THE PROPERTIES OF AQUEOUS SOLUTIONS OF THE PHENANTHRENE SULPHONIC ACIDS.

A contribution to the Study of Colloidal Electrolytes.

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INTRODUCTION.

The employment in industry of new types of wetting agents and detergents has led to a renewal of interest in the whole subject of colloidal electrolytes As originally defined by McBain,(1) colloidal electrolytes are "salts in which one ion has been replaced by a heavily hydrated polyvalent micelle that carries an equivalent sum-total of electrical charges and conducts electricity just as well or even better than the simple ion it replaces". As is well known, the conception of the ionic aggregate or ionic micelle was advanced by McBain to reconcile the relatively high electrical conductivity of soap solutions with their very low osmotic activity. The results of recent investigations have substantiated the value of this conception, while throwing some doubt on other features of McBain's theory.(2)

The bulk of the newer data has been obtained from the study of the properties of long paraffin-chain compounds such as alkyl sulphates, alkyl sulphonic acids, and alkyl pyridinium salts.(2)(3) It appears probable(2) that in the case of these compounds, as in

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(1) McBain and Salmon, J.A.C.S., 42 (1920) 426.
(2) Hartley, "Aqueous Solutions of Paraffin-chain Salts" (1936).
(3) Valkó "Kolloidchemische Grundlagen der Textilveredlung", (1937), Chap. 14.

that of the soaps, the aggregation of the fatty ions to form micelles is due primarily to the insolubility of the paraffin-chains. Harkins (1) has shown that the attraction of the chains for water is much less than that of water for water, so that considerable force is required to separate the chains and bring them into solution. On the other hand, the terminal (head) group of the fatty ion has a strong affinity for water and strives to drag the rest of the molecule into solution. At very low concentrations the influence of the terminal group predominates and the compound dissolves as a simple strong electrolyte. At higher concentrations, however, separation of the chains is achieved, in the main, only to the limited extent involved in the formation of micelles.

The water-water attraction cannot, however, be the sole factor responsible for the aggregation of organic ions in general, although it will probably always play some part. It is to be expected that the ions will exert attractive forces upon each other, according to the nature and disposition of the chemical groups present. (2)(3) That the degree of aggregation may be considerably influenced by quite small variations in molecular structure is indicated by the observations

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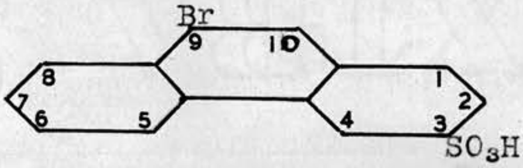
(1) Harkins, Alexander's "Colloid Chemistry", Vol. 1. (1926) 192.

(2) Hartley, "Aqueous Solutions of Paraffin-Chain Salts", (1936) 62-64.

(3) Valkó, "Kolloidchemische Grundlagen der Textilveredlung", (1937) 378-380.

of Robinson and others(1)(2)(3) on the behaviour of certain benzidine derivatives, and by those of Sandqvist(4) on the behaviour of some of the phenanthrene sulphonic acids.

The compound examined in greatest detail by Sandqvist was 9-bromo-phenanthrene-3-sulphonic acid:-



Sandqvist's interest in the properties of the aqueous solutions of this acid was aroused by the observation that the solution obtained by hydrolysing the sulphochloride possessed a very high viscosity. Investigation(5)(6) revealed that this effect was due to the presence of the hydrochloric acid produced by the hydrolysis, and that in general the addition of a mineral acid to a solution of the sulphonic acid gave rise to an extraordinary increase in the viscosity.

Sandqvist(6)(7) proceeded to study the electrical

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(1) Robinson and Mills, Proc. Roy. Soc., A <u>131</u> (1931) 576.
(2) Robinson and Garrett, Trans. Faraday Soc., <u>35</u> (1939) 771.
(3) Robinson and Selby, Trans Faraday Soc., <u>35</u> (1939) 780.
(4) McBain in Bogue's "Colloidal Behaviour", Vol. 1 (1924) 420.
(5) Sandqvist, Lieb. Ann., 398 (1913) 125.
(6) Sandqvist, Kolloid. Zeitschr., <u>19</u> (1916) 113.
(7) Sandqvist, Arkiv. for Kemi, Mineralogi och Geologi, <u>5</u> (1913-15) No. 17.

conductivity, at 18°C., of solutions of the sulphonic acid, both in the absence and in the presence of hydrochloric acid. He records (1) that at high dilutions the pure acid exhibited the conductivity characteristic of a strong acid, (2) that the conductivity of the pure acid underwent a marked decrease at a concentration of 0·02 - 0·03 N, and (3) that in the case of a mixture with hydrochloric acid, the conductivity of the mineral acid was not appreciably affected by the high viscosity. It was also observed (1)(2)(3) that a solution of the sulphonic acid became turbid and anisotropic at a certain temperature, the value of which depended upon the concentration of the solution. This change appeared to be accompanied by an increase in the conductivity, so that the conductivity curve for 18° passed through a minimum at some concentration between 0·3 and 0·5.

Sandqvist (3)(4) found further that the sulphonic acid passed through a dialysis membrane much more slowly at higher than at lower concentrations, suggesting that the acid possessed a strong tendency to associate with increase in concentration, a view which appeared to be supported by cryoscopic data.

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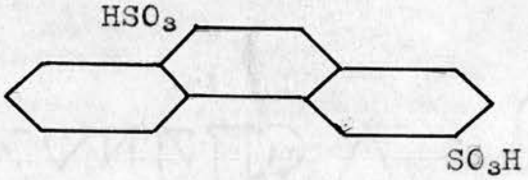
(1) Sandqvist, Kolloid. Zeitschr., 19 (1916) 113.
(2) Sandqvist, Berichte, 48 (1915) 2054.
(3) Sandqvist, Arkiv. for Kemi, Mineralogi och Geologi, 6 (1916-17) No. 9.
(4) Sandqvist, Arkiv. etc., 5 (1913-15) No. 17.

On the basis of the high conductivity and the evidence of aggregation, Sandqvist (1)(2)(3) concluded that 9-bromo-phenanthrene-3-sulphonic acid is a colloidal electrolyte, and the recent work on paraffin-chain compounds indicates that the shape of the conductivity curve is consistent with this conclusion.

Sandqvist prepared several other phenanthrene sulphonic acids but being primarily concerned with the chemistry of phenanthrene, he did not examine the behaviour of these acids in aqueous solution to any considerable extent. However, his recorded observations are sufficient to show that interesting results might be expected from an intensive study of the influence upon this behaviour of the position and nature of the substituent groups. He reports (4) that solutions of phenanthrene-9-3-disulphonic acids:-



in which bromine is replaced by the sulphonic group, showed neither anistropy nor high viscosity on the addition of hydrochloric acid. Loss of these properties also resulted on replacing the bromine by the group

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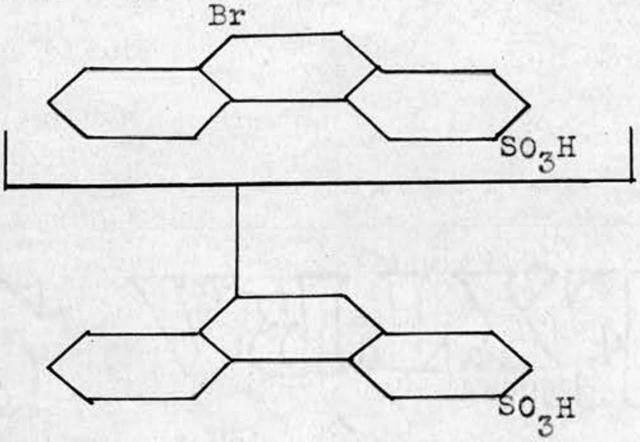
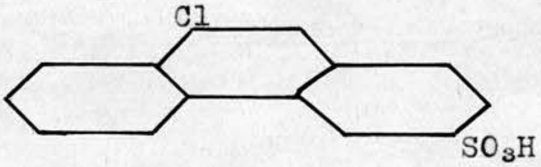
(1) Sandqvist, Kolloid. Zeitschr., 19 (1916) 113.
(2) Sandqvist, Arkiv. for Kemi, Mineralogi och Geologi, 5 (1912-13) No. 17.
(3) Sandqvist, Arkiv. etc., 6 (1916-17) No. 9.
(4) Sandqvist, Berichte, 50 (1917) 774.

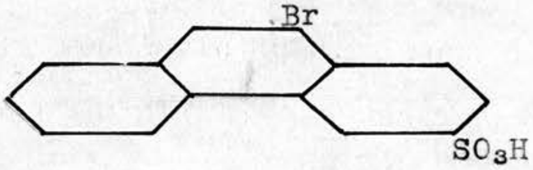
$C_{14}H_7BrSO_3CH_3$ to give a monobromodiphenanthryldisulphonic acid(1) :-



On the other hand, the anistropy and viscosity were much enhanced when chlorine was substituted for bromine, to give 9-chloro-phenanthrene-3-sulphonic acid(2) :-



Sandqvist(3) remarks that 10-bromo-phenanthrene-3-sulphonic acid:-



(which differs from the bromo-acid previously described only in regard to the position of the bromine

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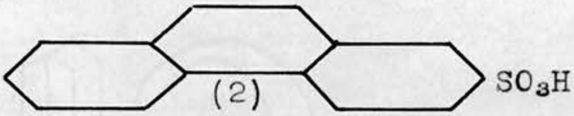
(1) Sandqvist, Arkiv. for Kemi, Mineralogi och Geologi, 7 (1918-20) No. 4.

(2) Sandqvist, Lieb. Ann., 417 (1918) 17.

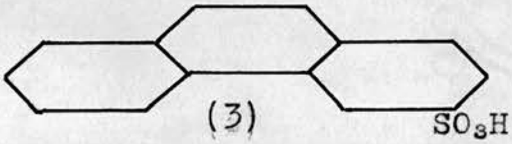
(3) Sandqvist, Lieb.Ann., 417 (1918) 1.

atom) showed no abnormal viscosity with hydrochloric acid. He suggests, however, that the concentration of the sulphonic acid may have been too low, since the 10-isomer was less soluble than the 9-isomer. Excess of the mineral acid induced separation of the 10-isomer in a slimy anisotropic form.

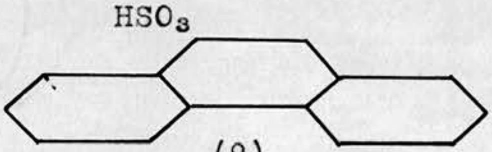
Sandqvist(1)(2)(3)(4) also determined the conductivity of certain solutions of the 2, 3, and 9 unsubstituted monosulphonic acids:-



(2)



(3)



(9)

The highest concentration investigated was about 0·03 N. In contrast with the behaviour of 9-bromo-phenanthrene-3-sulphonic acid, no sudden fall in conductivity was observed within the range 0·02 - 0·03 N. Moreover, in the case of the unsubstituted acids, the viscosity of the solution obtained by hydrolysing the sulphochloride was normal. Thus it would appear that the properties of the acid in aqueous solution are very considerably affected by the introduction of a halogen atom into the molecule.

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(1) Sandqvist, Lieb. Ann., 379 (1911) 79.
(2) Sandqvist, Lieb. Ann., 369 (1909) 104.
(3) Sandqvist, Lieb. Ann., 392 (1912) 76.
(4) Sandqvist, Arkiv. etc., 4 (1911-13) No. 33.

In addition to the foregoing survey of the work of Sandqvist, mention may be made of the observation due to Rinne(1)(2) that prior to dissolution, 9-bromophenanthrene-3-sulphonic acid forms, in succession, two distinct types of anisotropic systems, the smectic and the nematic respectively, the water content of the former being less than that of the latter.

The object of the present investigation was to make further advances in the interesting field opened up by Sandqvist and almost entirely neglected since his time, due possibly to the lack of practical application of the substances in question, and to the difficulties associated with their preparation. From the experimental standpoint, the ground covered has involved the following:-

(1) The preparation, in adequate amount, of pure samples of the 2, and 3-unsubstituted phenanthrene monosulphonic acids, and of the 9-bromo-, and 9-chlorophenanthrene-3-sulphonic acids.

(2) The measurement, at 18° and 25°, and over a wide range of concentration, of the following properties of aqueous solutions of these acids:

(a) Electrical conductivity
(b) Density
(c) Viscosity.

(3) The measurement, at 18° and 25°, and over a

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(1) Rinne, Zeitschr. Krystallogr. etc., 82 (1932) 379.
(2) Rinne, Trans. Faraday Soc., 29 (1933) 1016.

wide range of concentration, of the same properties in the case of p-toluene sulphonic acid.

(4) Observations on the "turbidity point" of the halogenated phenanthrene acid solutions, and the effect of hydrochloric acid on their viscosity and optical behaviour.

To some extent the ground covered by Sandqvist has been gone over again. This appeared desirable as a check, in any case, since Sandqvist's data stood alone. Actually, the results of the present work have revealed considerable errors in Sandqvist's data, so that the repetition was fully justified.

EXPERIMENTAL.

PREPARATION OF PHENANTHRENE-2 AND -3-SULPHONIC ACIDS.

Sulphonation of Phenanthrene and Separation of Isomers. Phenanthrene was obtained from two sources, viz., The British Drug Houses, Ltd., and Gesellschaft für Teerverwertung m.b.H., Duisburg-Meiderich. Both supplies were pure white crystalline plates, melting point 99°C.

Barium phenanthrene-2-sulphonate and potassium phenanthrene-3-sulphonate were prepared according to the method of Fieser,(1) as summarised below.

100 gm. phenanthrene were sulphonated for three hours at 120-125°C., using mechanical stirring. Sulphur dioxide was evolved and a dark brown syrup resulted. The hot syrup was dissolved in about 1 litre of water and a concentrated solution of 80 gm. sodium hydroxide added and the solution cooled in ice. The sodium salt which precipitated was filtered off and washed with half-saturated sodium chloride solution.

The sodium salt was dissolved in hot water containing 10 ml. concentrated hydrochloric acid solution to help in the dissolution of the salt. The filtered

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(1) Fieser, J.A.C.S., 51 (1929) 2460.

solution was neutralised with sodium hydroxide and the sodium salt allowed to crystallise. The crystals, mainly the 2-sulphonate, were dissolved in 1.5 litres hot water, and barium chloride added to bring down the barium salt. The barium salt was filtered off and repeatedly digested with boiling water until the residual salt was free from isomers.

The barium salt washings were now concentrated and the barium precipitated with sulphuric acid. After removing the barium sulphate, the solution was treated with potassium hydroxide to bring down a potassium salt mixture which was set aside.

