

151. The Viscosities of Aqueous Solutions of Some Phenanthrenesulphonic Acids.

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The viscosities of aqueous solutions of *p*-toluenesulphonic, phenanthrene-3-sulphonic, 9-bromophenanthrene-3-sulphonic, and 9-chlorophenanthrene-3-sulphonic acids have been measured at 18° over a considerable range of concentrations. Poiseuille's law was found to hold at the pressures employed. In the case of the halogenated acids there is an abnormal increase in the viscosity at concentrations in the neighbourhood of those at which the abnormal fall in conductivity occurs. The existence of two states of aggregation is indicated by a reversal in the behaviour of the acids: at relatively low concentrations the solutions of the bromo-acid are more viscous than those of the chloro-acid, but at higher concentrations the opposite is the case. It is confirmed that the addition of hydrochloric acid produces a very large increase in the viscosity of solutions of the halogenated acids. The clear isotropic mixed solutions possess "structural" viscosity.

SANDQVIST (*Arkiv Kemi, Min. Geol.*, 1916—1917, 6, No. 9) determined the viscosities of some aqueous solutions of 9-bromophenanthrene-3-sulphonic acid, and although these results were only approximate, they suggested that it would be of value to supplement our study of the conductivities of solutions of phenanthrenesulphonic acids (preceding paper) by an investigation of the viscous behaviour of these systems. We have accordingly measured the viscosities, at 18°, of solutions of the three phenanthrenesulphonic acids mentioned above and also of *p*-toluenesulphonic acid as representing simple aromatic sulphonic acids. The range of concentrations employed for the halogenated acids covers the isotropic region.

EXPERIMENTAL.

The preparation of the acids and the standardisation of the solutions are described in the previous paper. A viscometer of the Ostwald type was employed for the viscosity measurements; the capillary was 20 cm. long and 0.5 mm. in bore, and the timing marks were etched on 2.0 mm. tubing above and below the upper bulb. The pressure on the liquid in the viscometer was varied by the method of Bungenburg de Jong, Kruyt, and Lens (*Kolloid-Beih.*, 1932, 36, 429), the viscometer being attached to a litre bottle into which water flowed from a second similar bottle situated at a suitable height above the first. The extra pressure applied in this manner was read off a water manometer by means of a travelling telescope (reading to 0.001 cm.). Since the manometer levels altered slightly during a viscosity determination, the mean of the initial and the final difference between the levels was taken as the effective extra pressure. During measurements the viscometer was immersed in a water thermostat maintained at 18° ± 0.03°. The water in the pressure apparatus was kept at room temperature (about 18°), which was very constant.

Provided the change in the pressure of the liquid in the viscometer during measurement be sufficiently small compared with the total pressure, the following approximate equation should hold: $(h + p_1)t_1 = (h + p_2)t_2$, where h is the mean hydrostatic pressure of the column of liquid in the viscometer, p_1 and p_2 are any two values of the extra pressure (p), and t_1 and t_2 are the respective values of the time of flow (t). By rearrangement, we have $(p_2t_2 - p_1t_1)/(t_1 - t_2) = h = \text{constant}$. The constancy of h was tested by measurements with water, sucrose solution containing 39.98 g. in 100 g. of solution, and solutions of the halogenated phenanthrenesulphonic acids (0.03N and 0.3N). Over the range of p from *ca.* 8 to 18 (water and dilute solutions) and *ca.* 18 to 90 (more viscous solutions), the values of h differed from the mean by less than 0.3% (usually much less), and showed no systematic drift.

The values of relative viscosity (η) given in Table I were calculated from the formula $\eta = \eta_s/\eta_0 = th/t_0h_0$, where η_s = viscosity of solution, η_0 = viscosity of water, t and t_0 = times of flow without extra pressure, and h and h_0 = mean hydrostatic pressures of solution and water respectively; t_0 was taken as 196.4 secs., which is the mean of three determinations made at wide intervals during the work, and h_0 as 23.30 cm. In the tables times are given in seconds, pressures in cm. of water at room temperature, and concentrations (c) in terms of volume normality.

