behaviour is found at low ionic strengths. Fig. 1 shows these results.

TABLE 2. *Reproducibility of the mobilities for poly(acrylic acid).*

(Results expressed as $10^4\mu$, in cm. sec.$^{-1}$ v.$^{-1}$, the two series of experiments being given as pairs of comparable results.)

(*a*) Ascending boundaries.

pH / I	5·0	6·0	7·0	10·0
0·02	0·87, 0·85	1·15, 1·10	2·40, 2·38	— , 2·16
0·06	1·40, 1·37	1·55, 1·52	2·83, 2·78	2·48, 2·40
0·11	1·30, 1·28	1·43, 1·42	1·50, 1·50	1·47, —
0·20	1·20, 1·16	1·27, 1·23	1·33, 1·32	1·33, 1·28

(*b*) Descending boundaries.

pH / I	5·0	6·0	7·0	10·0
0·02	0·52, 0·50	0·90, 0·90	1·90, 1·88	1·98, 1·97
0·06	0·90, 0·93	1·22, 1·25	2·32, 2·30	2·23, 2·20
0·11	1·02, 1·00	1·07, 1·06	1·13, 1·10	1·18, —
0·20	0·97, 0·90	0·98, 0·95	1·00, 1·00	1·10, 1·08

In a procedure similar to that of Fitzgerald and Fuoss,[5] sodium hydroxide was used for neutralisation and aqueous sodium chloride as supernatant liquid of equal conductivity. The ascending boundary was always clear and sharp, developing more sharply towards the sodium

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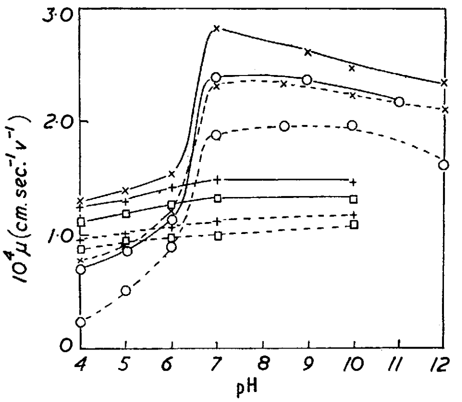
[29] Jordan, Mathieson, and Porter, *J. Polymer Sci.*, 1956, **21**, 463.

[30] Mathieson and Porter, *J. Polymer Sci.*, 1956, **21**, 495.

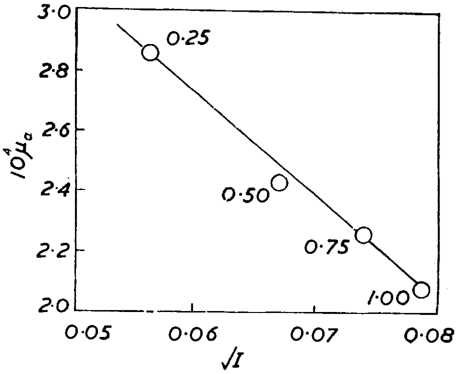
chloride solution, but the descending boundary became diffuse and hardly moved down the cell at all. This is similar to the result for poly-(1-n-butyl-4-vinylpyridinium bromide).[5] The ascending mobilities are given in Fig. 2, and show a linear decrease with $\sqrt{I}$ as well as the expected decrease with increased degree of ionisation (α_i).

FIG. 1. *Mobility of poly(acrylic acid).*



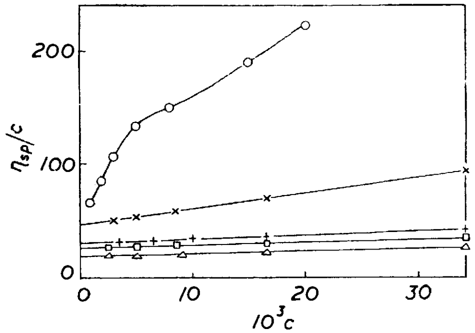
Full lines, ascending boundaries; broken lines, descending boundaries. Ionic strengths: ○, 0·02; ×, 0·06; +, 0·11; □, 0·20.