The mother liquor from the sodium salt recrystallisation was concentrated and the product converted to potassium salt. This was combined with the batch of potassium salt previously set aside, and recrystallised from water to give pure potassium-3-sulphonate. The mother liquor yielded more 2- and 3-sulphonate by repetition of the process of first precipitating barium-2-sulphonate and then potassium-3-sulphonate.

Evidence of the successful separation of the isomers was obtained from the melting points of the p-toluidine salts of the acids, as recommended by Fieser (loc. cit.), whose procedure is as follows:

The aqueous solution of the free acid or of an easily soluble salt is treated with excess p-toluidine and hydrochloric acid, and enough water added to form a solution at the boiling point. The barium salt of the 2-acid must be boiled with sulphuric acid and animal charcoal, filtered, and the filtrate, which contains the free acid, employed. If the amine salt separated in an oily state on cooling the solution, crystallisation may be induced by scratching the walls of the container. When the amine salts are pure, they should crystallise easily, but when impure they may remain indefinitely as oils. Fieser emphasises that reluctance to crystallise indicates the presence of mixed isomers. According to Fieser the presence of an unwanted isomer in one of the acids causes an abnormally large depression of the melting point of the amine salt of the wanted acid. The melting points of the p-toluidine salts, as given by Fieser, are

phenanthrene-2-sulphonate	291°C. (corr).
phenanthrene-3-sulphonate	222°C. (corr).

Preparation of the Pure Acids from the Salts. The potassium-3-salt was converted to the barium salt by precipitating from solution with barium chloride, and the procedure was then the same for both acids.

The free acid was obtained by boiling the barium salt with water containing a calculated excess of sulphuric acid. After filtering, the solution was concentrated to a small volume and the sulphonic acid precipitated by the addition of concentrated hydrochloric acid solution. The precipitation was repeated three times to eliminate the excess of sulphuric acid mentioned above. The sulphonic acid was then filtered off and dried in a vacuum desiccator over sodium hydroxide pellets.

When dry and free from hydrochloric acid, the acid was dissolved in a slight excess of acetone and filtered through a G3 sintered glass filter. On the addition of benzene to the solution, an oily liquid first separated, after which the pure sulphonic acid began to precipitate as a white solid. At this stage the solution was decanted from the oily layer and more benzene added to complete the precipitation of the acid. The oily liquid was redissolved in acetone, and the above process repeated. With each repetition the oily layer became smaller and darker in colour. The various batches of pure acid were finally combined.

CHARACTERISATION OF PHENANTHRENE-2- And -3-SULPHONIC ACIDS.

The characterisation of these acids depended mainly on the melting points of the p-toluidine salts, which are critical according to Fieser, and on the determination of the molecular weight by titration.

p-toluidine salts. The acids were precipitated from acetone solution, and the p-toluidine salts prepared as described above.

Phenanthrene-3-sulphonic acid: The salt precipitated at once without the appearance of oily drops, and had a melting point of 220.5°C. The melting point is 1.5°C. below Fieser's figure, but the fact that the acid crystallised without oily drops was considered to indicate that there was no serious contamination by isomers.

Phenanthrene-2-sulphonic acid: This acid proved more difficult to purify than the 3-acid, and even after repeated repurification by washing the barium salt, the melting point of the p-toluidine salt was 286°C., as compared with 291°C. obtained by Fieser. The salt darkened considerably near the melting point and decomposition seemed to set in. However, since the amine salt crystallised rapidly with little trace of oily drops, the acid was considered to be satisfactory.

<u>Molecular Weight.</u> The 2-acid was precipitated from acetone and dried over phosphorus pentoxide in vacuum at 100°C. for about 24 hours. The material was then anhydrous but rapidly took up water on exposure. The melting point was not very satisfactory and appeared to be about 143°C. Sandqvist(1) gives 150°C. as the approximate melting point of the monohydrate. Titration with alkali (see p. 24) gave the following data:

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(1) Sandqvist, Lieb. Ann., <u>379</u> (1911) 79. Quoted by Heilbron, "Dictionary of Organic Compounds".

Weight of 2-acid	0.2144 gm.	0.2184 gm.	
Volume of alkali	19.36 ml.	19.70 ml.	
Normality of alkali	0.04285	0.04285	
Mol. Wt. found	258.4	258.7	
Mol. Wt. calculated	258.2	2~~4~~8.2 5	258.2 ?

The 3-acid was precipitated from acetone and dried in vacuo over sodium hydroxide. Its melting-point at this stage was 88°C. which is that of the acid with two molecules of water of crystallisation.$^{(1)}$ The acid was therefore not dried at 100°C., since it would have melted. Titration with alkali (see p. 24) gave the following data:

Weight of 3-acid	0.2003	0.2003 gm.
Volume of alkali	17.45	17.50 ml.
Normality of alkali	0.03895	0.03895
Mol. Wt. found	294.7	294.3
Mol. Wt. calculated	294.2	for two molecules of water.

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(1) Sandqvist, Lieb. Ann., 369 (1909) 104, gives 88° - 89°. Quoted by Heilbron, "Dictionary of Organic Compounds".

PREPARATION OF 9-BROMO- AND 9-CHLORO-PHENANTHRENE SULPHONIC ACIDS.

Preparation of 9-bromo-phenanthrene. This compound was easily prepared by Sandqvist's (1) method, as follows. To a solution of 50 gm. phenanthrene in 700 ml. glacial acetic acid was added, drop by drop, 90 gm. bromine, the temperature being kept below 25°C. When all the bromine had been added, the mixture was left for two hours before filtering off the phenanthrene 9.10-dibromide which was then converted to 9-bromo-phenanthrene by heating at 100°C. on a steam-bath. When the evolution of hydrobromic acid had ceased, the resulting bromo-phenanthrene was recrystallised from petrol ether (B.P. 80-100°C.). Sandqvist used alcohol for the recrystallisation but the petrol ether was found to be preferable. The final product was almost white, having a light cream colour, and melted at 61-62°C. (Sandqvist 58-63°C., Hayduck (2) 63°C.).

Preparation of 9-chloro-phenanthrene. On attempting to follow Sandqvist's procedure, (3) it was found that the yields obtained were very erratic. Sometimes a good yield was obtained, but more

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(1) Sandqvist, Lieb. Ann., 398 (1913) 136.
(2) Hayduck, Lieb. Ann., 167 (1873) 181. This value also given by Heilbron, "Dictionary of Organic Compounds".
(3) Sandqvist, Lieb. Ann., 417 (1918) 17. Ber., 51 (1918) 1515.

frequently the product was largely a substance of high melting point. This substance could not be converted into 9-chloro-phenanthrene by heating, therefore it was not phenanthrene dichloride. When this substance of high melting point was present, the yield of 9-chloro-phenanthrene was low. Finally, it was found that consistently good yields were dependent on vigorous stirring of the reaction mixture during the chlorination. By this means the mixture was more efficiently freed from hydrochloric acid gas liberated by the chlorination and there was little or none of the high melting point substance in the final product.

50 gm. phenanthrene was dissolved in 120 c.c. carbon disulphide, and the solution cooled to 0°C. A solution of chlorine in 200 c.c. carbon disulphide was prepared by bubbling chlorine through ice-cold carbon disulphide until 30 gm. of chlorine had been absorbed. To the vigorously stirred phenanthrene solution, the chlorine solution was added continuously from an ice-cooled dropping funnel. The addition of the chlorine took 3-4 hours and the reaction mixture was ice-cooled to keep the temperature as near 0°C. as possible. Much hydrochloric acid gas was liberated by the reaction. When the addition of the chlorine solution was complete, stirring was continued for some time to remove from the solution as much as possible of the hydrochloric acid gas.

The mixture was left overnight and if a small quantity of solid matter had appeared it was filtered off and rejected. Most of the solvent was now removed by distillation and any solid filtered off and washed with carbon disulphide, the washings being added to the filtrate. If the chlorination has been successful there should be little or no solid precipitated from solution. The yellow oily solution was now transferred to a Pyrex distilling flask and the remainder of the carbon disulphide distilled. The temperature was raised and hydrochloric acid gas began to be evolved at 100°C. The colour of the solution darkens as heating is continued. The fraction distilling below 360°C. was collected as a yellow oil which eventually solidified. The yellow solid was recrystallised from 80-100 petrol ether, which gave an almost white product. Yield 25-30 gm. M.P. 48-50°C. (Sandqvist,(1) 53-53.5°C. corrected). A considerable amount of black carbonaceous matter remained in the distilling flask. An attempt at vacuum distillation of the chlorinated solution was unsuccessful on account of bumping (cf. Sandqvist).

<u>Sulphonation of 9-bromo- and 9-chloro-phenanthrene.</u> 20 gm. halogenated phenanthrene and 10 ml. concentrated sulphuric acid were stirred together in a wide test-tube

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(1) Sandqvist, Ber., 51 (1918) 1520.

immersed in a water bath at 100°C. After two hours, 4 ml. concentrated sulphuric acid was added, and again at the end of the next hour. The reaction mixture became viscous as the reaction proceeded and was semi-solid in the later stages.

Preparation of Pure Sulphunic Acids from Sulphonation Mixture. The sulphonation mixture was allowed to cool and the solid which separated was pressed on a sintered glass suction filter to remove excess sulphuric acid. The solid was dissolved in a small quantity of hot water, and boiled with animal charcoal and filtered to remove unsulphonated bromo-phenanthrene or chloro-phenanthrene. The solution was now cooled and on the addition of concentrated hydrochloric acid solution, a gelatinous precipitate of the sulphonic acid was obtained. The solid sulphonic acid was filtered off and purified by two further precipitations from aqueous solution by means of hydrochloric acid. Since the sulphonic acids, as precipitated from aqueous solution, are gelatinous and difficult to filter, it was found to be advantageous to separate the solid by centrifuging. The sulphonic acid was now transferred to a porous porcelain plate and dried in a vacuum desiccator which contained caustic soda pellets. When dry and free from hydrochloric acid, the sulphonic acid was dissolved in a slight excess of acetone. An insoluble white solid was removed at this stage by filtering the solution through a G3 sintered glass filter. The acetone solution was now boiled with animal charcoal for about 15 minutes, but the solution bumps badly and it is not completely decolourised. After filtering the solution, benzene was added until the sulphonic acid was all precipitated. The solid was removed by filtering through a G3 sintered glass filter and the precipitation from acetone repeated twice. The solid was finally dried in a vacuum desiccator. The acids resulting from this method were almost white in colour, having a slight yellow tinge. The bromophenanthrene sulphonic acid was slightly darker in colour than the chloro-phenanthrene sulphonic acid. During the purification process the acid solutions were shielded as much as possible from daylight, as it was noticed that the solutions tended to darken in colour when exposed to daylight, especially when they were hot.

The method described above for preparing the pure sulphonic acids from the sulphonation mixture was quite satisfactory for the present purpose. Sandqvist(1)(2) used a different and more elaborate method which is less convenient than the author's, since it involves the preparation and hydrolysis of the sulpho-chloride.

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(1) Sandqvist, Lieb. Ann., 398 (1913) 128; Arkiv. etc., 5 (1913-1915) No. 5, 6 (1916-1917) No. 9.
(2) Sandqvist, Lieb. Ann., 417 (1918) 17.

CHARACTERISATION OF THE HALOGENATED PHENANTHRENE SULPHONIC ACIDS.

It was considered that the acids would be adequately characterised if the melting points corresponded to those given by Sandqvist and if the molecular weights were correct.

Melting point. The test samples were precipitated from acetone solution with benzene as described, and were then dried at 100°C. The melting points were determined in a "pear bulb" apparatus and corresponded most closely to those given by Sandqvist for the anhydrous acids. At the melting point, the acids darkened in colour. The figures given below include a correction for the exposed stem of the thermometer, but Sandqvist's figures are not so corrected, in which case they may be low by 2 or 3°C.

Bromo-acid melted at 203.5 - 204°C. Sandqvist 200 - 201°C.

Chloro-acid melted at 208.8 - 209.3°C. Sandqvist 206 - 207°C.

Molecular Weight. A weighed amount of the anhydrous acid prepared as above was titrated with sodium hydroxide, taking the precautions described on page 24. The following data were obtained.

	Bromo-acid		Chloro-acid.		
Weight of acid (gm.)	0.2251	0.2265	0.2240	0.2220	0.1223
Volume of alkali (ml.)	14.46	14.55	17.97	16.45	9.08
Normality of alkali	0.04627	0.04627	0.04276	0.04611	0.04611
Mol. Wt. found.	336.5 ~~337.2~~	336.5 ~~337.2~~	291.5	292.7	292.0
Mol. Wt. calculated	337.1 ~~339.1~~	337.1 ~~339.1~~	292.6	292.6	292.6

p-TOLUENE SULPHONIC ACID.

The acid was "B.D.H. Micro-Analytical Reagent" and was in the form of small white hygroscopic crystals. The material was free from inorganic impurities, apart from a little iron. The latter was found in the residue left after incinerating a quantity of the acid. 1.022 gm. of p-toluene sulphonic acid gave 0.0006 gm. of light-brown residue which gave a precipitate of prussian blue with potassium ferrocyanide.

Some of the acid was dried over phosphorus pentoxide for several weeks and it was then titrated with barium hydroxide, using the procedure later described. Due to its hygroscopic nature, the acid has to be weighed rapidly to prevent absorption of water.

Weight of acid	0.2006 gm.	0.2001 gm.
Volume of 0.04233N barium hydroxide	24.89 ml.	24.75 ml.
Mol. Wt. found	190.4	191.0
Mol. Wt. calculated	190.2	190.2
Difference	0.1%	0.42%

The divergence in the second result is rather more than the probable error in titration, but absorption of water during weighing would give a high result for the molecular weight.

PREPARATION AND STANDARDISATION OF SULPHONIC ACID SOLUTIONS.

For a series of determinations, a suitable solution of approximately known concentration was first prepared in the usual manner. The remaining solutions were derived from this by dilution by weight, that is to say, a weighed amount of one solution was diluted by the addition of a weighed amount of water. One or two solutions of the series were titrated with alkali, and since the densities of all the solutions were known, it was possible to calculate the concentrations for the whole series in terms of normality (N). In the tables, solutions belonging to the same series are distinguished by a particular letter, e.g., A_1 , A_2 , A_3 , etc.

