150. *The Electrical Conductivities of Aqueous Solutions of Some Phenanthrenesulphonic Acids.*

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The conductivities and densities of aqueous solutions of *p*-toluenesulphonic acid, phenanthrene-2-sulphonic acid, phenanthrene-3-sulphonic acid, 9-chlorophenanthrene-3-sulphonic acid, and 9-bromophenanthrene-3-sulphonic acid have been determined at 18° and 25° over a wide range of concentrations. In sufficiently dilute solutions the conductivity varies with the concentration according to the Onsager theory. Although the conductivity curve for the toluene acid is essentially that of a simple strong electrolyte, the curves for the phenanthrene acids show features characteristic of the behaviour of colloidal electrolytes. The tendency to form micelles at relatively low concentrations increases in the order 3-acid, 2-acid, chloro-acid, bromo-acid. The conductivities of isotropic solutions of the halogenated acids do not pass through minima, and have practically identical values at the highest concentrations. It is confirmed that the chloro-acid shows anisotropy more readily than the bromo-acid. As a whole, the data for the halogen derivatives indicate that these compounds form two types of aggregate in aqueous solution. In all cases the density varies linearly with the concentration over a considerable range. No breaks were detected in the density curves for the halogenated acids.

SANDQVIST (*Annalen*, 1913, **398**, 125; *Arkiv Kemi, Min. Geol.*, 1913—1915, **5**, No. 17; 1916—1917, **6**, No. 9; *Kolloid-Z.*, 1916, **19**, 113; *Ber.*, 1920, **53**, 158, 168) prepared 9-bromophenanthrene-3-sulphonic acid and examined certain physical properties of its aqueous solutions. Since, on the one hand, the solutions were good conductors of electricity, and, on the other, diffusion and cryoscopic data indicated that aggregation occurred to an increasing degree as the concentration was increased, he concluded that the acid should be regarded as a colloidal electrolyte.

Sandqvist prepared several other phenanthrenesulphonic acids but did not investigate their behaviour in aqueous solution in detail; however, he noted that under certain conditions of concentration and temperature solutions of the bromo-acid became turbid and anisotropic, and also that the viscosity of the solutions was enormously increased by the addition of mineral acids. Consequently, he examined the related acids for the presence or absence of such phenomena, and his observations suggested that further study of the influence of chemical constitution upon the properties of these compounds should be of interest in the field of colloidal electrolytes.

We now report an extensive investigation of the electrical conductivities at 18° and 25° of aqueous solutions of phenanthrene-2-, phenanthrene-3-, 9-bromophenanthrene-3-, and 9-chlorophenanthrene-3-sulphonic acids. For comparison, measurements were also made with *p*-toluenesulphonic acid over a wide range of concentrations, this acid being selected as representing simple aromatic sulphonic acids.

EXPERIMENTAL.

Phenanthrene-2- and -3-sulphonic Acids.—Phenanthrene (m. p. 99°) was sulphonated at 120—125° for 3 hours, and barium phenanthrene-2-sulphonate and potassium phenanthrene-3-sulphonate prepared as described by Fieser (*J. Amer. Chem. Soc.*, 1929, **51**, 2465). The free acids were obtained by boiling the barium salts with suitable excess of sulphuric acid, removing barium sulphate, and adding concentrated hydrochloric acid. After three precipitations, the sulphonic acid was kept over sodium hydroxide until dry and free from hydrochloric acid, then dissolved in acetone, and benzene carefully added. The oily liquid which first separated was removed before precipitation of the purified white solid acid by further addition of benzene. Titration (with alkali) of the 2-acid, dried over phosphoric oxide at 100° for 24 hours, gave *M*, 258·4, 258·7 (Calc.: *M*, 258·2). The m. p. of the *p*-toluidine salt was 286°, whereas Fieser (*loc. cit.*) gives 291°, but the salt readily crystallised, a sign, according to Fieser, that it was free from isomers. Titration of the 3-acid, dried over sodium hydroxide, gave *M*, 294·7 (Calc. for dihydrate: *M*, 294·2). The m. p. of the acid was 88° (Sandqvist, *Annalen*, 1909, **369**, 104, gives 88—89°), and that of the easily crystallised *p*-toluidine salt, 220·5° (Fieser gives 222°).