FIG. 2. *Mobility of poly(acrylic acid) at constant conductivity.*



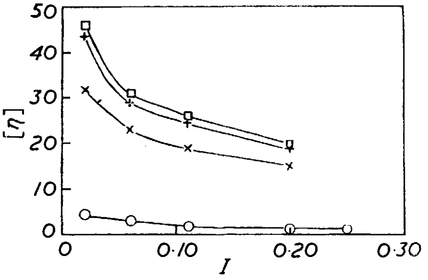
Numerals at points are α_i.

FIG. 3. *Reduced viscosity of poly(acrylic acid).*



Upper curve, 60% *neutralised, in water. Remainder, polyacid in solutions of constant ionic strengths at* pH 10. *Ionic strengths:* ×, 0·02; +, 0·06; □, 0·11; △, 0·20.

FIG. 4. *Effect of* pH *and ionic strength on the limiting viscosity number of poly(acrylic acid).*



pH *values:* ○, 3·0 *and* 3·5; ×, 5·0; +, 7·0; □, 10·0 *and* 12·0.

Experiments carried out at pH 7·0 and ionic strength 0·02 showed the effect of polyacid concentration to be small over the range examined (Table 3). The results do not rule out a very small decrease of μ with c, and it has been concluded from transport experiments that this should occur.[31]

TABLE 3. *Mobility of poly(acrylic acid) at different concentrations.*
pH = 7·0, I = 0·02.

c (g./100 ml.)	0·043	0·090	0·17	0·34
$10^4\mu_a$	2·32	2·44	2·38	2·43
$10^4\mu_d$	1·93	2·04	1·97	2·01

Effect of pH, *Ionic Strength, and Concentration on the Viscosity.*—The viscosity of 60% neutralised poly(acrylic acid) in aqueous solution is shown in Fig. 3. The plot of reduced

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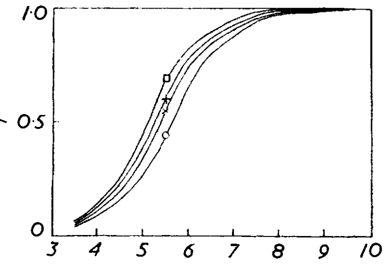
[31] Huizenger, Greiger, and Wall, *J. Amer. Chem. Soc.*, 1950, **72**, 2636.

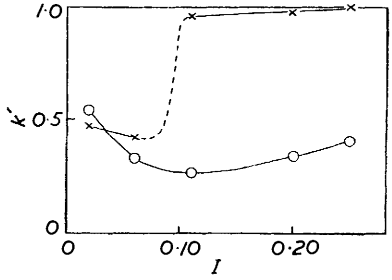
viscosity against concentration is of the ascending variety characteristic of polyelectrolytes of very high molecular weight in aqueous solution.[30] Typical results on the effect of ionic strength on the reduced viscosity are also given in Fig. 3 for pH 10. The reduced viscosity decreases with increased ionic strength and is linear in concentration for all ionic strengths studied, allowing limiting viscosity numbers $[\eta]$ to be obtained for each ionic strength. In agreement with earlier results,[32] it was found that iso-ionic dilution did not produce a family of straight lines. Fig. 4 shows the limiting viscosity numbers for different ionic strengths and pH values. They are smaller at high ionic strength and low pH, as is to be expected, showing little change with pH above pH 7, and reaching a minimum value at $I = 0{\cdot}2$ and pH 3·5 and below. The values for pH 3·0 and 3·5 are identical and so are those for pH 10·0 and 12·0.

FIG. 5. *Degree of ionisation of poly(acrylic acid).*



Ionic strengths: ○, 0·02; ×, 0·06; +, 0·11; □, 0·20.

FIG. 6. *The Huggins constant for poly(acrylic acid).* ○, pH 10·0; ×, pH 3·0.



Electrometric Titration.—The results of the titrations at constant ionic strength gave a series of straight lines when plotted as $\log\,[(1 - \alpha_i)/\alpha_i]$ against pH, as found for poly(methacrylic acid).[5] The degrees of ionisation calculated by Katchalsky, Shavit, and Eisenberg's method [28] for various pH values and ionic strengths are shown in Fig. 5.