Standardisation was performed as follows. A suitable quantity of the acid solution was weighed out by means of a weighing-pipette and titrated with carbonate-free alkali in an atmosphere free from carbon dioxide, phenolphthalein being the indicator. The titration was carried out in a Büchner filter flask of about 250 ml. capacity. Before commencing the addition of alkali, the flask containing the solution was freed from atmospheric carbon dioxide by sweeping it out with a stream of nitrogen. The nitrogen supply was then attached to the side tube of the flask and a brisk stream of gas maintained during the addition of the alkali. The nitrogen used was the commercial grade and was passed through a "Sofnolite" tower as a precaution against traces of carbon dioxide. Near the end-point, the flask was again swept out with nitrogen and the supply re-attached to the side tube. In this way, the interference of atmospheric carbon dioxide was reduced to a minimum, and it was possible to titrate to a very pale pink colour, which persisted for a minute or more.

Barium hydroxide proved to be quite suitable for titrations with p-toluene sulphonic acid, since the barium salt did not precipitate from the dilute solutions used. The barium salts of the phenanthrene sulphonic acids are, however, much less soluble and a white precipitate appeared early in the titration.

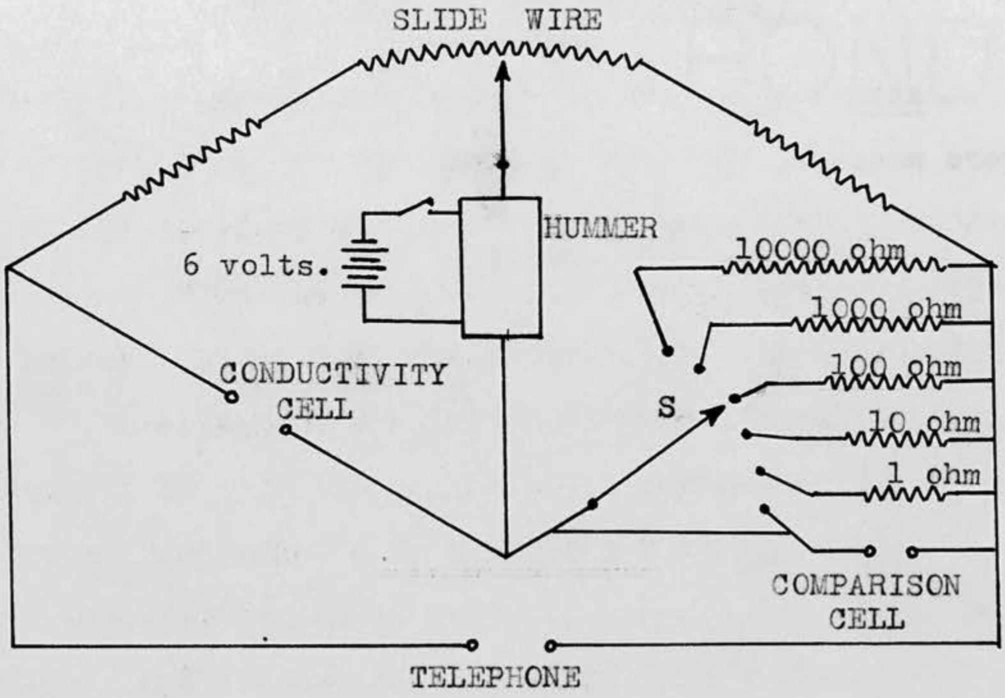
In the case of the halogenated phenanthrene acids, the barium salt precipitate obscured the end-point so much that some other alkali had to be tried. It was found possible to employ sodium hydroxide. The sodium salt of the chloro-acid was not precipitated during the titrations at room temperature, but in the case of the bromo-acid, it was necessary to heat the solution to about 30°C. before starting the titration, in order to keep the salt in solution. The carbonate-free sodium hydroxide was prepared from the metal.

Barium hydroxide was at first used for titrating the 2- and 3-phenanthrene acids, since the precipitate was fairly compact and seemed not to interfere with the end-point. This, however, was later shown to be incorrect, since somewhat different values were obtained by titration with sodium hydroxide, which gave no precipitate. A suitable correction was accordingly applied to the earlier data, to bring them into line with the later .

Owing to the limited quantities of sulphonic acid available, it was desirable that only small amounts of the acids should be used up in standardising the solutions. For this reason the standard alkali was made approximately 0.05 Normal, the quantity of acid being such that 12 - 20 ml. (usually about 17 ml.) of alkali was necessary for neutralisation.

In the earlier part of the work, Kahlbaum's succinic acid was the substance against which the alkali was standardised. However, the succinic acid was found to give a low result when compared with a sample of potassium hydrogen phthalate obtained from the U.S. Bureau of Standards. Results obtained with Hopkin and Williams "Analar" brand potassium hydrogen phthalate agreed well with those from the Bureau of Standards sample. "Analar" potassium hydrogen phthalate was therefore adopted as standard, the necessary correction being applied to the succinic acid data. The same precautions were taken in standardising the alkali as were employed in the case of the sulphonic acids. Also, when standardising alkali to be used against a bromo-acid solution, the solution of potassium hydrogen phthalate was heated to about 30°C. so as to have identical conditions for both titrations.

FIGURE 1.



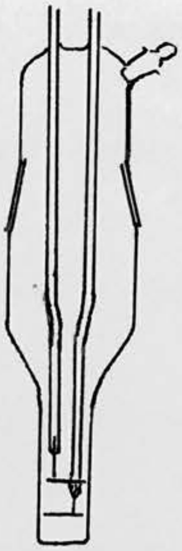
CONDUCTIVITY BRIDGE - CIRCUIT DIAGRAM.

MEASUREMENT OF CONDUCTIVITY.

Apparatus. The conductivities of the solutions were measured by means of a "CAMBRIDGE" conductivity bridge. The values obtained on the scale of the bridge refer to resistance or conductivity according to the position of a change-over switch, but as in practice only resistances were measured, the change-over switching is omitted from the circuit diagram (Figure 1). The bridge circuit consists of an alternating current Wheatstone Bridge, energised by a "CAMBRIDGE Reed Hummer" vibrating at 1000 cycles/second. When the switch S is in the 1 ohm position, the slide wire scale reads directly .25 ohm to 3 ohms. By turning S to the 10, 100, 1000, or 10,000 ohms positions, the scale reading, multiplied by 10, 100, 1000, 10,000 respectively, gives the resistance in ohms. A 6 volt accumulator supplies the current for operating the "Hummer". The telephone for detecting the balance point of the circuit is a specially sensitive single earphone supplied with the instrument. Many of the more concentrated solutions did not give a sharp point of balance and some improvement was obtained by connecting a large air-spaced variable condenser, adjusted as required, across the terminals marked "Comparison Cell".

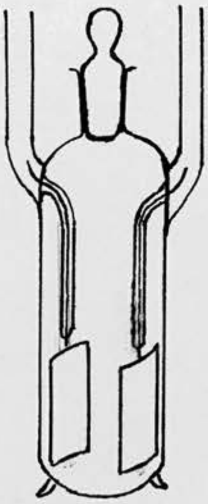
The calibration of the conductivity bridge was frequently checked against a GAMBRELL Class B Resistance

FIGURE 2.

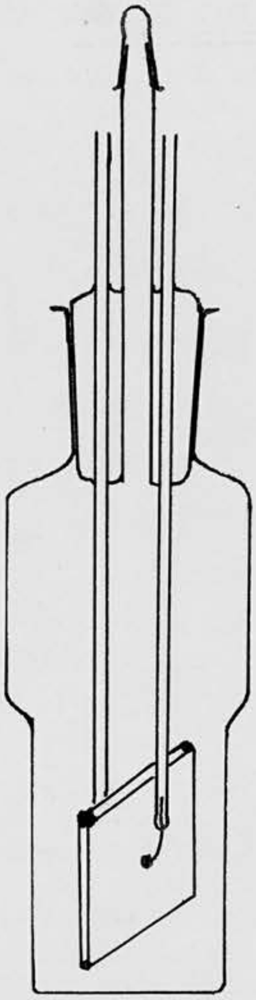


Cells No.
1,~~3~~, and 5.

2



Cell No. 3.



Cell No. 4.

Box, accuracy 1 in 1000. Resistances of 1 ohm to 10,000 ohms, in 1 ohm steps, are obtainable with this box.

The leads, for connecting the conductivity cell to the bridge, were thick flexible wires, rubber-covered and with a piece of heavy gauge copper wire soldered to one end for dipping into the cell.

Five cells of three distinct types were used. Cells numbered 1, 2 and 5 (Figure 2) were small cells of borosilicate glass with platinised platinum electrodes. Since the electrodes were attached to the cap they could be lifted out for cleaning. The electrodes were approximately 1 cm. diameter and were separated by about 1 cm. In use the cell was filled up to the top of the narrow cylinder surrounding the electrode, about 5 ml. of solution being required. There was no advantage in using a larger volume of solution in the cell. The cell constants were .7 to .8 for cells 1 and 2, and approximately .5 for cell 5. Cell 3 was of about 50 ml. capacity and had platininsed platinum electrodes measuring 1.5 cm. × 3 cm. and approximately 2.5 cm. apart. The two lower corners of each electrode were attached to the wall of the cell. This type of cell was found to be very convenient in use and gave a sharp point of balance, but due to its large capacity its use had to be restricted to moderately dilute solutions. Cell 4, made by Baumbach, was a large cell of the Hartley type, similar to that employed by Howell and Handford.(1) It was used only for solutions of extreme dilution. The body of the cell was of silica, the detachable electrode assembly being of borosilicate glass, with grey platinum electrodes. The electrodes were 12 cm.^{2} in area, and were situated 2 mm. apart. Four pieces of glass sealed between the electrodes, one at each of the four corners, kept the electrodes rigid. When in use, the cell contained 135 ml. of solution.

Procedure. Each of the three types of conductivity cell required a different method of handling and a routine procedure was developed in each case.

Cells 1, 2 and 5. Since these cells were intended for use with concentrated solutions of which only small quantities were available, the following procedure was adopted in order to minimise waste.

The cell was first washed with four changes of distilled water and was then taken apart. The internal surfaces of the two parts were washed with absolute alcohol, care being taken to avoid wetting the plates with alcohol. When the alcohol had evaporated, the cell was reassembled. The cell was now dry except for a little water on the electrodes which were not allowed to become dry on account of the trouble involved in re-wetting platinised electrodes which

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(1) Howell and Handford, Trans. Faraday Soc., 29 (1933)640.

have been dried. The cell was now rinsed with three or four small quantities of the solution which was to be measured, after which the cell was charged with the solution and the resistance measured. Next, without dismantling the cell, it was well washed with distilled water, filled with the standard potassium chloride solution, and the cell constant determined.

The constant was redetermined after each measurement because when the cell was dismantled for cleaning, the constant was liable to alter on account of the plates touching the sides of the cell while withdrawing the electrodes.

Cell 3. The cell was well washed with distilled water and then rinsed with four 10 ml. portions of the solution to be measured, after which the cell was charged with solution to a fixed mark near the neck. The cell constant was determined at the beginning and end of each series of determinations.

Cell 4. The cell was washed with distilled water and then with at least four 50 ml. portions of solution. The cell was now charged with solution, about 135 ml., and the resistance measured, after which the cell was emptied, refilled with the same solution and the resistance measured again.

When this cell was first put into use, a few unaccountably low conductivities were obtained. Since the resistance did not change on refilling the cell, it appeared that the low results were not due to adsorption. Whatever the explanation, anomalous results were eventually eliminated. The employment of only freshly-prepared solutions was adopted as a possible precaution, but it cannot be stated how far this was responsible for the improvement.

The constant for this cell could not be determined by direct measurement with the standard potassium chloride solution, since the resistance was too small to be measured accurately. Hence, the cell constant was obtained by comparison with cell 3. A suitable hydrochloric acid solution was made up and its resistance determined with the two cells. Since the constant for cell 3 was known, the constant for cell 4 could be calculated. The constant remained at the same value (0.01445) throughout the work.

The values of the cell constants are given on pages 38 and 39.

Experimental Conditions. Two thermostat baths were used, each consisting of a large rectangular glass vessel containing water. The heating element was a carbon filament lamp immersed in the bath and controlled by the usual system of thermal-expansion regulator and relay. The regulator was of the type which is partly filled with an organic liquid, to obtain greater sensitivity; carbon tetrachloride was used in preference to toluene, since it has less chemical action on the mercury. By maintaining the contacts of the regulator in a clean condition, it was possible to control the temperature to 18 or 25°C. within ± 0.03°C. Conductivity measurements were made while the temperature of the bath was passing through 18 or 25°C. Thermometers graduated to 0.05°C., and calibrated against a N.P.L. standard thermometer, were used to indicate the temperature of the thermostat. The water in the thermostat was efficiently circulated by a mechanical stirrer.

When the conductivity cell was placed in the thermostat, the resistance was immediately read. Readings were then made at intervals until reasonably constant values were obtained. The final value was taken as the mean of a number of readings, since the balance point was usually not absolutely sharp.

All measurements were carried out in subdued artificial light, to avoid any trouble from the action of sunlight on the compounds.(1)

Preparation of pure water. Starting with good quality distilled water of specific conductivity about 1.5 gemmhos, "equilibrium" conductivity water was prepared in a Vogel and Jeffery still.(2) This apparatus is designed to give water of specific conductivity 0.75 gemmhos (at 18°), which is in equilibrium with the carbon dioxide of the stmosphere.

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(1) See Sandqvist, Arkiv. etc., 7 (1918-20) No. 4.
(2) Vogel and Jeffery, J.C.S., 1931, 1201.

At first, the apparatus was operated according to the instructions of the designers, but the water so obtained was not always up to specification, having on occasion a specific conductivity of about 1 gemmho. The cause of the occasional erratic behaviour were not discovered but were probably related to the method of distillation under reduced pressure, i.e., the requisite amount of vacuum was difficult to control. However, by passing a stream of purified nitrogen through the apparatus and thus operating with the pressure slightly above atmospheric pressure, water of specific conductivity 0.65 - 0.75 gemmho was easily prepared as required. A sample of water from each preparation was tested for conductivity and was used only if the specific conductivity was 0.8 gemmho or less.

For the following reasons, it was considered unnecessary to apply any solvent correction to solutions prepared with this water. Apart from carbon dioxide, the impurity most likely to be present in the water was ammonia, but tests with Nessler's solution failed to reveal any trace. On bubbling purified nitrogen for several hours through a sample of the conductivity water in the large cell, an appreciable decrease in the conductivity was observed, which indicated that the main impurity was volatile. It appears safe to say that the conductivity of the water was chiefly due to carbonic acid,(1) so that there was no need to apply

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(1) See paper by Wynne-Jones (J. Physical Chem., <u>31</u> (1927) 1653) for further evidence in support of this view.

a solvent correction to the solutions under consideration.