The values of h for the chlorophenanthrenesulphonic acid were derived from the expression $h = h_0 + 1.9 c$, which was found to reproduce the experimental values of h to within 0.1%. The corresponding equation for the bromo-acid was $h = h_0 + 3.1 c$. For the *p*-toluene- and unsubstituted phenanthrene-sulphonic acids the viscosities may be slightly low, since they were calculated by assuming $h = h_0 W/W_0$, where W and W_0 are the respective weights of equal volumes of solution and water at 18°, but any error involved is without significance in the present connection.

TABLE I.
Viscosities of sulphonic acids at 18°.

Sulphonic acid.	c (N).	η .	c (N).	η .	c (N).	η .	c (N).	η .
<i>p</i> -Toluene	0.01031	1.004	0.05049	1.023	0.1008	1.046	0.2528	1.120
Phenanthrene	0.01021	1.006	0.02341	1.015	0.08433	1.056	0.3402	1.351
	0.01575	1.010	0.04939	1.031	0.2357	(1.264)	0.7474	2.323
Chloro-phenanthrene	0.01234	1.009	0.03912	1.030	0.07796	1.086	0.1472	1.309
	0.03009	1.021	0.06122	1.059	0.1214	1.199	0.2439	2.723
Bromo-phenanthrene	0.01181	1.009	0.03875	1.036	0.07591	1.094	0.1409	1.247
	0.02397	1.017	0.04948	1.052	0.09028	1.120	0.2166	1.630
							0.3190	3.679

TABLE II.
Viscosities of aqueous solutions of halogenated phenanthrenesulphonic acids containing hydrochloric acid.

p .	h .	t .	$(h + p)t/h_0t_0$.	p .	h .	t .	$(h + p)t/h_0t_0$.
Chloro-acid, $c = 0.02055N$; HCl, $c = 0.410N$.				Bromo-acid, $c = 0.02003N$; HCl, $c = 0.415N$.			
0.0	23.52	2759.0	14.180	0.0	23.55	454.9	2.341 (mean)
30.27		990.6	11.644			454.8	
30.36		998.3	11.754			454.5	
66.67		443.9	8.749			455.0	
98.24		264.3	7.032	Bromo-acid, $c = 0.04948N$; HCl, $c = 0.410N$.			
98.68		262.2	7.002	0.0	23.65	2891.0	14.94
98.67		262.8	7.017	0.0		2889.0	(mean)
	HCl, $c = 0.412N$.			98.17		536.0	14.25 (mean)
0.0	23.44	199.7	$\eta = 1.022$	98.03		535.8	
				97.88		535.5	
				98.15		537.0	

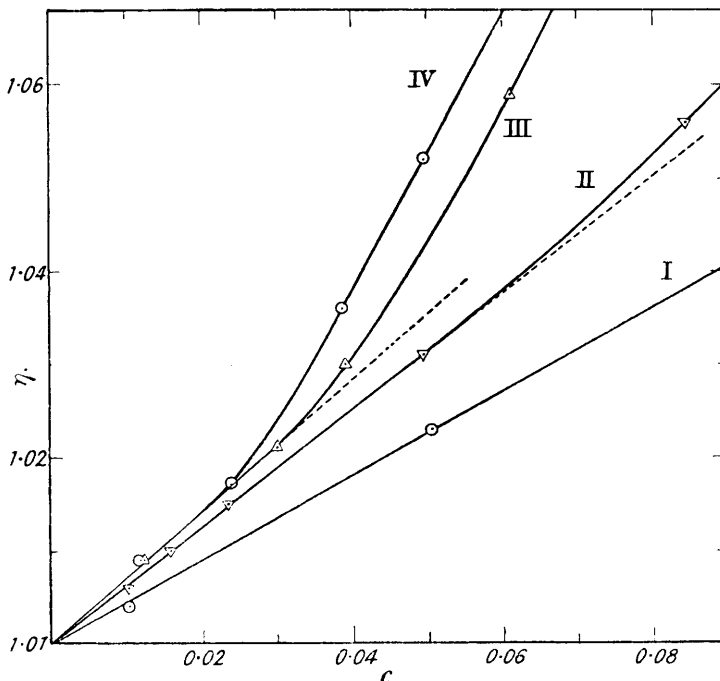
DISCUSSION.