DISCUSSION FOR POLY(ACRYLIC ACID)

Effect of Concentration on Viscosity.—Poly(acrylic acid) in salt solutions obeys the Huggins formula [33]

$$\eta_{sp}/c = [\eta] + k'[\eta]c + \ldots\ldots$$

and values of k' for pH 3 and 10, corresponding to negligible and complete ionisation respectively, are shown in Fig. 6. At pH 10 the value of k' falls with ionic strength to a minimum of 0·27 at $I = 0{\cdot}11$ and then rises gradually. Fujita, Mitsuhashi, and Homma [32] found a minimum of 0·33 at $I = 0{\cdot}10$ for poly(acrylic acid) of lower molecular weight ($1{\cdot}8 \times 10^6$) at 30°. They suggested that k' could be expressed as the sum of a hydrodynamic interference term and a term due to electrostatic interaction between polyions and smaller ions. The initial decrease of k' with I was considered to be due to decreased molecular asymmetry and reduced net charge, giving a random coil at the ionic strength corresponding to the minimum in k', further increase in I producing " hypercoiling " and a tendency for the molecules to become impenetrable to solvent. The values of k' at pH 3, where there is negligible ionisation, show a more gradual fall with I at first than do those at pH 10, in agreement with the suggestion of an electrostatic contribution, but at an ionic strength of about 1·0 there is a sudden large increase in k' which thereafter changes little with increased ionic strength. This effect for the virtually un-ionised polyacid is surprising, and if the hypothesis of hypercoiling be invoked it implies a very sharp transition from the random coil to the impenetrable hypercoiled structure. It may be, however, that at this low pH incipient phase separation is occurring.

Molecular Dimensions of Poly(acrylic Acid).—For a molecular weight of $2{\cdot}5 \times 10^6$

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[32] Fujita, Mitsuhashi, and Homma, *J. Colloid Sci.*, 1954, **9**, 466.
[33] Huggins, *J. Amer. Chem. Soc.*, 1942, **64**, 2716.

there are $3{\cdot}47 \times 10^4$ monomer units and so $6{\cdot}94 \times 10^4$ bonds in the chain if this is linear. If the molecule were a random coil with free rotation, the root-mean-square end-to-end distance ($\sqrt{\bar{r}_0^2}$) would be 578 Å. Using the minimum value of the limiting viscosity number (1·5), the Flory–Fox theory [34] gives a value for $\sqrt{\bar{r}_0^2}$ of 1260 Å, which is reasonable for the undissociated molecule at low pH and high ionic strength if this is a random coil with restricted rotation and the possibility of hypercoiling is ignored. With this limited encouragement the Flory–Fox theory was applied, and the molecular dimensions calculated by using

$$[\eta] = 2{\cdot}1 \times 10^{21}(\bar{r}^2)^{3/2}/M$$

for various pH values and ionic strengths, expressed in terms of the molecular expansion factor $\alpha_e = \sqrt{\bar{r}^2}/\sqrt{\bar{r}_0^2}$, where $\sqrt{\bar{r}^2}$ represents the root-mean-square end-to-end distance for extensions beyond the minimum, are shown in Fig. 7. The theory predicts much smaller molecular extensions than might have been expected, the maximum predicted extension being just less than 3-fold, whereas the fully extended length (contour length) would be 107,500 Å representing an 85-fold increase. From light-scattering measurements Oth and Doty [24] reported a maximum increase of 5-fold and so the predictions of the Flory–Fox theory are in reasonable accord with these experiments. With $\sqrt{\bar{r}_0^2} = 1260$ Å there are 7300 Kuhn statistical chain elements, so Kuhn statistics are clearly applicable to this system, each chain element being 14·7 Å in length. These calculations, which are in accord with similar ones on a sample of lower molecular weight,[32] suggest that the Flory–Fox theory gives at least an approximate picture of the molecular extension, sufficient to make comparison with the predictions of polyelectrolyte theories.