9-Bromo- and 9-Chloro-phenanthrene.—9-Bromophenanthrene, prepared by Sandqvist's method (*Annalen*, 1913, **398**, 136) and recrystallised from petroleum (b. p. 80—100°), was almost white and had m. p. 61—62°. Sandqvist (*loc. cit.*) gives 58—63°, and Haydruck (*Annalen*, 1873, **167**, 181), 63°.

9-Chlorophenanthrene was prepared as described by Sandqvist and Hagelin (*Ber.*, 1918, **51**, 1515). Vigorous stirring of the reaction mixture during chlorination was necessary for good yields (25—30 g. from 50 g. of phenanthrene). After crystallisation from petroleum (b. p. 80—100°), the product was almost white; m. p. 48—50°. Sandqvist and Hagelin give 53—53·5°.

9-Bromo- and 9-Chloro-phenanthrene-3-sulphonic Acids.—The halogenated phenanthrene (20 g.) was treated with concentrated sulphuric acid (18 ml.) for some hours at about 100°, the acid being added in several portions, and the mixture kept constantly stirred. The very viscous sulphonated mass was cooled, filtered off under suction to remove sulphuric acid, dissolved in a small quantity of water, and boiled with charcoal. After cooling, concentrated hydrochloric acid was added, and the gelatinous precipitate of sulphonic acid separated by means of a centrifuge. The precipitation was repeated twice, and the acid then kept over sodium hydroxide to remove water and hydrogen chloride. Further purification was effected by dissolving the acid in acetone and reprecipitating it by addition of benzene, the procedure being twice repeated. Since solutions of the acids darkened on exposure to light, they were kept shielded as far as possible. The almost white product was finally dried in a vacuum desiccator. The following data were obtained with samples reprecipitated from acetone and dried at 100°. Bromo-acid (Found, by titration: M, 337·2. Calc.: M, 339·1), m. p. 203·5—204°; Sandqvist (*loc. cit.*, 1916—1917) gives m. p. 200—201°. Chloro-acid (Found, by titration: M, 291·5, 292·7, 292·0. Calc.: M, 292·6), m. p. 208·8—209·3°. Sandqvist (*Annalen*, 1918, **417**, 17) gives m. p. 206—207°.

p-Toluenesulphonic Acid.—" B. D. H. Micro-analytical Reagent " was used without further purification. Apart from a trace of iron, it was free from inorganic matter. Titration of the acid, dried over phosphoric oxide for several weeks, gave M, 190·4, 191·0 (Calc.: M, 190·2).

Conductivities.—The conductivities were measured by means of a Cambridge bridge, which was provided with a " reed hummer " supplying A.C. at 1000 cycles/sec. A large silica cell, similar to that described by Howell and Handford (*Trans. Faraday Soc.*, 1933, **29**, 640), was employed for concentrations below 0·001N. Cell constants were determined with 0·1 " demal " potassium chloride, the specific conductivity of this solution being taken as 0·011163 ohm^{-1} cm.$^{-1}$ (Parker and Parker, *J. Amer. Chem. Soc.*, 1924, **46**, 312) at 18°.