Standard Potassium Chloride Solution. Cell constants were determined by means of 0.1 "demal" potassium chloride solution (0.1 equivalents per decimetre at 0°C.), as recommended by Parker and Parker.(1)

"ANALAR" potassium chloride, as supplied by Hopkin and Williams, was used, without further purification. The potassium chloride was dried by heating in a porcelain basin directly in contact with a bunsen flame. The material at the bottom of the basin became partially fused. After cooling in a desiccator, chloride was removed from the top as required.

7.4790 gm. of potassium chloride were weighed out, and transferred to a clean, dry and weighed litre standard flask. Weights corresponding to weight of flask + weight of chloride and an additional 1000 gm. were now put on the pan, and conductivity water added to the potassium chloride until exact balance was attained. The solution was stored in a glass-stoppered Jena glass bottle.

According to Parker and Parker, a solution of potassium chloride containing 7.4789(6) gm. in 1000 gm. water (weighed in air), has a specific conductivity of 0.011163(6) mho at 18°C. This value was employed in the present investigation.

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(1) H. C. Parker and E. W. Parker, J.A.C.S., 46 (1924) Table X, p. 332.

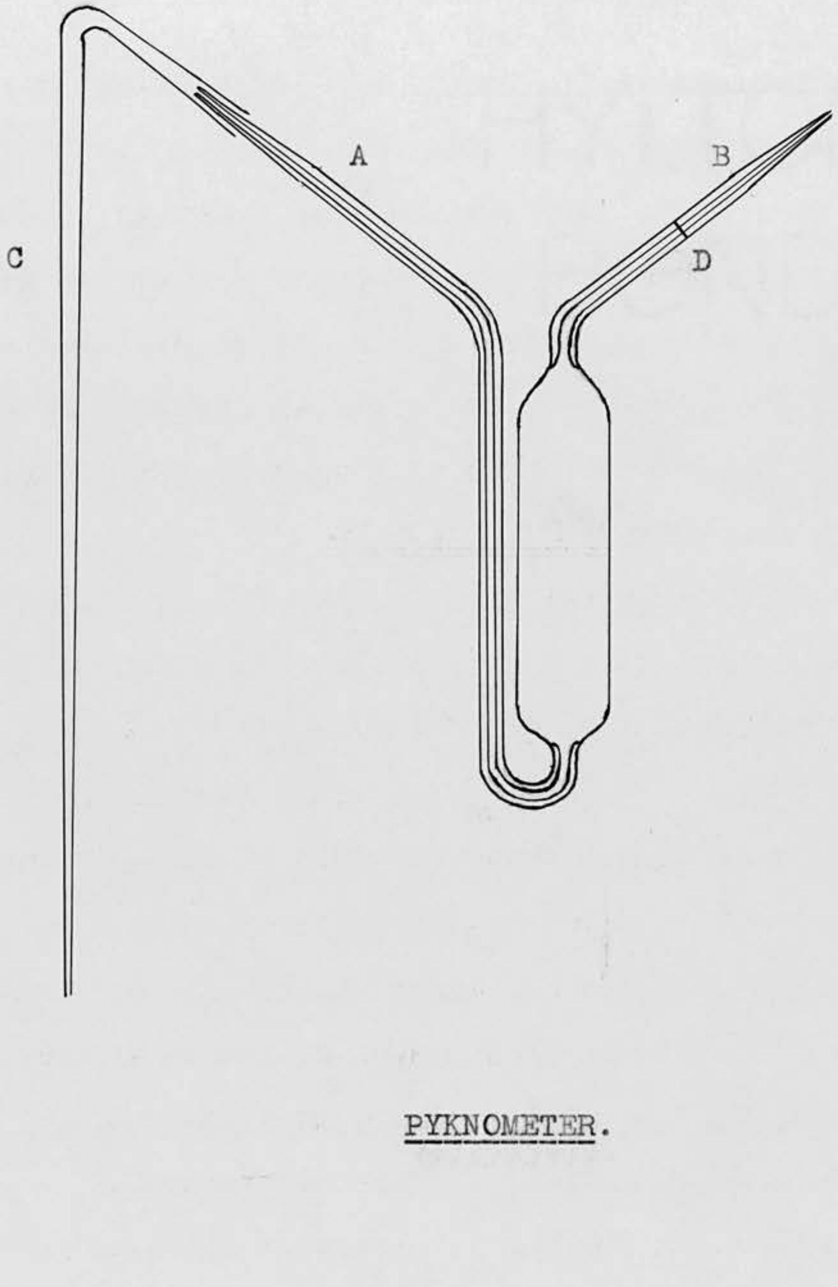
Cell Constants.

Solutions	Cell constant	Solutions	Cell constant
p-toluene sulphonic acid (Tables I and II).			
A_1 A_3 A_5	0.7954	C_4	0.8032
A_2	0.7850	C_6 C_8	0.8026
A_4	0.7920	C_9	0.8294
A_7 A_8 A_9	0.1832	C_{10} C_{12}	0.8035
B_1 B_3	0.7977	C_{11}	0.1832
B_2 B_4	0.7954	C_{14} to C_{17}	"
B_6 to B_{12}	0.1827	D_2 D_3	"
C_1	0.8023	D_4 to D_8	0.01445
C_2	0.8254	E_1	0.1832
C_3 C_5 C_7	0.8266	E_2 E_3 E_4	0.01445
Phenanthrene-3-sulphonic acid (Tables III and IV)			
C_1 C_2 C_3	0.8222	H_7 H_9	0.8143
C_4	0.8260	H_{10} to H_{13}	0.1832
C_5 C_6 C_7	0.8333	H_{14} H_{15} H_{16}	0.01445
D_1 to D_4	0.8360	I_2	0.8143
E_2 E_3 E_4	0.1832	I_3 I_4	0.8132
F_1 F_2	0.7954	I_5 I_6	0.8277
F_3	0.8087	J_1	0.1832
F_4	0.7966	J_4 to J_8	0.1832
G_1 to G_5	0.1832	J_2 J_3	0.01445
G_6	0.7966	J_5 J_8	0.01445
H_6 H_8	0.8245		

Cell Constants (cont.)

Solutions	Cell constant	Solutions	Cell constant
Phenanthrene-2-sulphonic acid (Tables V and VI).			
B_1	0.7987	C_5	0.8273
B_3	0.8254	C_6	0.8009
B_2 B_4	0.8081	D_1 D_3	0.8310
B_5	0.8065	D_2	0.8281
B_6 to B_{10}	0.1832	D_4	0.1832
B_{12} B_{13}	"	D_5 D_6 D_7	0.01445
C_1	0.7998	D_8	0.8215
C_2 C_4	0.8065	E_1	0.8305
C_3	0.8277	E_2	0.8281
9-bromo-phenanthrene-3-sulphonic acid (Tables VII and VIII).			
A_1 A_5	0.8277	B_1 B_5	0.8305
A_2 A_3	0.8269	B_2	0.8285
A_4	0.8281	B_3 B_4	0.8292
A_6 to A_9	0.1832	C_1	0.8226
A_{10} A_{11} A_{12}	0.01445	C_5	0.8247
9-chloro-phenanthrene-3-sulphonic acid (Tables IX and X).			
A_1	0.8219	B_{10} B_{11} B_{12}	0.1832
A_2	0.8221	B_{13}	0.01445
A_3	0.8247	B_{14}	0.01445
A_4 to A_8	0.1832	C_1	0.8268
B_1	0.8258	C_2	0.8262
B_2	0.8287	C_3	0.8292
B_3	0.8269	C_4	0.8269
B_4	0.5608	D_6	0.8243
B_5 to B_9	0.1832	D_8	0.8231
B_7 (a)	0.1832	X	0.5599

FIGURE 3.



PYKNOMETER.

DETERMINATION OF DENSITY.

The pyknometer (Figure 3) was of the usual form and had a capacity of between 4 and 5 ml. The tubes A and B were 1 mm. bore capillaries, B having a line etched round it at D. A was tapered and ground to make a good joint with the tube C, which was designed to enable the pyknometer to be filled directly from bottles. In this way loss or contamination of the solutions was minimised.

The pyknometer was cleaned with chromic acid occasionally and it was maintained in a sufficiently clean condition for long periods merely by washing it thoroughly with distilled water after each determination. After the cleansing with water, the pyknometer was rinsed with absolute alcohol, dried by drawing a stream of air through it, and weighed. C was then attached to A, and the pyknometer filled with liquid by applying suction at B. The pyknometer was now placed in the thermostat, and liquid removed by drawing a piece of filter paper across the mouth of A until the liquid exactly filled the pyknometer from the mouth of A to the mark at D. This adjustment was repeated until the liquid showed no change of level while immersed for a further 15 minutes in the thermostat. The pyknometer and its contents were then weighed.

The density was calculated from the formula,(1)

$$d_4^{t^\circ} = \frac{W\,D - 0.0012(W - W_0)}{W_0},$$

where t° = temperature

W = weight of solution filling pyknometer at t°

W_0 = weight of water filling pyknometer at t°.

D = density of water at t°.

The results obtained are given in Tables XI to XX. The value of D was taken as 0.99707 at 18°C. and 0.99863 at 25°C.(2)

99863
99707

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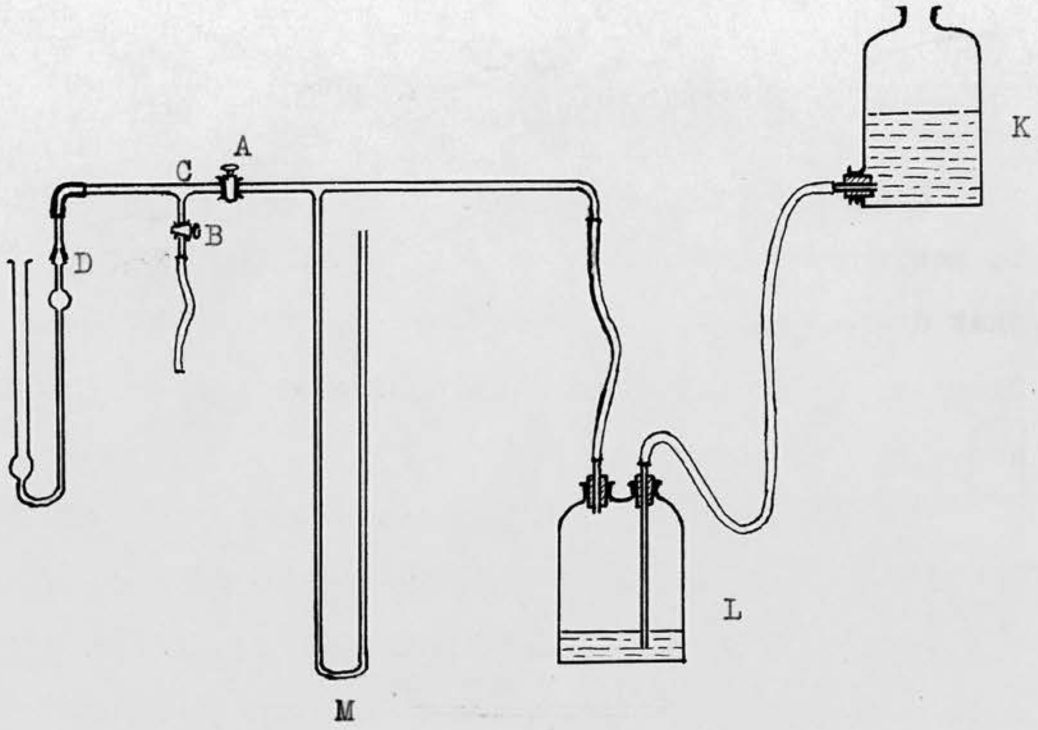
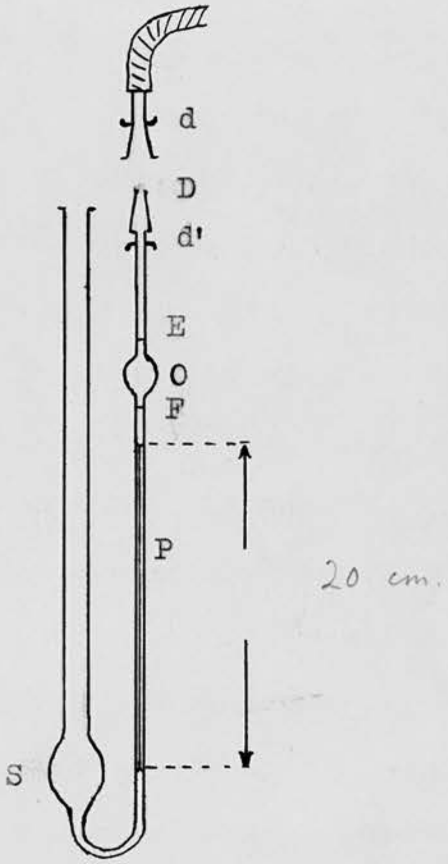
(1) Findlay, "Practical Physical Chemistry" (1935) 63.
(2) Findlay, "Practical Physical Chemistry" (1935). Table on page 64.

FIGURE 4.


A
C
B
D
V
M
K
L


d
D
d'
E
O
F
P
20 cm.
S

MEASUREMENT OF VISCOSITY.

Description of Apparatus. The method employed to measure the viscosity of a solution was essentially that described by Bungenburg de Jong, Kruyt and Lens (1) Diagrams showing the principal features of the apparatus are given in Figure 4.

The specially constructed viscometer V was of the Ostwald type. The volume of the bulb O was between 3 and 4 ml. and the capillary P was a 20 cm. length of $\frac{1}{2}$ mm. bore glass tube. E and F, the marks between which the liquid was timed, were etched on tubing of 2 mm. bore. With 5 ml. of liquid in the viscometer and the upper level of the liquid just above E, the lower level came to the bottom of the bulb S.

The bottles K and L (capacity about 1 litre) were partly filled with water and K was mounted on a vertical lift so that the pressure on the liquid in the viscometer could be varied by altering the height between K and L. By means of the water manometer M, the excess pressure obtained in this fashion was measured. A travelling telescope, reading to 0.001 cm., was employed to determine the positions of the levels in M. The maximum excess pressure obtained was about 100 cm. of water.

The viscometer was connected to the rest of the

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(1) Bungenburg, Kruyt and Lens. Kolloid Beih., 36 (1932) 429.

apparatus by the ground glass joint D, the two sections of which were kept securely together by rubber bands looped over the hooks d and d'. Connections elsewhere were made by means of rubber pressure tubing. The functions of the glass taps A and B, on the glass T-piece C, are described below.