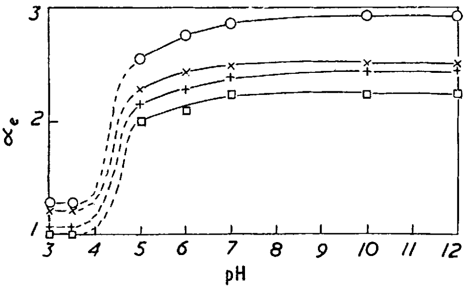

FIG. 7. *Molecular expansion factor for poly(acrylic acid). Ionic strengths:* ○, 0·02; ×, 0·06; +, 0·11; □, 0·20.

The frictional factor calculated from the Flory–Fox theory, with use of the Kirkwood–Riseman hydrodynamic treatment,[35] has the value of $f = 5{\cdot}75 \times 10^{-7}$ per polymer molecule for pH 3 and ionic strength 0·2, and values for the other pH's and ionic strengths are obtained by multiplying by the appropriate value of the expansion factor. Calculated by Stokes's Law, $f = 1{\cdot}06 \times 10^{-6}$ for pH 3 and ionic strength 0·2, although the Flory value of $\sqrt{\bar{r}_0^2}$ is used.

Dissociation Constant and Charge of Poly(acrylic Acid).—Fig. 5 shows that the degree of ionisation is negligible at pH 3 and almost unity at pH 8, and that it increases with increased ionic strength. The average number of fixed charges per molecule can be calculated from the values of α_i and the molecular weight of $2{\cdot}5 \times 10^6$, it being assumed there is one carboxyl group attached to each repeating unit; 34,700 is obtained when $\alpha_i = 1{\cdot}0$.

For poly(methacrylic acid), Katchalsky, Shavit, and Eisenberg [28] calculated the dissociation constant pK_0' from

$$\mathrm{pH} = pK_0' - \log\,[(1 - \alpha_i)/\alpha_i] + 0{\cdot}4343e\psi_0/kT$$

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[34] Flory and Fox, *J. Phys. Chem.*, 1949, **53**, 197; *J. Polymer Sci.*, 1950, **5**, 745; *J. Amer. Chem. Soc.*, 1951, **73**, 1904, 1909, 1915; Flory, " Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, New York, 1953.

[35] Kirkwood and Riseman, *J. Chem. Phys.*, 1948, **16**, 565.

where ψ_0 is the electrostatic potential, and e and k are the electronic charge and Boltzmann constant respectively. They calculated ψ_0 from electrophoretic measurements using Henry's equations [36] for spheres at low degrees of ionisation, and Gorin's equation [37] for cylinders at high degrees of ionisation. Relaxation effects, uncertain particularly for cylinders,[38] were neglected, and the results on molecular extension given here and elsewhere [16,17,24] show that it is unjustified to treat the molecules as cylinders even at high degrees of ionisation. Nevertheless, linear plots of pH against $\log [(1 - \alpha_i)/\alpha_i]$ were found, and a constant value of pK_0' was obtained, close to the value for the monomer. The results given here for poly(acrylic acid) lead to similar conclusions, pH being linear in $\log [(1 - \alpha_i)/\alpha_i]$, and the values of pK_0' are shown in Table 4. The appropriate monomer, propionic acid, has $pK_0 = 4{\cdot}87$, and there is evidence of a slow fall in pK_0' with ionic strength from the monomer value, probably to be ascribed to the approximate nature of the theory from which the values of pK_0' were derived.

TABLE 4. *Dissociation constant of poly(acrylic acid).*

I	0·02	0·06	0·11	0·20
pK_0'	4·88	4·59	4·58	4·45

Effect of pH *and Ionic Strength on Mobility.*—The initial increase of μ with I to the maximum may be due in part to the rapid fall in reduced viscosity with ionic strength over this range. Beyond this point, μ falls with increased I, which is the usual result, and although the degree of ionisation increases this is presumably more than compensated for by double-layer effects and ionic association. The minimum in k' occurs at an ionic strength only a little higher than the maximum in μ. The rise of μ with pH at higher ionic strengths to a constant value at complete ionisation is the expected result, but at the lower ionic strengths this is modified and a maximum appears in μ at pH 7—9. The cause of this is not clear. Quantitative comparison of the mobilities and expansion factors with the predictions of the polyelectrolyte theories will be made in a later publication.