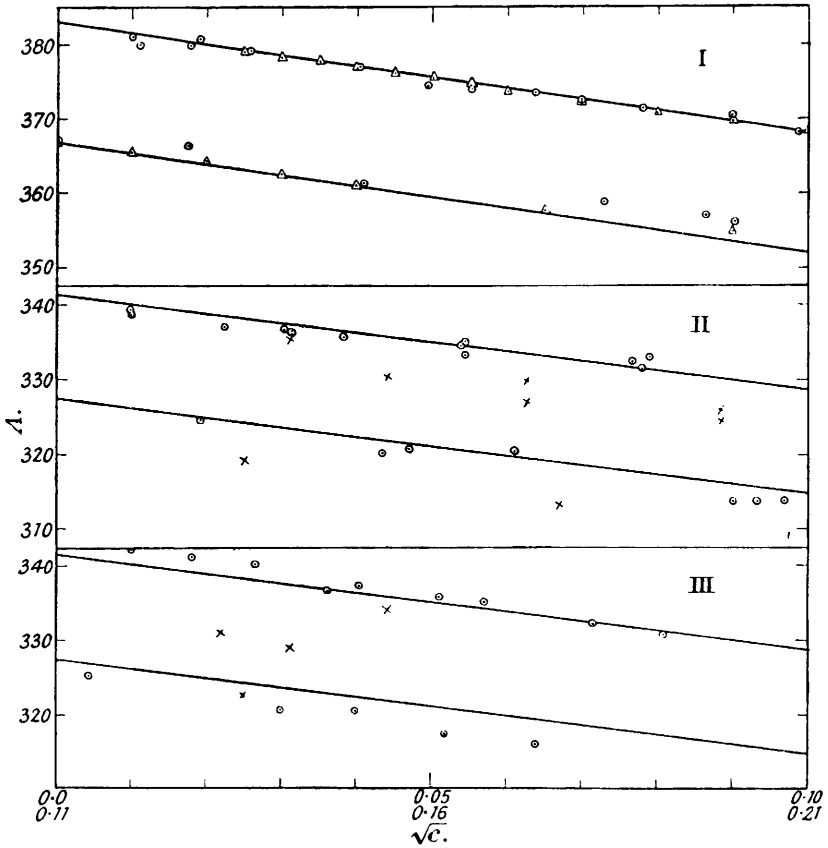
All solutions were prepared from water distilled in the apparatus designed by Vogel and Jeffery (J., 1931, 1201). By passing a stream of purified nitrogen through the still, and thus operating slightly above atmospheric pressure, water of specific conductivity 0·65—0·75 × 10^{-6} ohm^{-1} cm.$^{-1}$ at 18° was easily prepared as required. Although tests with Nessler's solution showed the complete absence of ammonia, yet an appreciable decrease in the conductivity was observed when purified nitrogen was bubbled for several hours through a sample of the water in the silica cell. It appeared safe to assume that the conductivity was chiefly due to carbon dioxide (see Wynne-Jones, *J. Physical Chem.*, 1927, **31**, 1653), and no solvent correction was applied.

Each series of solutions was prepared by dilution, by weight, of a suitable solution of approximately known concentration. The composition of one or two of the solutions was determined by titrating a known weight with alkali, the densities of all the solutions were measured, and the volume normalities calculated.

DISCUSSION.