It will be seen from Fig. 1 that, within the experimental error, the viscosity-concentration curves for all four acids are linear over the range of concentrations for which Onsager's conductivity equation holds (cf. preceding paper). In the case of the *p*-toluene acid the linear relation persists up to 0.1N at least, and there is, at the most, only a slight amount of divergence between 0.1N and 0.25N. The unsubstituted phenanthrenesulphonic acid, however, shows appreciable divergence between 0.05N and 0.08N, and the halogenated acids give marked inflections at still lower concentrations. Comparison with the conductivity results reveals that the inflections in the viscosity curves occur at concentrations in the neighbourhood of those at which the respective conductivity curves markedly diverge from the Onsager relation. The abnormal rise in viscosity must, therefore, be brought about by that change in the condition of the dissolved acid responsible for the abnormal fall in conductivity, *i.e.*, by the formation of micelles. Tartar and Wright (*J. Amer. Chem. Soc.*, 1939, **61**, 544) and Hess, Philippoff, and Kiessig (*Kolloid-Z.*, 1939, **88**, 40) have observed a marked inflection in the viscosity curve of sodium dodecyl sulphate in the region of incipient aggregation, and Hess and his co-workers also report an inflection in the case of sodium laurate. None of these workers has, however, attempted to explain how an increase in the viscosity may result from the formation of micelles in dilute solutions of colloidal electrolytes.

It has been shown (see, *e.g.*, Dole, "Electrochemistry," 1935, p. 100) that the viscosity of dilute solutions of many strong electrolytes can be represented by $1/\eta = 1 - A\sqrt{c} \pm Bc$,

where the constant A is expressible in terms of the valency and mobility of the ions. In an interesting attempt to account for the viscous behaviour of solutions of arsphenamine, Robinson and Morrell (*Trans. Faraday Soc.*, 1934, **30**, 339) point out that the rapid increase in the value of A with increasing ionic valency suggests that "a large fraction of the viscosity could be accounted for by the electrical forces arising out of the high valency of the ion-aggregates." The question of the effective valency of the micelles is a difficult one (McBain and Searles, *J. Physical Chem.*, 1936, **40**, 493; McBain and Betz, *J. Amer. Chem. Soc.*, 1935, **57**, 1905; Hartley, *Kolloid-Z.*, 1938, **88**, 22), but it can at least be said that the work of Schmid and Larsen (*Z. Elektrochem.*, 1938, **44**, 657) on the high-frequency conductivity of colloidal electrolytes appears to indicate that the interionic attraction is increased by the formation of micelles.

FIG. 1.
Viscosities of solutions of sulphonic acids at 18°.

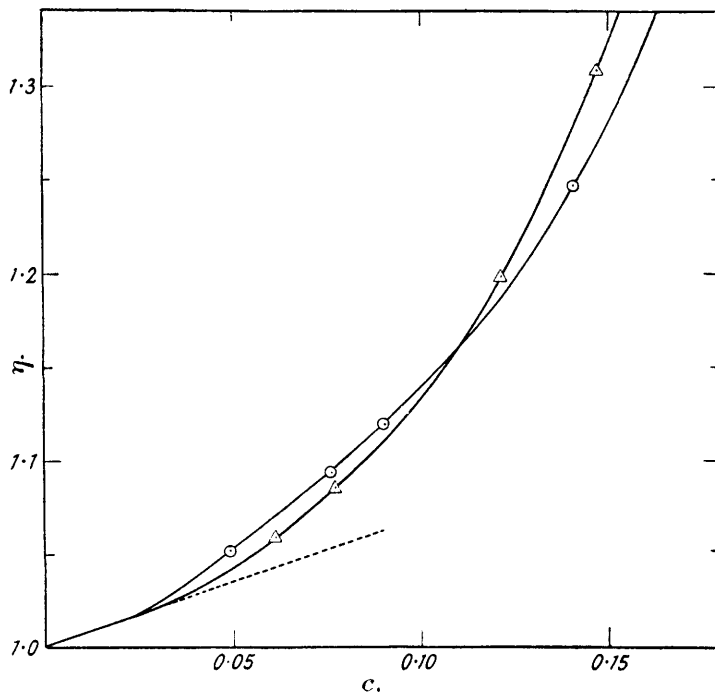


I. *p*-Toluenesulphonic acid. II. Phenanthrene-3-sulphonic acid. III. 9-Chlorophenanthrene-3-sulphonic acid. IV. 9-Bromophenanthrene-3-sulphonic acid.