RESULTS AND DISCUSSION FOR POLY(METHACRYLIC ACID)

A few results were also obtained with a sample of poly(methacrylic acid) of much lower molecular weight, for comparison. The mobility decreases with increased concentration at pH 7 and ionic strength 0·02 (Fig. 8) as previously found by Katchalsky, Shavit, and Eisenberg.[28] It follows approximately the relation $\mu \propto 1/c$. The ascending mobilities at various pH's and ionic strengths are shown in Fig. 9. Over the range examined, μ decreases with I and increases with pH. This behaviour is much simpler than that of the high-molecular-weight poly(acrylic acid). The reduced viscosities of aqueous and 0·2M-sodium nitrate solutions of poly(methacrylic acid) are given in Fig. 10. The aqueous solution gives a concave upward curve, characteristic of polyelectrolytes of relatively low molecular weight.[30] It may be then that the more complex mobility behaviour of the poly(acrylic acid) is due to its higher molecular weight.

TABLE 5. *Dissociation constant of poly(methacrylic acid).*

pH \ I	0·02	0·06	0·11	0·20
5	4·77	4·72	4·82	4·90
6	4·82	4·87	4·88	4·85
7	4·90	4·91	4·90	4·92

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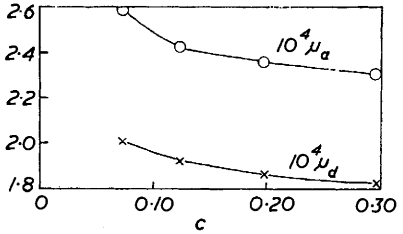
[36] Henry, *Proc. Roy. Soc.*, 1931, *A*, **133**, 106.
[37] Gorin, *J. Chem. Phys.*, 1939, **7**, 405.
[38] Booth, *Proc. Roy. Soc.*, 1950, *A*, **203**, 514.

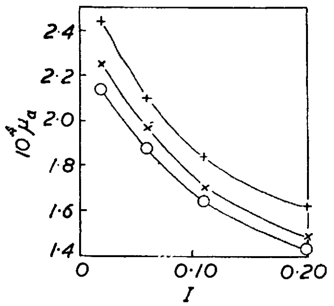
Titrations of polyacid against polysalt at constant ionic strength were carried out as for poly(acrylic acid) at a polymer concentration of 0·124 g./100 ml. Plots of log $[(1 - \alpha_i)/\alpha_i]$ were again linear in pH, and dissociation constants calculated by the method of Katchalsky, Shavit, and Eisenberg [28] are given in Table 5. The average of the twelve values of pK_0' is 4·86, while the monomer, butyric acid, has pK_0 4·84. Excellent agreement with Katchalsky, Shavit, and Eisenberg's theory is found here in confirmation of their own results. There is no trend of pK_0' with ionic strength as found for the high-molecular-weight poly(acrylic acid) but there is evidence of a trend of pK_0' with pH.

FIG. 8. *Effect of concentration on the mobility of poly(methacrylic acid).*



pH = 7; I = 0·02.

FIG. 9. *Ascending mobilities of poly(methacrylic acid).*



c = 0·124%; pH *values*: ○, 5·0; ×, 6·0; +, 7·0.

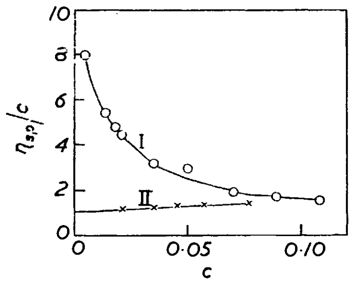


FIG. 10. *Reduced viscosity of poly(methacrylic acid).* (I), *aqueous solution*; (II) 0·2M-aq. $NaNO_3$ *solution at complete ionisation.*

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THE UNIVERSITY, NOTTINGHAM.
DEPARTMENT OF TEXTILE INDUSTRIES,
THE UNIVERSITY, LEEDS 2.

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