p-Toluenesulphonic Acid.—In Fig. 1 (I) the equivalent conductivity (Λ) at 25° is plotted against the square root of the volume normality up to a concentration of about 0·04N. The curve is shown in two portions, the upper one extending to about $\sqrt{c} = 0{\cdot}01$ and the lower comprising the remaining concentrations. The straight line corresponds to the equation $\Lambda = \Lambda_0 - (0{\cdot}2274\Lambda_0 + 59{\cdot}79)\sqrt{c}$, Λ_0 being taken as 383·0. This is the version of Onsager's equation (for a uni-univalent electrolyte at 25°) commonly found in the literature. According to the data quoted by Falkenhagen (" Electrolytes," 1934, 193) the constants should be 0·2271 and 59·78, but the differences are of no importance in the present instance. Up to $\sqrt{c} = 0{\cdot}10$ the authors' data are fairly well represented by the Onsager line, the divergence in regard to Λ seldom exceeding 0·5 unit. The most reliable previous work is that of Wegscheider and Lux (*Monatsh.*, 1909, **30**, 411; cf. da Monte and Zoso, *Gazzetta*, 1897, **27**, ii, 467; Wightman and Jones, *Amer. Chem. J.*, 1911, **46**, 56; Dawson and Crann, J., 1916, **109**, 97), whose values show good agreement with the Onsager line up to about $\sqrt{c} = 0{\cdot}18$, but their results may be subject to a slight experimental error, since they are based on the value for the specific conductivity of 0·02N-potassium chloride obtained by Kohlrausch, Holborn, and Diesselhorst (*Wied. Annalen*, 1898, **64**, 417), whose values for 1·0N-, 0·10N-, and 0·01N-solutions have been shown by Jones and Prendergast (*J. Amer. Chem. Soc.*, 1937, **59**, 731; see also Davies, J., 1937, 1326) to be probably in error by + 0·60, − 0·048, and + 0·110%, respectively. Between $\sqrt{c} = 0{\cdot}10$ and $\sqrt{c} = 0{\cdot}20$ the experimental curve diverges from the Onsager line, the conductivity falling *less* rapidly than at the lower concentrations. The figure does not include one further value obtained by Wegscheider and Lux, *viz.* $\Lambda = 352{\cdot}6$ for $\sqrt{c} = 0{\cdot}225$, *i.e.*, 2·6 units higher than the theoretical value.

FIG. 1.



I. p-*Toluenesulphonic acid at* 25° (△ *Wegscheider and Lux*). II. *Phenanthrene*-3-*sulphonic acid at* 18° (× *Sandqvist*). III. *Phenanthrene*-2-*sulphonic acid at* 18° (× *Sandqvist*).

Up to about $\sqrt{c} = 0{\cdot}10$, the data for dilute solutions at 18° showed fairly good agreement with the Onsager equation (see Falkenhagen, *op. cit.*, p. 193)

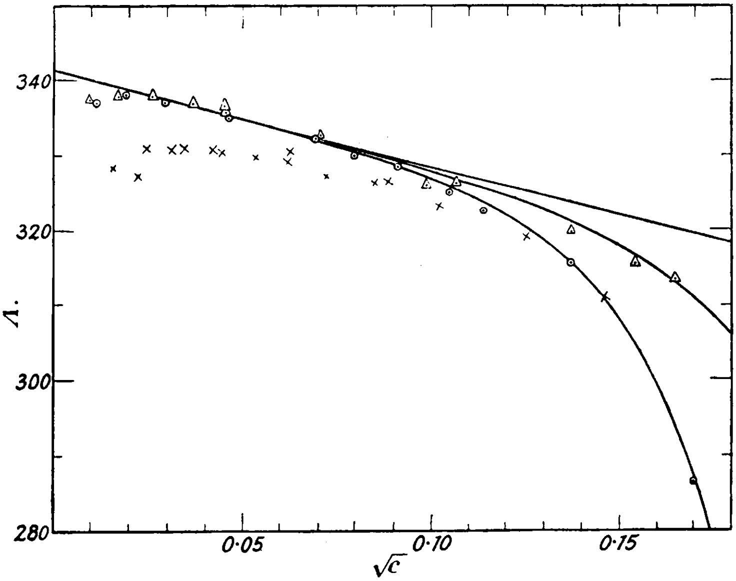
$$\Lambda = \Lambda_0 - (0{\cdot}2238\Lambda_0 + 50{\cdot}49)\sqrt{c},$$