Procedure. Before starting the determinations, the viscometer was cleaned with chromic acid cleaning mixture and well washed with distilled water. To dry the viscometer, it was rinsed with absolute alcohol, allowed to drain and a current of air drawn through it. For a determination, 5 ml. of the required solution was run into the viscometer from a cleaned and dried pipette. The viscometer was then clamped in position in the thermostat (kept at 18°C± 0.03°), so that the capillary was vertical, this being verified with the aid of a plumb line held near the glass sides of the thermostat. The remainder of the apparatus was now connected to the viscometer and the liquid allowed to come to the required temperature.

To make a determination without extra pressure, tap A was closed, tap B opened, and the liquid drawn up a little above E by applying suction at the tube attached to B. On withdrawing the suction, the level of the liquid began to fall and the time taken for the meniscus to pass from E to F was measured on a stop-watch reading to 0.1 second.

In making a determination with extra pressure, the procedure was as follows. Tap A was closed and K was raised to give a suitable increase in pressure. The solution was drawn up above E, so that when tap B was closed the liquid came to rest with the meniscus still above E. The levels of the manometer were then read, tap A was opened and the flow of liquid was timed as before. Tap A was closed again as soon as possible after the meniscus passed F, and the manometer levels were read again. It was observed that the levels always altered slightly during the flow of liquid, therefore the mean of the initial and final differences of level was taken as the effective extra pressure.

Test of Viscometer. Measurements with water and with 39.98% sucrose solution (39.98 gm. sucrose in 100 gm. solution) were carried out to ensure that the design of the viscometer was satisfactory. The requisite condition is that the following relation (Poiseuille's Law) should hold;

$$p't = \text{constant},$$

where p' = total pressure acting on the liquid in the viscometer;

t = time of flow.

In the present instance,

$$p' = h + p,$$

where h = the mean hydrostatic pressure of the column of liquid in the viscometer,

and p = the effective extra pressure applied by the method described.

For any two values, p_1 and p_2, of the extra pressure, Poiseuille's Law thus becomes

$$(h + p_1)t_1 = (h + p_2)t_2$$

where t_1 and t_2 are the respective times of flow. Hence,

$$\frac{p_1t_1 - p_2t_2}{t_2 - t_1} = h = \text{constant.}$$

The data in Tables XXI and XXII show that actually the constancy of h was satisfactory, the variation from the mean value being usually less than about 0.1%. In all the viscosity tables, p and h are expressed in terms of centimetres of water at room temperature (very constant).

Calculation of Relative Viscosity. The values of relative viscosity (η) given in Tables XXV to XXVIII, were calculated from the expression,

$$\frac{\eta_s}{\eta_0} = \eta = \frac{t\,h}{t_0h_0}$$

where η_s = viscosity of solution.

η_0 = viscosity of water.

t = time of flow (seconds) of solution without extra pressure.

t_0 = time of flow (seconds) of water without extra pressure.

h = mean hydrostatic pressure of solution.

h_0 = mean hydrostatic pressure of water.

The value of t_0 was taken as 196.4 sec., which is the mean of three determinations made at different times during the work and recorded in Table XXI. The agreement amongst these values showed that the degree of reproducibility of the viscosity data was satisfactory.

The value of h_0 was taken to be 23.30 cm. (Table XXI).

Bungenburg de Jong, Kruyt and Lens (loc. cit.) assumed that the value of h was given by,

$$h = h_0 W/W_0$$

where W and W_0 are the respective weights of equal volumes of solution and water. In the present investigation, however, it was ascertained that this relation does not necessarily hold. Some values of h were determined experimentally in the case of the chloro-phenanthrene acid (Table XXIII). They were found to be expressible to within 0.1% by the equation,

$$h = h_0 + 1.9 N.$$

where N = normality of solution. If, on the other hand, h is calculated as $h_0 W/W_0$, using the values of W and W_0 given in Table XIX, then the relation obtained is,

$$h = h_0 + 2.3 N.$$

which differs slightly but significantly from the experimental equation. The values of η given in Table XXVIII were calculated by means of the experimental equation.

In the case of the bromo-phenanthrene acid the values of h in Table XXIV correspond to

$$h = h_0 + 3.1 N.$$

and the viscosities given in Table XXVII are based on this equation. If h is taken as h_0W/W (see Table XVII for values of W and W_0) the relation is,

$$h = h_0 + 3.5 N.$$

which again differs slightly but significantly from the experimental equation.*

The values of η for the solutions of the p-toluene and phenanthrene-3-acid given in Tables XXV and XXVI were, however, calculated by taking $h = h_0W/W_0$, since no experimental determinations were made. Thus the true values of η for these acids are probably a little less than those recorded here but the latter amply suffice to establish the most important features of the viscosity-concentration curves.

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* A difference was also observed with the sucrose solution. h, calculated from h_0W/W_0 (W = 5.464 g.; W_0 = 4.634 g.), was 27.46 cm., as compared with 27.32 cm., the value found.

DETERMINATION OF TURBIDITY-POINT.

Sandqvist(1)(2) observed that solutions of the halogenated phenanthrene sulphonic acids were turbid below a definite temperature, the "turbidity-point", the value of which depended upon the concentration, the temperature being the higher the greater the concentration.

In the present investigation, determinations of the turbidity-points of two solutions of the chloro-acid were carried out in the following manner. The bulb of a thermometer was immersed in the solution, which was contained in a glass vessel suitably arranged for gradual variation of the temperature. Commencing with the temperature high enough to give a quite clear system, the solution was cooled, with constant stirring, and the temperature read when the first sign of turbidity was detected. The solution was now heated and observation made of the temperature at which the turbidity just disappeared. The mean of the two observations was taken as the value of the turbidity-point.

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(1) Sandqvist, Arkiv, etc., 6 (1916-17) No. 9; Kolloid-Zeitschr., 19 (1916) 113.
(2) Sandqvist, Lieb. Ann., 417 (1918) 17.

The following data were obtained:

Solution	N	Turbidity-point (°C.)		
		Heating	Cooling	Mean
C_1	0.3115	17.75	17.69	17.72
C_2	0.2302	9.78 9.78	9.73 9.75	9.76

Sandqvist found that his values for both bromo-(1) and chloro-(2) acid could be represented to within about 0.05°C. by an equation of the form

$$t^\circ = a + b \log C,$$

where t° = turbidity-point, C = concentration of solution in mols per 100 mols solution, and a and b are constants. For the chloro-acid Sandqvist obtained a = 34.3 and b = 60.2, whereas the present data give a = 31.03 and b = 58.28. However, Sandqvist states that his values of C are only approximate, and a proper comparison is therefore not possible. Adopting the values of a and b obtained in the present work, it was deduced that the concentration of the solution whose turbidity-point is 18° will be 0.315 N., Sandqvist's approximate value being 0.284 N.

For the bromo-acid Sandqvist obtained a = 23.31 and b = 63.45, from which it has been calculated that

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(1) Sandqvist, Arkiv. etc., 6 (1916-17) No. 9 ; Kolloid-Zeitschr., 19 (1916) 113.

(2) Sandqvist, Lieb. Ann., 417 (1918) 17.

the concentration of the solution whose turbidity-point is 18° will be 0.425 N., which is considerably higher than in the case of the chloro-acid. No determinations were carried out in this research, but it was observed that a 0.3190 N. solution of the bromo-acid was still quite clear at a temperature below the turbidity-point of a 0.3115 N. solution of the chloro-acid. Since the solutions show double refraction when turbid, it follows that the chloro-acid becomes anisotropic more readily than does the bromo-acid.

Sandqvist's observation that an anisotropic solution of the chloro-acid slowly separates into two layers was confirmed. The upper layer was clear and the lower one turbid and streaky in appearance. Such separation was not observed by Sandqvist in the case of the bromo-acid.

CONDUCTIVITY DATA.

TABLE I.

Conductivity p-toluene sulphonic acid at 18°C.

Solution	N	$\sqrt{N}$	Spec. cond.	Λ
B_1	1.6280	1.2760	0.2319	(142.5)
D_1	1.2842	1.1333	0.2400	186.8
C_1	1.0235	1.0211	0.2133	208.4
A_1	0.9792	0.9895	0.2040	(208.3)
B_2	0.8140	0.9022	0.1846	226.8
C_2	0.7648	0.8745	0.1756	229.6
C_3	0.6113	0.7819	0.1500	245.3
C_4	0.5117	0.7152	0.1310	256.0
C_5	0.4082	0.6389	0.1085	265.8
B_3	0.4070	0.6380	0.1086	267.1
A_2	0.3917	0.6259	0.1047	267.2
C_6	0.3056	0.5528	0.08519	278.8
C_7	0.2562	0.5062	0.07302	285.0
C_8	0.2046	0.4523	0.05971	291.9
B_4	0.2035	0.4511	0.05937	291.7
B_6	0.1628	0.4034	0.04833	296.9
A_3	0.1565	0.3958	0.04662	297.7
C_9	0.1529	0.3910	0.04560	298.3
C_{10}	0.1222	0.3495	0.03704	303.1
A_4	0.09792	0.3129	0.03003	306.7
B_7	0.08140	0.2853	0.02520	309.7
C_{11}	0.07643	0.2765	0.02376	310.6
C_{12}	0.06100	0.2470	0.01919	314.6
B_8	0.04070	0.2018	0.01304	320.4
A_5	0.03917	0.1979	0.01261	(321.8)
D_2	0.03863	0.1966	0.01238	320.5
E_1	0.03351	0.1831	0.01080	322.2
C_{14}	0.02284	0.1511	0.007419	324.8
B_9	0.01628	0.1276	0.005346	328.4
C_{15}	0.01218	0.1104	0.004024	330.3
A_7	0.009792	0.09895	0.003247	331.6
B_{10}	0.008140	0.09022	0.002704	332.2
C_{16}	0.006092	0.07803	0.002030	333.3
A_8	0.004898	0.06998	0.001637	334.3
B_{11}	0.004070	0.06380	0.001363	334.9
C_{17}	0.003048	0.05521	0.001026	336.7
A_9	0.002449	0.04949	0.0008266	337.5
B_{12}	0.001628	0.04034	0.0005412	338.6
E_2	0.0006674	0.02584	0.0002274	340.8
D_5	0.0006222	0.02494	0.0002111	(339.3)
D_3	0.0006108	0.02471	0.0002065	(338.2)
E_3	0.0003655	0.01912	0.0001249	341.7
D_7	0.0003136	0.01771	0.0001069	340.8
E_4	0.0001221	0.01105	0.00004182	342.5
D_8	0.0001027	0.01013	0.00003507	341.6
D_6	0.00009460	0.009726	0.00003137	(332.1)
D_4	0.00009442	0.009717	0.00003074	(325.6)

TABLE II.

Conductivity p-toluene sulphonic acid at 25°C.

Solution	N	$\sqrt{N}$	Spec. cond.	Λ
B_1	1.6240	1.2750	0.2557	(157.4)
D_1	1.2810	1.1318	0.2698	210.8
C_1	1.0211	1.0106	0.2392	233.3
A_1	0.9769	0.9883	0.2280	(233.4)
B_2	0.8119	0.9010	0.2072	255.2
C_2	0.7630	0.8736	0.1965	257.5
C_3	0.6100	0.7809	0.1670	273.8
C_4	0.5107	0.7146	0.1467	267.2
C_5	0.4075	0.6383	0.1209	296.7
B_3	0.4062	0.6374	0.1213	298.5
A_2	0.3909	0.6253	0.1171	299.7
C_6	0.3050	0.5522	0.09475	310.7
C_7	0.2556	0.5057	0.08116	317.6
C_8	0.2043	0.3519	0.06633	324.8
B_4	0.2032	0.4508	0.06619	325.7
B_6	0.1626	0.4032	0.05373	330.5
A_3	0.1563	0.3952	0.05176	331.2
C_9	0.1526	0.3907	0.05093	333.7
C_{10}	0.1220	0.3493	0.04121	337.8
A_4	0.09775	0.3126	0.03346	342.3
B_7	0.08127	0.2850	0.02798	344.3
C_{11}	0.07630	0.2762	0.02636	345.5
C_{12}	0.06090	0.2468	0.02130	349.8
B_8	0.04064	0.2016	0.01447	356.1
A_5	0.03911	0.1978	0.01401	(358.0)
D_2	0.03857	0.1964	0.01377	356.9
E_1	0.03346	0.1829	0.01200	358.7
C_{14}	0.02281	0.1510	0.008235	361.2
B_9	0.01626	0.1275	0.005957	366.4
C_{15}	0.01216	0.1103	0.004466	367.2
A_7	0.009777	0.09888	0.003600	368.3
B_{10}	0.008127	0.09012	0.003011	370.5
C_{16}	0.006082	0.07799	0.002257	371.2
A_8	0.004890	0.06992	0.001822	372.6
B_{11}	0.004064	0.06375	0.001517	373.4
C_{17}	0.003043	0.05516	0.001138	373.9
A_9	0.002445	0.04944	0.0009156	374.4
B_{12}	0.001626	0.04032	0.0006131	377.0
E_2	0.0006664	0.02582	0.0002527	379.2
D_5	0.0006212	0.02492	0.0002347	(377.9)
D_3	0.0006098	0.02469	0.0002311	(378.9)
E_3	0.0003650	0.01911	0.0001390	380.7
D_7	0.0003131	0.01769	0.0001189	379.8
E_4	0.0001219	0.01104	0.00004631	379.9
D_8	0.0001025	0.01012	0.00003905	381.0
D_6	0.00009447	0.009720	0.00003490	(369.4)
D_4	0.00009427	0.009709	0.00003438	(364.7)

TABLE III.

Conductivity phenanthrene-3-sulphonic acid at 18°C.