As will be seen from Fig. 3, the viscosity of solutions of the halogenated phenanthrene-sulphonic acids increases very rapidly as the concentration is increased above about 0.1N. However, even at the highest concentrations examined, Poiseuille's relation was found to hold over the range of pressures employed. Hence, there was no indication, under the given conditions, of the existence of "structural" viscosity in the case of these solutions.

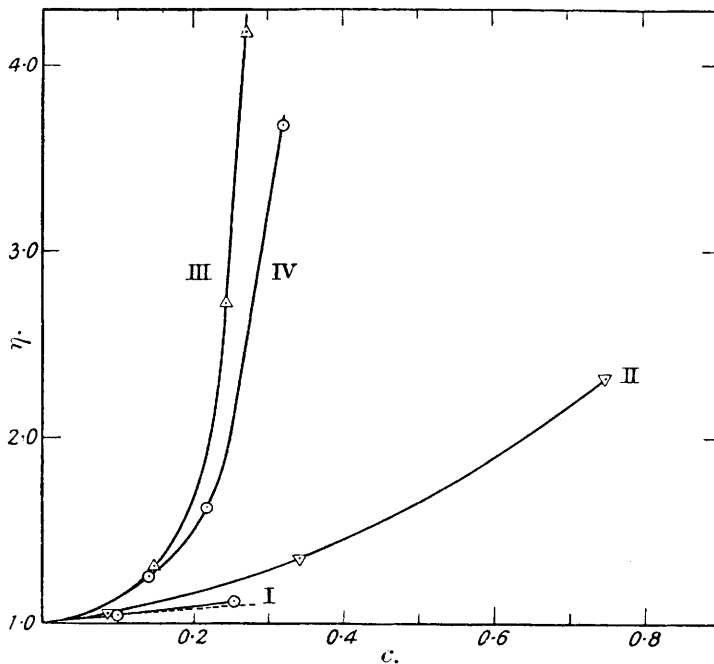
A very interesting feature of the results is the intersection of the curves for the halogenated acids in the neighbourhood of 0.12N (Fig. 2), concentrated solutions of the chloro-acid being much more viscous than corresponding solutions of the bromine derivative. This reversal in viscous behaviour suggests that two states of aggregation occur, each affecting the viscosity in a specific manner. One predominates at low concentrations and is more marked with the bromo-acid, while the other predominates at high concentrations and is more characteristic of the chloro-acid. The electrical conductivities and optical behaviour of the solutions are consistent with the existence of two types of micelle (see preceding paper). It seems possible that aggregation may take place in two stages, the first consisting in the aggregation, at low concentration, of sulphonate ions to form

FIG. 2.
Viscosities of solutions of halogenated phenanthrenesulphonic acids at 18°.



○ 9-Bromophenanthrene-3-sulphonic acid. △ 9-Chlorophenanthrene-3-sulphonic acid.

FIG. 3.
Viscosities of solutions of sulphonic acids at 18°.



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relatively small micelles, and the second, in the aggregation, at high concentrations, of these micelles to form larger units. This is the view taken by Stauff (*Kolloid-Z.*, 1939, **89**, 224) for the case of paraffin-chain electrolytes, but McBain (*J. Physical Chem.*, 1939, **43**, 458) prefers to postulate the existence of two types of independent origin (see, also, Hartley, *loc. cit.*).

It is evident from Tables I and II that the addition of hydrochloric acid to solutions of the halogenated phenanthrenesulphonic acids produces a very striking increase in the apparent viscosity, even at quite low concentrations of the sulphonic acids. This phenomenon was first observed by Sandqvist (*Kolloid-Z.*, 1916, **19**, 113; *Annalen*, 1918, **417**, 17), but the present data reveal the additional fact that the mixed solutions do not conform to Poiseuille's law: the value of $(h + p)t/h_0t_0$ is not constant, but decreases with increase in the rate of flow. Hence, the mixed solutions possess "structural" viscosity. In agreement with Sandqvist, it was found that the effect is much more marked with the chloro- than with the bromo-acid. The mixed solutions were quite clear, and examination in the polarising microscope gave no evidence of anisotropy.

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