Λ_0 being taken as 343·5. With one exception ($\Lambda = 186{\cdot}8$ for $\sqrt{c} = 1{\cdot}133$), the data for the higher concentrations at 18° are plotted in Fig. 3 (II). Although the general shape of the curve resembles that for hydrochloric acid (I) (I.C.T., 1929, VI, 242), there are appreciable differences. For the present purpose, the theoretical line for hydrochloric acid may be obtained with sufficient accuracy by assuming that Onsager's theory applies at 0·001N, and estimating the value of Λ at this concentration, by interpolation, from the data of Shedlovsky and MacInnes (*J. Amer. Chem. Soc.*, 1935, **57**, 1705). This gives Λ_0 = 381·7. Divergence from the Onsager line is always less marked with the sulphonic acid than with hydrochloric acid. Whereas the theoretical and the experimental curve for the former acid meet at about $\sqrt{c}$ = 0·85, those for the latter are still wide apart in this region.

Phenanthrene-3-*sulphonic Acid*.—The data for the more dilute solutions at 18° are shown in Fig. 1 (II), and those for the higher concentrations in Fig. 3 (III) (excluding Λ = 167·2 at $\sqrt{c}$ = 1·124). Onsager values have been calculated by assuming Λ_0 = 341·5. Although the measurements are less accurate than those for the toluene acid, the theoretical curve fairly represents the actual data up to about $\sqrt{c}$ = 0·15. With one exception, Sandqvist's values (*Annalen*, 1909, **369**, 104; *Arkiv Kemi, Min. Geol.*, 1911—1913, **4**, No. 33, 23, 24) lie on a straight line much below those of the authors. All of Sandqvist's figures appear to be based on the value given by Kohlrausch and Holborn (" Leitvermögen der Elektrolyte," 1898, p. 77; measurements by Kohlrausch, Holborn, and Diesselhorst, *loc. cit.*) for the specific conductivity of 0·01N-potassium chloride at 18°. Jones and Prendergast (*loc. cit.*) have shown that the value is probably too low by 0·017%, but this is quite inadequate to account for the present discrepancy.

FIG. 2.

Conductivities of halogenated phenanthrenesulphonic acids at 18°.

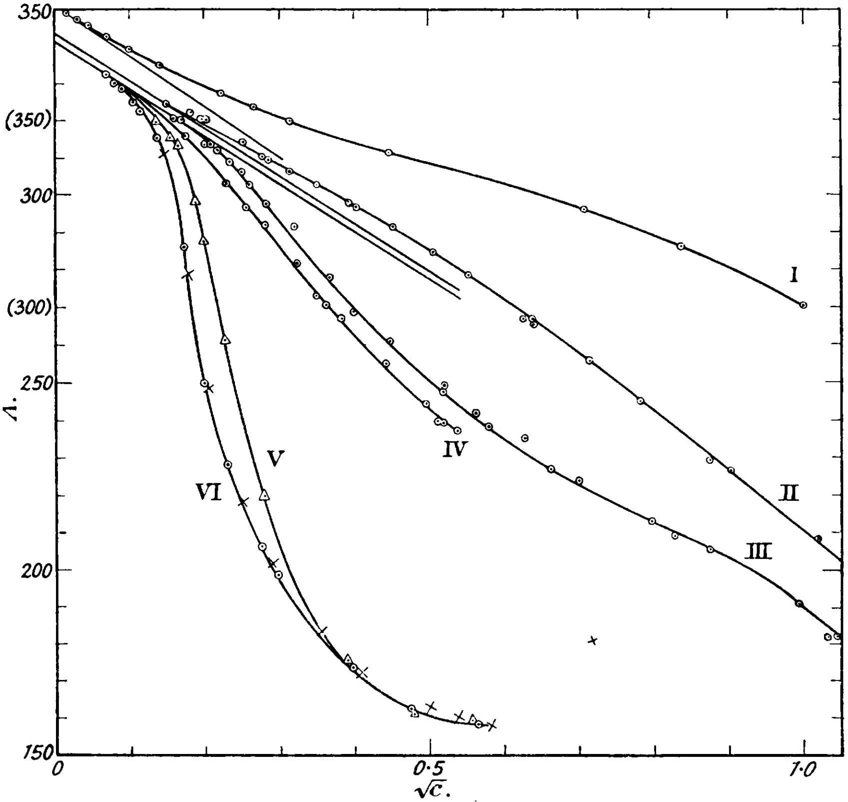


△ 9-*Chlorophenanthrene*-3-*sulphonic acid*. ⊙ 9-*Bromophenanthrene*-3-*sulphonic acid* (× *Sandqvist*).