Solution	N	$\sqrt{N}$	Spec. cond.	Λ
C_1	1.2640	1.1240	0.2114	167.2
D_5	1.0930	1.0460	0.1995	182.5
I_4	1.0660	1.0330	0.1941	182.0
D_1	0.9851	0.9924	0.1882	191.1
D_2	0.7638	0.8740	0.1569	205.4
I_2	0.6861	0.8283	0.1436	209.2
C_2	0.6349	0.7968	0.1353	213.1
I_5	0.4903	0.7001	0.1097	223.9
H_6	0.4400	0.6633	0.09982	226.9
D_4	0.3936	0.6273	0.09258	235.3
I_3	0.3365	0.5801	0.08030	238.6
C_3	0.3176	0.5635	0.07686	242.0
H_7	0.2716	0.5212	0.06770	249.2
F_1	0.2690	0.5187	0.06662	247.7
H_8	0.1962	0.4429	0.05125	261.2
C_4	0.1604	0.4004	0.04314	268.9
F_2	0.1346	0.3667	0.03741	278.1
H_9	0.1030	0.3210	0.03008	291.8
C_5	0.08034	0.2834	0.02394	298.0
F_3	0.06720	0.2592	0.02038	303.3
I_6	0.06707	0.2590	0.02030	302.7
E_2	0.06261	0.2502	0.01919	306.5
F_4	0.05380	0.2319	0.01661	308.7
G_1	0.04747	0.2169	0.01470	312.3
H_{10}	0.04284	0.2069	0.01344	313.7
J_1	0.04134	0.2033	0.01397	313.7
C_6	0.04004	0.2001	0.01256	313.7 8333
E_3	0.02927	0.1711	0.009383	320.5
H_{11}	0.02461	0.1569	0.007894	320.7
G_6	0.02354	0.1534	0.007536	320.2 8333
C_7	0.02027	0.1424	0.006485	(319.9)
J_4	0.01671	0.1293	0.005430	324.8
G_2	0.01177	0.1085	0.003860	328.0
H_{12}	0.01146	0.1070	0.003752	327.4
E_4	0.006261	0.07912	0.002084	332.9
H_{13}	0.006073	0.07793	0.002014	331.6
G_3	0.005883	0.07670	0.001956	332.4
J_5	0.002970	0.05450	0.0009900	333.3

TABLE III. (cont.)

Solution	N	$\sqrt{N}$	Spec. cond.	Λ
J_5	0.002970	0.05450	0.0009954	335.2
G_4	0.002942	0.05424	0.0009847	334.7
J_6	0.002905	0.05389	0.0009718	334.6
H_{14}	0.002844	0.05332	0.0009456	(332.5)
G_5	0.001471	0.03835	0.0004939	335.7
J_2	0.0009900	0.03147	0.0003332	336.6
J_2	0.0009900	0.03147	0.0003329	336.2
J_7	0.0009335	0.03055	0.0003143	336.7
H_{15}	0.0006501	0.02550	0.0002192	337.1
H_{16}	0.0001104	0.01051	0.00003715	(336.5)
J_8	0.000100	0.01001	0.00003393	338.8
J_8	0.0001001	0.01001	0.00003393	339.3
J_3	0.00009800	0.009900	0.00003323	339.0

TABLE IV.

Conductivity phenanthrene-3-sulphonic acid at 25°C.

Solution	N	$\sqrt{N}$	Spec. cond.	Λ
D_3	1.0910	1.0470	0.2235	204.8
I_4	1.0640	1.0350	0.2174	204.3
D_1	0.9831	0.9913	0.2106	213.0
D_2	0.7623	0.8730	0.1769	232.1
I_2	0.6850	0.8275	0.1606	234.5
I_5	0.4893	0.6995	0.1228	250.9
H_6	0.4392	0.6627	0.1128	256.8
D_4	0.3928	0.6266	0.1041	259.0
I_3	0.3359	0.5794	0.09065	269.9
H_7	0.2712	0.5207	0.07632	281.4
F_1	0.2685	0.5181	0.07498	279.2
H_8	0.1959	0.4425	0.05775	295.0
F_2	0.1344	0.3664	0.04200	312.6
H_9	0.1028	0.3206	0.03378	328.4
F_3	0.06710	0.2590	0.02274	338.8
I_6	0.06694	0.2587	0.02267	338.6
E_2	0.06250	0.2500	0.02133	341.3
F_4	0.05371	0.2317	0.01849	344.3
G_1	0.04699	0.2168	0.01633	347.5
H_{10}	0.04277	0.2067	0.01491	348.6
J_1	0.04128	0.2032	0.01441	348.9
E_3	0.02922	0.1709	0.01045	357.5
H_{11}	0.02458	0.1568	0.007838	357.1
G_6	0.02349	0.1532	0.007467	356.9
J_4	0.01669	0.1292	0.006017	360.6
G_2	0.01175	0.1083	0.004285	364.7
H_{12}	0.01144	0.1069	0.004179	364.5
E_4	0.006250	0.07905	0.002314	370.2
H_{13}	0.006063	0.07785	0.002240	369.3
G_3	0.005874	0.07668	0.002166	368.7
J_5	0.002965	0.05444	0.001096	369.7
J_5	0.002965	0.05444	0.001101	371.3
G_4	0.002937	0.05417	0.001093	372.3
J_6	0.002900	0.05382	0.001077	371.4
H_{14}	0.002839	0.05326	0.001050	370.0
G_5	0.001469	0.03831	0.0005470	372.4
J_2	0.0009884	0.03144	0.0003695	373.8
J_2	0.0009884	0.03144	0.0003701	374.5
J_7	0.0009321	0.03054	0.0003489	374.4
H_{15}	0.0006491	0.02548	0.0002434	375.1
H_{16}	0.0001102	0.01050	0.00004141	(375.0)
J_8	0.0000999	0.01000	0.00003784	378.5
J_8	0.0000999	0.01000	0.00003777	377.8
J_3	0.0000979	0.00989	0.00003688	376.9

TABLE V.

Conductivity phenanthrene-2-sulphonic acid at 18°C.

Solution	N	$\sqrt{N}$	Spec. cond.	Λ
D_1	0.2897	0.5383	0.06876	237.3
E_1	0.2688	0.5184	0.06446	239.8
B_1	0.2616	0.5115	0.06285	240.0
C_1	0.2460	0.4960	0.06019	244.6
C_2	0.1968	0.4434	0.05020	255.2
D_8	0.1469	0.3833	0.03927	267.3
D_2	0.1320	0.3634	0.03575	270.8
B_2	0.1309	0.3616	0.03549	271.1
C_3	0.1230	0.3506	0.03362	273.4
B_3	0.1046	0.3235	0.02951	281.9
C_4	0.07871	0.2806	0.02310	293.3
B_4	0.06542	0.2558	0.01945	297.1
B_5	0.05223	0.2287	0.01587	303.2
C_5	0.03935	0.1983	0.01182	(300.4)
D_3	0.03032	0.1742	0.009579	315.9
B_6	0.02616	0.1618	0.008303	317.3
E_2	0.02242	0.1497	0.007181	320.4
C_6	0.01967	0.1402	0.006305	320.6
B_7	0.01309	0.1144	0.004259	325.3
B_8	0.006544	0.08089	0.002164	330.6
D_4	0.005121	0.07157	0.001701	332.1
B_9	0.003273	0.05719	0.001096	335.0
B_{12}	0.002617	0.05114	0.0008786	335.7
B_{10}	0.001637	0.04044	0.0005520	337.3
B_{13}	0.001309	0.03617	0.0004404	336.6
D_6	0.0007079	0.02661	0.0002408	340.2
D_5	0.0003294	0.01814	0.0001124	341·3
D_7	0.0001007	0.01003	0.00003443	342.2

TABLE VI.

Conductivity phenanthrene-2-sulphonic acid at 25°C.

Solution	N	$\sqrt{N}$	Spec. cond.	Λ
D_1	0.2893	0.5378	0.07714	266.7
E_1	0.2683	0.5180	0.07285	271.5
B_1	0.2612	0.5112	0.07076	270.9
C_1	0.2456	0.4956	0.06753	275.1
C_2	0.1964	0.4430	0.05632	286.8
D_8	0.1467	0.3830	0.04410	300.6
D_2	0.1318	0.3631	0.04010	304.2
B_2	0.1307	0.3611	0.03996	305.9
C_3	0.1228	0.3504	0.03777	307.5
B_3	0.1044	0.3232	0.03312	317.2
C_4	0.07858	0.2803	0.02575	327.7
B_4	0.06531	0.2565	0.02166	331.5
B_5	0.05224	0.2285	0.01730	331.2
C_5	0.03929	0.1981	0.01357	345.4
D_3	0.03028	0.1740	0.01060	350.0
B_6	0.02613	0.1616	0.009234	353.4
E_2	0.02239	0.1496	0.007956	355.4
C_6	0.01964	0.1402	0.005546	(282.3)
B_7	0.01307	0.1143	0.004721	361.3
B_8	0.006534	0.08081	0.002405	368.2
D_4	0.005112	0.07150	0.001891	369.9
B_9	0.003278	0.05716	0.001217	372.5
B_{12}	0.002613	0.05108	0.0009745	373.3
B_{10}	0.001635	0.04041	0.0008963	375.1
B_{13}	0.001307	0.03615	0.0008392	375.1
D_6	0.0007068	0.02659	0.0002675	378.5
D_5	0.0003287	0.01813	0.0001248	379.4
D_7	0.0001006	0.01003	0.00003829	380.7

TABLE VII.

Conductivities 9-bromo-phenanthrene-3-sulphonic acid at 18°.

Solution	N	$\sqrt{N}$	Spec. cond.	Λ
C_1	0.3190	0.5648	0.05051	158.3
B_1	0.3174	0.5633	0.05027	158.4
B_2	0.2258	0.4752	0.03667	162.5
B_4	0.1579	0.3973	0.02742	173.7
B_3	0.08837	0.2973	0.01752	198.3
C_5	0.07591	0.2756	0.01564	206.1
A_1	0.05355	0.2314	0.01221	228.0
B_5	0.04051	0.2013	0.01013	250.0
A_2	0.02901	0.1703	0.008312	286.5
A_3	0.01872	0.1369	0.005907	315.6
A_4	0.01293	0.1137	0.004172	322.5
A_5	0.01097	0.1047	0.003567	324.9
A_6	0.008299	0.09109	0.002727	328.6
A_9	0.006320	0.07950	0.002085	330.1
A_7	0.004780	0.06915	0.001590	332.4
A_8	0.002129	0.04614	0.0007131	334.9
A_{10}	0.0008612	0.02935	0.0002903	337.1
A_{11}	0.0003642	0.01908	0.0001231	338.1
A_{12}	0.0001272	0.01127	0.00004284	337.0

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TABLE VIII.

Conductivities 9-bromo-phenanthrene-3-sulphonic acid at 25°.

Solution	N	$\sqrt{N}$	Sp. cond.	Λ
C_1	0.3185	0.5643	0.05982	187.8
B_1	0.3168	0.5628	0.05967	188.3
B_2	0.2254	0.4747	0.04481	198.8
B_4	0.1576	0.3969	0.03333	211.4
B_3	0.08820	0.2970	0.02052	232.6
C_5	0.07580	0.2754	0.01837	242.3
A_1	0.05348	0.2313	0.01428	266.9
B_6	0.04046	0.2011	0.01185	292.9
A_2	0.02896	0.1702	0.009594	331.3
A_3	0.01869	0.1368	0.006573	351.7
A_4	0.01292	0.1137	0.004634	358.7
A_5	0.01096	0.1047	0.003968	361.9
A_6	0.008287	0.09103	0.003028	365.4
A_9	0.006311	0.07943	0.002316	367.0
A_7	0.004775	0.06910	0.001766	369.8
A_8	0.002126	0.04612	0.0007932	373.1
A_{10}	0.0008599	0.02933	0.0003220	374.3
A_{11}	0.0003637	0.01907	0.0001367	375.7
A_{12}	0.0001270	0.01127	0.00004763	375.1

TABLE IX.

Conductivity 9-chloro-phenanthrene-3-sulphonic acid at 18°.

Solution	N	$\sqrt{N}$	Sp. cond.	Λ
C_1	0.3115	0.5581	0.04975	159.7
A_1	0.2402	0.4901	0.03941	(164.1)
C_2	0.2302	0.4797	0.03718	161.5
C_3	0.1517	0.3895	0.02665	175.6
A_2	0.1192	0.3453	0.02290	(192.0)
D_6	0.07796	0.2793	0.01715	220.0
B_1	0.05202	0.2281	0.01361	261.6
A_3	0.04763	0.2182	0.01282	(269.3)
D_8	0.03912	0.1978	0.01127	287.8
X	0.03545	0.1882	0.01057	298.3
B_2	0.02726	0.1651	0.008545	313.4
A_4	0.02388	0.1545	0.007516	(314.8)
B_3	0.02379	0.1543	0.007504	315.5
B_4	0.01848	0.1359	0.005909	319.7
C_4	0.01562	0.1249	0.004940	(316.2)
B_5	0.01132	0.1064	0.003694	326.3
B_6	0.009757	0.09879	0.003181	326.0
A_5	0.009545	0.09770	0.003119	(326.7)
B_7	0.004998	0.07069	0.001663	332.7
A_6	0.003811	0.06173	0.001268	(332.8)
B_7(a)	0.003789	0.06156	0.001270	(335.1)
B_8	0.002083	0.04564	0.0006993	335.7
B_{13}	0.002027	0.04502	0.0006825	336.7
A_7	0.001905	0.04365	0.0006380	(334.8)
B_9	0.001348	0.03672	0.0004541	336.9
A_8	0.0009523	0.03086	0.0003198	(335.7)
B_{10}	0.0006717	0.02592	0.0002270	337.8
B_{11}	0.0002926	0.01711	0.00009886	337.8
B_{12}	0.00009436	0.009736	0.00003184	337.4
B_{14}	0.00008511	0.009226	0.00002871	337.3

TABLE X.

Conductivity 9-chloro-phenanthrene-3-sulphonic acid at 25°.

Solution	N	$\sqrt{N}$	Sp.Cond.	Λ
C_1	0.3111	0.5577	0.05822	187.2
A_1	0.2398	0.4897	0.04735	(197.4)
C_2	0.2300	0.4794	0.04502	195.9
C_3	0.1515	0.3892	0.03321	219.3
A_2	0.1191	0.3450	0.02810	(236.0)
D_6	0.07786	0.2790	0.02046	262.7
B_1	0.05196	0.2280	0.01588	305.6
A_3	0.04757	0.2181	0.01491	(313.4)
D_8	0.03907	0.1977	0.01289	330.0
X	0.03540	0.1881	0.01196	337.8
B_2	0.02722	0.1650	0.009526	349.9
A_4	0.02384	0.1544	0.008337	(349.6)
B_3	0.02375	0.1541	0.008354	351.7
B_4	0.01846	0.1358	0.006579	356.3
C_4	0.01560	0.1248	0.005303	(353.0)
B_5	0.01131	0.1064	0.004102	362.7
B_6	0.009745	0.09870	0.003551	364.4
A_5	0.009535	0.09763	0.003453	(362.1)
0 B_7	0.004991	0.07065	0.001846	369.9
A_6	0.003806	0.06169	0.001409	(370.4)
B_7(a)	0.003784	0.06152	0.001410	(372.7)
B_8	0.002080	0.04560	0.0007764	373.4
B_{13}	0.002023	0.04498	0.0007578	374.5
A_7	0.001902	0.04361	0.0007098	(373.2)
B_9	0.001346	0.03668	0.0005048	375.1
A_8	0.0009508	0.03084	0.0003555	(373.9)
B_{10}	0.0006705	0.02589	0.0002514	374.9
B_{11}	0.0002922	0.01710	0.0001099	376.1
B_{12}	0.00009419	0.009705	0.00003556	377.6
B_{14}	0.00008496	0.009217	0.00003188	375.3

DENSITY DATA.

TABLE XI.

Densities p-toluene sulphonic acid at 18°.

Solution	N	W	d^{18}_{4}	Calcd.	Per cent Diff.
D_1	1.2842	4.9466	1.06575	1.06638	-0.059
C_1	1.0235	4.8788	1.05249	1.05263	-0.013
C_2	0.7648	4.8160	1.03883	1.03898	-0.015
C_3	0.6113	4.7849	1.03096	1.03088	+0.008
C_4	0.5117	4.7544	1.02567	1.02563	+0.004
C_5	0.4082	4.7351	1.02017	1.02017	0.000
C_6	0.3056	4.7041	1.01474	1.01475	-0.001
C_7	0.2562	4.6919	1.01220	1.01215	+0.005
C_8	0.2046	4.6790	1.00943	1.00942	+0.001
C_9	0.1529	4.6661	1.00663	1.00670	-0.007
C_{10}	0.1222	4.6589	1.00506	1.00508	-0.002
C_{11}	0.07643	4.6482	1.00277	1.00266	+0.011
* C_{11}	0.07643	4.6535	1.00265	1.00266	-0.001
C_{12}	0.06100	4.6441	1.00192	1.00185	+0.007
D_2	0.03863	4.6444	1.00076	1.00067	+0.009
C_{14}	0.02284	4.6343	0.99973	0.99983	-0.010
* C_{14}	0.02284	4.6405	0.99985	0.99983	+0.002
C_{15}	0.01218	4.6321	0.99928	0.99927	+0.001
C_{16}	0.006092	4.6305	0.99893	0.99895	-0.002
C_{17}	0.003048	4.6296	0.99873	0.99879	-0.006
D_3	0.0006108	4.6346	0.99863	0.99866	-0.003
Water (C)	-	4.6289	0.99863	-	-
Water (C)	-	4.6294※	"	-	-
*Water (C)	-	4.6349※	"	-	-
*Water (C)	-	4.6349※	"	-	-
Water (D)	-	4.6346※	"	-	-

※ Value of Wo

TABLE XII.

Densities p-toluene sulphonic acid at 25°.

Solution	N	W	d_4^{25}	Calcd.	Diff. Per cent.
D_1	1.2810	4.9345	1.06320	1.06400	-0.075
C_1	1.0211	4.8687	1.05008	1.05042	-0.033
C_2	0.7630	4.8067	1.03672	1.03694	-0.022
C_3	0.6100	4.7753	1.02884	1.02894	-0.010
C_4	0.5107	4.7460	1'02371	1.02375	-0.004
C_5	0.4075	4.7267	1.01846	1.01827	-0.009
C_6	0.3050	4.6966	1.01306	1.01301	+0.005
C_7	0.2556	4.6843	1.01048	1.01037	+0.011
C_8	0.2043	4.6719	1.00769	1.00774	-0.005
C_9	0.1526	4.6595	1.00506	1.00504	+0.002
C_{10}	0.1220	4.6523	1.00363	1.00344	+0.009
C_{11}	0.07630	4.6412	1.00113	1.00106	+0.007
* C_{11}	0.07630	4.6466	1.00113	1.00106	+0.007
C_{12}	0.06090	4.6373	1.00023	1.00025	-0.002
D_2	0.03857	4.6377	0.99908	0.99908	+0.008
C_{14}	0.02281	4.6278	0.99818	0.99826	-0.008
* C_{14}	0.02281	4.6336	0.99829	0.99826	+0.003
C_{15}	0.01216	4.6254	0.99770	0.99771	-0.001
C_{16}	0.006082	4.6239	0.99735	0.99739	-0.004
C_{17}	0.003043	4.6229	0.99714	0.99723	-0.009
D_3	0.0006098	4.6280	0.99707	0.99710	+0.003
Water (C)	-	4.6226※	0.99707	-	-
"	-	4.6226※	"	-	-
* "	-	4.6280※	"	-	-
* "	-	4.6280※	"	-	-
Water (D)	-	4.6280※	"	-	-

※ Value of Wo

TABLE XIII.

Densities phenanthrene-3-sulphonic acid at 18°.

Solution	N	W	d_4^{18}	Calcd.	Per cent Diff.
I_1	1.522	5.2008	1.12045	1.12350	-.272
I_4	1.073	5.0376	1.08540	1.08667	-.117
I_2	0.6905	4.8936	1.05443	1.05528	-.081
I_5	0.4933	4.8215	1.03885	1.03911	-.025
H_6	0.4428	4.8033	1.03496	1.03496	0.000
I_3	0.3386	4.7618	1.02607	1.02641	-.034
H_7	0.2733	4.7392	1.02107	1.02105	+.002
H_8	0.1974	4.7102	1.01498	1.01483	+.015
H_9	0.1038	4.6747	1.00729	1.00715	+.014
I_6	0.06741	4.6594	1.00399	1.00416	-.017
H_{10}	0.04310	4.6507	1.00214	1.00217	-.003
J_1	0.04160	4.6501	1.00192	1.00204	-.012
H_{11}	0.02477	4.6441	1.00072	1.00066	+.006
J_4	0.01682	4.6410	1.00004	1.00001	+.003
H_{12}	0.01153	4.6388	0.99954	0.99958	-.004
H_{13}	0.006112	4.6368	0.99912	0.99913	-.001
J_5	0.002989	4.6353	0.99882	0.99887	-.005
H_{14}	0.002861	4.6358	0.99892	0.99886	+.006
J_2	0.0009961	4.6348	0.99870	0.99871	-.001
H_{15}	0.0006542	4.6348	0.99870	0.99868	+.002
H_{16}	0.0001111	4.6346	0.99866	0.99864	+.002
J_3	0.00009860	4.6343	0.99859	0.99864	-.005
Water	-	4.6345*	0.99863	-	-

* Value of Wo

TABLE XIV.

Densities phenanthrene-3-sulphonic acid at 25°.

Solution	N	W	d_4^{25}	Calcd.	Per cent Diff.
I_1	1.5183	5.1881	1.11763	1.62029	-0.239
I_4	1.0708	5.0262	1.08274	1.08397	-0.113
I_2	0.6893	4.8847	1.05234	1.05301	-0.064
I_5	0.4924	4.8128	1.03681	1.03703	-0.021
H_6	0.4420	4.7946	1.03294	1.03296	0.000
I_3	0.3380	4.7538	1.02415	1.02450	-0.034
H_7	0.2729	4.7312	1.01927	1.01922	+0.005
H_8	0.1971	4.7025	1.01312	1.01307	+0.005
H_9	0.1035	4.6675	1.00555	1.00563	-0.008
I_6	0.06736	4.6525	1.00233	1.00254	-0.021
H_{10}	0.04303	4.6442	1.00058	1.00056	+o.002
J_1	0.04154	4.6434	1.00041	1.00044	-0.003
H_{11}	0.02473	4.6373	0.99905	0.99908	-0.003
J_4	0.01679	4.6346	0.99847	0.99843	+0.004
H_{12}	0.01103	4.6323	0.99800	0.99797	+0.003
H_{13}	0.006102	4.6304	0.99758	0.99757	+0.001
J_5	0.002984	4.6288	0.99721	0.99731	-0.010
H_{14}	0.002856	4.6293	0.99732	0.99730	+0.002
J_2	0.0009945	4.6285	0.99714	0.99715	-0.001
H_{13}	0.0006532	4.6285	0.99714	0.99712	+0.002
H_{16}	0.0001109	4.6283	0.99710	0.99708	+0.002
J_3	0.00009846	4.6279	0.99701	0.99707	-0.007
Water	0 -	4.6282*	0.99707	-	-

*Value of Wo

TABLE XV.

Densities phenanthrene-2-sulphonic acid at 18°.

Solution	N	W	d_4^{18}	Calcd.	Per cent Diff.
D_1	0.2897	4.7432	1.02213	1.02240	-0.026
E_1	0.2688	4.7378	1.02093	1.02068	+0.025
D_8	0.1469	4.6901	1.01073	1.01068	+0.005
D_2	0.1320	4.6840	1.00941	1.00946	-0.005
D_3	0.03032	4.6460	1.00122	1.00112	+0.010
E_2	0.02242	4.6433	1.00062	1.00047	+0.015
D_4	0.005121	4.6363	0.99907	0.99905	+0.002
D_5	0.0003294	4.6346	0.99870	0.99866	+0.004
H_2O	-	4.6343*	0.99863	-	-

* Value of Wo

TABLE XVI.

Desnities phenanthrene-2-sulphonic acid at 25°.

Solution	N	W	d_4^{25}	Calcd.	Per cent Diff.
D_1	0.2893	4.7352	1.02021	1.02055	-0.034
E_1	0.2683	4.7303	1.01921	1.01884	+0.036
D_8	0.1467	4.6827	1.00891	1.00896	-0.005
D_2	0.1318	4.6766	1.00757	1.00777	-0.020
D_3	0.03028	4.6394	0.99954	0.99953	+0.001
E_2	0.02239	4.6367	0.99896	0.99889	+0.007
D_4	0.005112	4.6289	0.99728	0.99749	-0.021
D_5	0.0003287	4.6283	0.99714	0.99710	+0.004
H_2O	-	4.6280*	0.99707	-	-

* Value of Wo

TABLE XVII.

Densities 9-bromo-phenanthrene-3-sulphonic acid at 18°.

Solution	N	W	d_4^{18}
C_1	0.3190	4.8575	1.04676
B_1	0.3174	4.8561	1.04648
B_2	0.2258	4.7917	1.03257
C_2	0.2166	4.7855	1.03135
B_4	0.1579	4.7443	1.02233
C_3	0.1409	4.7323	1.01980
C_4	0.09028	4.6968	1.01218
B_3	0.08837	4.6958	1.01194
C_5	0.07591	4.6870	1.01007
A_1	0.05355	4.6711	1.00661
C_6	0.04948	4.6687	1.00607
B_5	0.04051	4.6619	1.00460
C_7	0.03875	4.6613	1.00453
A_2	0.02901	4.6545	1.00301
C_8	0.02397	4.6511	1.00234
A_3	0.01872	4.6475	1.00150
A_4	0.01293	4.6434	1.00064
C_9	0.01181	4.6428	1.00052
A_5	0.01097	4.6421	1.00035
A_6	0.008299	4.6405	1.00000
A_9	0.006320	4.6388	0.99959
A_7	0.004780	4.6380	0.99941
A_8	0.002129	4.6361	0.99902
Water	-	4.6343*	0.99863

* Value of Wo

TABLE XVIII.

Densities 9-bromo-phenanthrene-3-sulphonic acid at 25°.

Solution	N	W	d_4^{25}
B_1	0.3168	4.8474	1.04440
B_2	0.2254	4.7838	1.03098
B_4	0.1576	4.7368	1.02059
B_3	0.08820	4.6889	1.01031
A_1	0.05348	4.6646	1.00502
B_5	0.04046	4.6555	1.00304
A_2	0.02896	4.6479	1.00141
A_3	0.01869	4.6410	0.99990
A_4	0.01292	4.6371	0.99905
A_5	0.01096	4.6357	0.99875
A_6	0.008287	4.6341	0.99840
A_9	0.006311	4.6324	0.99807
A_7	0.004775	4.6316	0.99788
A_8	0.002126	4.6297	0.99744
Water	-	4.6280*	0.99707

*Value of Wo

TABLE XIX.

Densities 9-chloro-phenanthrene-3-sulphonic acid at 18°.

Solution	N	W	d_4^{18}
C_1	0.3115	4.7922	1.03267
D_1	0.2717	4.7739	1.02874
D_2	0.2439	4.7595	1.02567
A_1	0.2402	4.7566	1.02507
C_2	0.2302	4.7509	1.02377
C_3	0.1517	4.7109	1.01514
D_4	0.1472	4.7094	1.01478
D_5	0.1214	4.6960	1.01200
A_2	0.1192	4.6940	1.01154
D_6	0.07796	4.6738	1.00711
D_7	0.06122	4.6652	1.00533
B_1	0.05202	4.6603	1.00430
A_3	0.04763	4.6583	1.00380
D_8	0.03912	4.6541	1.00293
X	0.03545	4.6530	1.00268
D_{10}	0.03009	4.6495	1.00198
B_2	0.02726	4.6480	1.00158
A_4	0.02388	4.6454	1.00108
B_3	0.02379	4.6461	1.00124
B_4	0.01848	4.6433	1.00062
C_4	0.01562	4.6419	1.00029
D_9	0.01234	4.6405	1.0000
B_5	0.01132	4.6396	0.99978
B_6	0.009757	4.6391	0.99966
A_5	0.009545	4.6389	0.99961
B_7	0.004998	4.6367	0.99914
A_6	0.003811	4.6363	0.99907
B_7(a)	0.003789	4.6361	0.99902
B_8	0.002083	4.6352	0.99884
B_{13}	0.002027	4.6351	0.99882
A_7	0.001905	4.6355	0.99891
B_9	0.001348	4.6349	0.99877
A_8	0.0009523	4.6347	0.99873
B_{10}	0.0006717	4.6346	0.99870
B_{11}	0.0002926	4.6346	0.99870
Water	-	4.6343 *	0.99863

* Value of Wo

TABLE XX.

Densities 9-chloro-phenanthrene-3-sulphonic acid at 25°.

Solution	N	W	d_4^{25}
C_1	0.3111	4.7841	1.03079
D_1	0.2713	4.7662	1.02700
A_1	0.2398	4.7486	1.02306
C_2	0.2300	4.7432	1.02189
C_3	0.1515	4.7031	1.01331
A_2	0.1191	4.6866	1.00955
D_6	0.07786	4.6669	1.00549
B_1	0.05196	4.6538	1.00265
A_3	0.04757	4.6516	1.00225
D_8	0.03907	4.6476	1.00135
X	0.03540	4.6465	1.00114
B_2	0.02722	4.6415	1.00002
A_4	0.02384	4.6392	0.99950
B_3	0.02375	4.6398	0.99964
B_4	0.01846	4.6374	0.99912
C_4	0.01560	4.6356	0.99873
B_5	0.01131	4.6335	0.99829
B_6	0.009745	3.6331	0.99820
A_5	0.009535	4.6331	0.99820
B_7	0.004991	4.6306	0.99765
A_6	0.003806	4.6299	0.99751
B_7(a)	0.003784	4.6298	0.99748
B_8	0.002080	4.6289	0.99728
B_{13}	0.002023	4.6288	0.99725
A_7	0.001902	4.6292	0.99735
B_9	0.001346	4.6288	0.99725
A_8	0.0009508	4.6285	0.99719
B_{10}	0.0006705	4.6284	0.99716
B_{11}	0.0002922	4.6283	0.99714
Water	-	4.6280 *	0.99707

* Value of Wo

VISCOSITY DATA.