The behaviour of the phenanthrene acid differs considerably from that of the toluene acid. In the neighbourhood of $\sqrt{c}$ = 0·15 the experimental curve commences to fall *below* the theoretical line, and up to about $\sqrt{c}$ = 0·35 bends markedly in the direction of the x-axis (Fig. 3). Over the range $\sqrt{c}$ = 0·35—0·85 a second inflection, in the opposite sense, occurs, and at still higher concentrations the curve again changes direction. Altogether, the curve closely resembles that obtained by Laing-McBain, Dye, and Johnston (*J. Amer. Chem. Soc.*, 1939, **61**, 3210) for the straight-chain sulphonic acid $C_9H_{19}{\cdot}SO_3H$, the inflections, however, being more marked in the case of the aromatic acid. Those workers determined the conductivities of a number of the straight-chain acids at 25°, and their results show that, as the number of carbon atoms increases from 2 to 14, there is a gradual transition from typical fully dissociated electrolytes to well-marked colloidal electrolytes, the heptyl and nonyl acids occupying an intermediate position. It would therefore appear from the shape of the conductivity curve that the formation of micelles occurs to an appreciable extent in aqueous solutions of phenanthrene-3-sulphonic acid.

Phenanthrene-2-sulphonic Acid.—The data for dilute solutions at 18° are plotted in Fig. 1 (III), which also includes the highest values obtained by Sandqvist (*Arkiv Kemi, Min. Geol.*, 1911—1913, **4**, No. 33, p. 55; *Annalen*, 1911, **379**, 79) in three independent series of measurements. The straight line is Onsager's curve with $\Lambda_0 = 341{\cdot}5$, as for the 3-acid. Over the range $\sqrt{c} = 0{\cdot}035$—$0{\cdot}08$ the experimental points are close to the theoretical line.

FIG. 3.
Conductivities at 18°.



I. *Hydrochloric acid (ordinates in parentheses).* II. p-*Toluenesulphonic acid.* III. *Phenanthrene-*3-*sulphonic acid.* IV. *Phenanthrene-*2-*sulphonic acid.* V. 9-*Chlorophenanthrene-*3-*sulphonic acid.* VI. 9-*Bromophenanthrene-*3-*sulphonic acid* (× *Sandqvist*). *Straight lines = Onsager equation.*

It seems preferable to attribute the lack of agreement at the three lowest concentrations to experimental error, rather than to assume a higher value for Λ_0, since it is not likely that the difference in the position of the sulphonic group would influence the mobility of the sulphonate ion to an appreciable extent.

The experimental curve diverges from the straight line in the same manner as that of the 3-acid, but the divergence commences at a lower concentration, *viz.*, about $\sqrt{c} = 0{\cdot}1$. Careful repurification of the acids produced no significant change in the results, and it would therefore appear that there is a genuine difference in behaviour. Since, presumably, the earlier divergence indicates that the 2-acid shows a greater tendency to form micelles than does the 3-acid, it is surprising that at the higher concentrations (Fig. 3) the curves for the two acids are practically parallel. Owing to the restricted solubility of the 2-acid, it was not possible to extend the measurements above about 0·3N.

Halogenated Phenanthrenesulphonic Acids.—The data for 18° are shown in Figs. 2 and 3, which include the higher set of values for the bromo-acid obtained by Sandqvist (*Arkiv Kemi, Min. Geol.*, 1913—1915, **5**, No. 17, 39, 40; 1916—1917, **6**, No. 9, 34, 35; *Kolloid-Z.*, 1916, **19**, 113) in two independent series of measurements. Although our results are in quite good agreement with his above about $\sqrt{c} = 0{\cdot}15$, below this there is marked discrepancy. Up to roughly $\sqrt{c} = 0{\cdot}06$ the present data, except those for the lowest concentrations studied, agree fairly well with the Onsager equation obtained by taking $\Lambda_0 = 341{\cdot}3$. With further increase in concentration the curves undergo inflections similar in nature to those observed with the unsubstituted acid, but very much more pronounced. The general shape of the curves is similar to that of the higher straight-chain sulphonic acids and sulphonates (see, *e.g.*, Murray and Hartley, *Trans. Faraday Soc.*, 1935, **31**, 183; Hartley, *J. Amer. Chem. Soc.*, 1936, **58**, 2347; Tartar *et al.*, *ibid.*, p. 322; 1939, **61**, 549; Laing-McBain, Dye, and Johnston, *loc. cit.*), and it is evident that the introduction of a halogen atom at the 9-position markedly increases the tendency to micelle formation.

Determinations of the turbidity points of two solutions of the chloro-acid gave the following results:

	Turbidity point.		
c (N).	Heating.	Cooling.	Mean.
0·3115	17·75°	17·69°	17·72°
0·2302	9·78, 9·78	9·73, 9·75	9·76

Sandqvist (*Kolloid-Z.*, 1916, **19**, 113; *Annalen*, 1918, **417**, 17) found that his values for the turbidity point could be represented to within about 0·05° by an equation of the form $t° = a + b \log C$, where a and b are constants, and C is the concentration in mols. per 100 mols. of solution. For the chloro-acid, Sandqvist obtained $a = 34{\cdot}3$ and $b = 60{\cdot}2$, whereas our data give $a = 31{\cdot}03$ and $b = 58{\cdot}28$. However, Sandqvist states that his values are only approximate, and a proper comparison is therefore not possible. The values now obtained being adopted, it follows that the concentration of the solution with a turbidity point of 18° will be 0·315N, Sandqvist's approximate figure being 0·284N. (A turbid, and therefore anisotropic, solution of the chloro-acid separated into two distinct layers, as reported by Sandqvist. The upper layer was quite clear, and the lower one turbid and streaky.) According to Sandqvist's data for the bromo-acid, the concentration of the solution with a turbidity point of 18° will be 0·425N, and we have observed that a 0·3115N-solution is still quite clear at a temperature below the turbidity point of an equally concentrated solution of the chloro-acid. Hence, the chlorine derivative shows a greater tendency to give anisotropic systems.

It will be seen from the foregoing that the conductivity measurements stop short of the region of anisotropy. Sandqvist determined the conductivity of one anisotropic solution (0·508N) of the bromo-acid and obtained an average value of 181·0 for Λ. If this figure is correct, the conductivity must pass through a minimum. It should be pointed out, however, that Sandqvist records that the specific conductivity could be varied between 0·091 and 0·096 by shaking the solution between measurements. A minimum in the conductivity curve is a very characteristic feature of colloidal electrolytes of the long paraffin-chain type, but in the range of concentrations concerned, the solutions are homogeneous, clear, and isotropic (see, *e.g.*, Hartley, *Kolloid-Z.*, 1939, **88**, 22), and the conductivity depends only on the concentration and temperature.

The curve for the chloro-acid diverges less rapidly from the Onsager line than does that of the bromo-acid, and it would seem that at the lower concentrations the formation of micelles is less extensive when bromine is replaced by chlorine. At about $\sqrt{c} = 0{\cdot}25$ the curves commence to approach one another, and beyond about $\sqrt{c} = 0{\cdot}4$ they are practically coincident. This behaviour is not observed with a homologous series of paraffin-chain electrolytes, for in this case the more abrupt the divergence from the theoretical line, *i.e.*, the more colloidal the compound, the lower is the minimum value of Λ. Moreover, the more marked anisotropy shown by the chloro-acid suggests that at the higher concentrations this acid possesses a greater tendency to form aggregates. It seems probable, therefore, that two states of aggregation are to be distinguished, one predominating at the lower concentrations, and more marked with the bromo-acid, and the other becoming prominent at the higher concentrations, and shown to a greater degree by the chloro-acid.

The data at 25° up to about $\sqrt{c} = 0{\cdot}07$ showed fair agreement with Onsager's theory, Λ_0 being taken as 379·5. With increase in temperature the curve flattens out less rapidly at the highest concentrations, owing probably to a decrease in the degree of aggregation, as with other types of colloidal electrolytes. The concentration at which the two curves meet is somewhat higher at 25° than at 18°, and at the higher temperature the conductivity of the chloro-acid is slightly less than that of the bromo-acid in the most concentrated solutions.

It was established by actual experiment that the low values of Λ obtained for the most dilute solutions were not due to adsorption on the electrodes or cell walls. In view of the experimental conditions, however, it would be premature to assume the existence of a maximum in this region of the conductivity curve (cf. Robinson and Moillet, *Proc. Roy. Soc.*, 1934, *A*, **143**, 630; Laing-McBain, Dye, and Johnston, *loc. cit.*).

Densities.—In general, over a considerable range of concentrations the density varied linearly with the concentration according to equations of the type $d^{18^\circ}_{4^\circ} = 0{\cdot}99862 + ac$ or $d^{25^\circ}_{4^\circ} = 0{\cdot}99707 + bc$, where the constants a and b have the values given below:

Sulphonic acid.	*a.*	*b.*
Toluene (up to *ca* 0·6N)	0·052756	0·052248
Phenanthrene (up to *ca.* 0·4N)	0·082048	0·081154
Chlorophenanthrene (isotropic range)	0·11013	0·10837
Bromophenanthrene (isotropic range)	0·15110	0·14993

At higher concentrations of the toluene and phenanthrene acids, the experimental values diverge from the linear relation and fall towards the concentration axis. Similar behaviour was observed by Laing-McBain, Dye, and Johnston with the lower members of the paraffin-chain series of sulphonic compounds. There was no indication of a break in the curves of the halogenated phenanthrene acids, similar to that observed by Bury and Parry (J., 1935, 626; Bury, *Chem. and Ind.*, 1938, **57**, 1167) at the "critical concentration for micelles" in the case of potassium laurate.

Influence of Chemical Constitution.—The contrast between the behaviour of the unsubstituted phenanthrene acids and that of tetradecylsulphonic acid (Laing-McBain, Dye, and Johnston, *loc. cit.*), or its sodium salt (Tartar *et al.*, *loc. cit.*), is an illustration of the fact that aromatic sulphonate ions form micelles much less readily than paraffin-chain sulphonate ions containing the same number of carbon atoms (cf. Norris, J., 1922, **121**, 2161). That increase in the size of the aromatic nucleus favours aggregation is shown by the difference between the behaviour of *p*-toluenesulphonic acid and of the unsubstituted phenanthrene acids. Similarly, Norris found that sodium anthraquinonesulphonate is more colloidal than sodium naphthalenesulphonate. The data for the unsubstituted phenanthrene acids further indicate that the position of the sulphonic group exerts an appreciable influence upon the tendency to form micelles. This agrees with Norris's observation that the sodium salt of β-naphthalenesulphonic acid is more colloidal than the α-isomer. With regard to the effects of substitution, the present results confirm that the introduction of a halogen atom at the 9-position in phenanthrene-3-sulphonic acid increases, in striking fashion, the colloidal character of the compound. It would appear that there exist, between the halogenated sulphonate ions, specific forces of attraction, which vary in strength with the nature of the halogen.

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