TABLE XXI.

Viscometric data for water at 18°.

p	t	h_0	Mean h_0	Variation in h_0
0.0	196.3	-		-
"	196.3	-		-
"	196.3	-		-
"	196.3	-		-
"	196.4	-		-
8.676	143.1	23.33		+0.03
8.761	142.6	23.26		-0.04
8.849	142.3	23.32	23.30	+0.02
18.88	108.4	23.29		-0.01
19.06	108.0	23.31		+0.01
19.14	107.7	23.29		-0.01
0.0	196.5	-	-	-
"	196.4			
"	196.3			
"	196.5			
0.0	196.5	-	-	-
"	196.6			
"	196.5			

TABLE XXII.

Viscometric data for 39.98% sucrose solution at 18°.

p	t	h	Mean h	Variation in h
0.0	1048.5	-		-
"	1048.4	-		-
16.39	655.0	27.29		-0.03
16.48	653.7	27.29		-0.03
60.82	325.0	27.32	27.32	0.00
60.94	324.9	27.36		+0.04
92.67	238.9	27.35		+0.03
92.80	238.4	27.30		-0.02
96.82	230.6	27.30		-0.02

TABLE XXIII.

Viscosity 9-chloro-phenanthrene-3-sulphonic acid at 18°.

<table>
<tr><td colspan="5">Concentration = 0.03912 N (Solution D_8)</td></tr>
<tr><th>p</th><th>t</th><th>h</th><th>Mean h</th><th>Variation in h</th></tr>
<tr><td>0.0</td><td>201.7</td><td>-</td><td rowspan="7">23.36</td><td>-</td></tr>
<tr><td>7.417</td><td>153.1</td><td>23.36</td><td>0.00</td></tr>
<tr><td>7.510</td><td>152.6</td><td>23.33</td><td>-0.03</td></tr>
<tr><td>7.597</td><td>152.2</td><td>23.35</td><td>-0.01</td></tr>
<tr><td>14.08</td><td>125.8</td><td>23.33</td><td>-0.03</td></tr>
<tr><td>14.34</td><td>125.0</td><td>23.36</td><td>0.00</td></tr>
<tr><td>14.43</td><td>124.8</td><td>23.42</td><td>+0.06</td></tr>
<tr><td colspan="5">Concentration = 0.2439 N (Solution D_2)</td></tr>
<tr><td>0.0</td><td>524.5</td><td>-</td><td rowspan="3">23.79</td><td>-</td></tr>
<tr><td>28.32</td><td>239.4</td><td>23.78</td><td>-0.01</td></tr>
<tr><td>28.43</td><td>239.0</td><td>23.80</td><td>+0.01</td></tr>
<tr><td colspan="5">Concentration = 0.2717 N (Solution D_1)</td></tr>
<tr><td>0.0</td><td>803.1</td><td>-</td><td rowspan="6">23.82</td><td>-</td></tr>
<tr><td>24.75</td><td>394.0</td><td>23.84</td><td>+0.02</td></tr>
<tr><td>24.84</td><td>393.1</td><td>23.82</td><td>0.00</td></tr>
<tr><td>96.90</td><td>158.2</td><td>23.78</td><td>-0.04</td></tr>
<tr><td>96.94</td><td>158.0</td><td>(23.74)</td><td>-</td></tr>
<tr><td>97.63</td><td>157.6</td><td>23.83</td><td>+0.01</td></tr>
</table>

TABLE XXIV.

Viscosity 9-bromo-phenanthrene-3-sulphonic acid at 18°.

Concentration = 0.3190 N (Solution C_1)

p	t	h	Mean h	Variation in h
0.0	693.4	-		-
29.924	310.6	24.28	24.30	-0.02
30.038	310.1	24.31		+0.01
89.067	148.6	24.30		0.00
89.208	148.4	24.30		0.00

TABLE XXV.

Viscosity p-toluene sulphonic acid at 18°.

Solution	N	t	W	h	η
F_1	0.2528	217.0	4.6965	23.61	1.120
F_2	0.1008	204.3	4.6591	23.37	1.046
F_3	0.05049	200.4	4.6466	23.36	1.023
F_4	0.01013	197.1	4.6368	23.31	1.004
Water	-	-	4.6343 *	-	-

* Value of Wo

TABLE XXVI.

Viscosity phenanthrene-3-sulphonic acid at 18°.

Solution	N	t	W	h	η
K_1	0.7474	429.8	4.9184	24.73	2.323
K_2	0.3402	258.1	4.7644	23.95	1.351
K_3	0.2357	232.5	4.7249	23.75	(1.264)
K_4	0.08433	206.0	4.6669	23.46	1.056
K_5	0.04939	201.7	4.6534	23.40	1.031
K_6	0.02341	198.9	4.6432	23.34	1.015
K_8	0.01575	198.0	4.6402	23.33	1.010
K_7	0.01021	197.4	4.6386	23.32	1.006
Water	-	-	4.6343*	-	-

* Value of Wo

TABLE XXVII.

Viscosity 9-bromo-phenanthrene-3-sulphonic acid at 18°.

Solution	N	h	t	η
C_1	0.3190	24.29	693.4	3.679
C_2	0.2166	23.97	311.3	1.630
C_3	0.1409	23.74	240.4	1.247
C_4	0.09028	23.58	217.5	1.120
C_5	0.07591	23.54	212.8	1.094
C_6	0.04948	23.45	205.4	1.052
C_7	0.03875	23.42	202.5	1.036
C_8	0.02397	23.37	199.2	1.017
C_9	0.01181	23.34	197.8	1.009

TABLE XXVIII.

Viscosity 9-chloro-phenanthrene-3-sulphonic acid at 18°.

Solution	N	h	t	η
D_1	0.2717	23.82	803.1	4.180
D_2	0.2439	23.76	524.5	2.723
D_4	0.1472	23.58	254.2	1.309
D_5	0.1214	23.53	233.2	1.199
D_6	0.07796	23.45	212.0	1.086
D_7	0.06122	23.42	206.9	1.059
D_8	0.03912	23.37	201.7	1.030
D_{10}	0.03009	23.36	200.1	1.021
D_9	0.01234	23.32	197.9	1.009

TABLE XXIX.

Viscosity 9-chloro-phenanthrene-3-sulphonic acid + hydrochloric acid at 18°.

Sulphonic acid = 0.02055 N.
Hydrochloric acid = 0.410 N.

p	t	W	$\frac{(h + p)t}{h_o t_o}$
0.0	2759.0	4.6796	14.180
30.27	990.6	"	11.644
30.36	998.3	"	11.754
66.67	443.9	"	8.749
98.24	264.3	"	7.032
98.68	262.2	"	7.002
98.67	262.8	"	7.017

Viscosity 0.412 N Hydrochloric acid.

p	t	W	$\frac{(h + p)t}{h_o t_o}$
0.0	199.7	-	1.022
Water	-	4.6343 *	-

* Value of Wo

TABLE XXX.

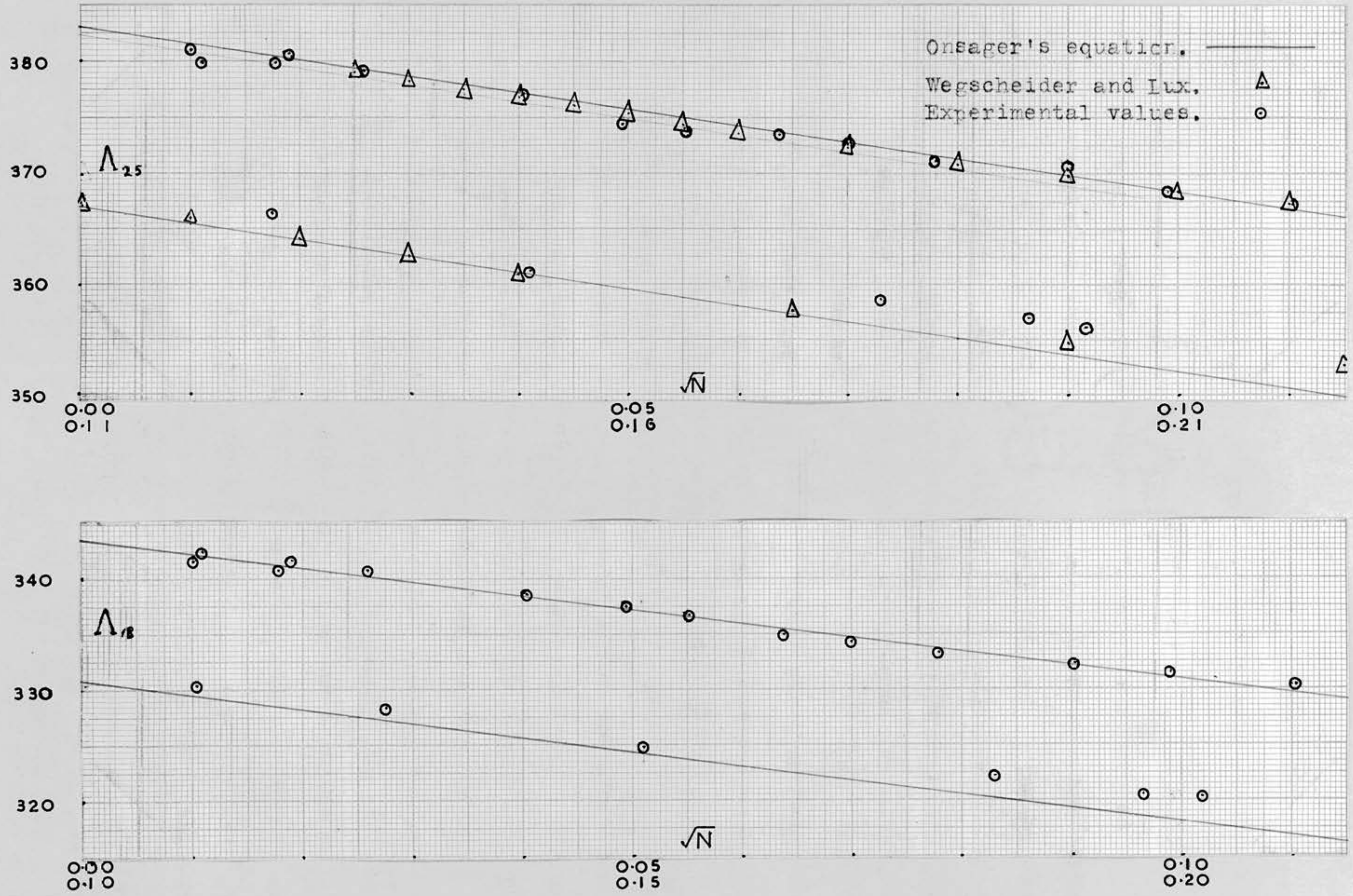
Viscosity 9-bromo-phenanthrene-3-sulphonic acid + hydrochloric acid at 18°.

Solution D_1. Sulphonic acid = 0.02003 N. HCl = 0.415 N.
Solution D_2. " " = 0.04948 N. HCl = 0.410 N.

Solution	p	t	W	$\frac{(h + p)t}{h_o t_o}$
D_1	0.0	454.9	4.6839	2.341
	"	454.8	"	
	"	454.5	"	
	"	455.0	"	
D_2	0.0	2891.0	4.7041	14.94
	"	2889.0	"	
	98.17	536.0	"	14.25
	98.03	535.8	"	
	97.88	535.5	"	
	98.15	537.0	"	
Water	-	-	4.6343 *	-

* Value of Wo

FIGURE 5.



CONDUCTIVITY OF p-TOLUENE SULPHONIC ACID AT 18° AND 25°C.

DISCUSSION.

CONDUCTIVITY.

As previously stated, the conductivity data here presented are based upon the value obtained by Parker and Parker(1) for the specific conductivity, at 18°, of a 0.1 demal solution of potassium chloride. Parker and Parker's values were adopted as the basis of the conductivity data given in the International Critical Tables (Vol. VI), and they are also frequently used in the general literature. It is, however, becoming the practice to employ the slightly higher values obtained by Jones and Bradshaw(2). These values are preferred by Dole(3), Shedlovsky(4), Davies(5), and others, who consider them more accurate than those of Parker and Parker. The two standards differ by 0.028 per cent. for the 0.1 demal solution, so that the present conductivity values should be increased by this amount to bring them in line with the work of Jones and Bradshaw.

Actually, the correction is of minor importance in the present connection. No extreme degree of accuracy was aimed at, since the primary object was to establish the main features of the conductivity curves over a wide range of concentrations.

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(1) Parker and Parker, J.A.C.S., 46 (1924) 312.
(2) Jones and Bradshaw, J.A.C.S., 55 (1933) 1780.
(3) Dole, "Electrochemistry", (1935) page 58.
(4) Shedlovsky and Brown, J.A.C.S., 56 (1934) 1066.
(5) Davies J.C.S., 1937, 432.

DILUTE SOLUTIONS.

p-Toluene Sulphonic Acid.

In order to ascertain the characteristic features in the behaviour of the phenanthrene sulphonic acids, it is obviously desirable to make comparison with the behaviour of the simplest type of aromatic sulphonic acid. A survey of the literature revealed that previous investigations on such acids have been confined to limited ranges of low concentrations, so that it became necessary to measure the conductivity of some appropriate compound up to a suitably high concentration. The simplest acid is, of course, benzene monosulphonic acid, but it was decided to employ p-toluene mono-sulphonic acid, which can differ only slightly from the benzene acid, and is much more convenient to handle. The results of the measurements are given in Tables I and II.

In Figure 5 (p. 79) the values of the equivalent conductivity, at both 18° and 25°, are plotted against the square-root of the normality, up to a concentration of about 0.04 N ($\sqrt{N} = 0.2$). For the purpose of covering this range of concentrations on a large enough scale, the points for each temperature are plotted in two portions, the upper one extending to a concentration of about 0.0121 N ($\sqrt{N} = 0.11$), and the lower one including the higher concentrations.

In the theory of Onsager, the value of the equivalent conductivity (Λ), in aqueous solution, of a uni-univalent electrolyte at a finite concentration (N) is related to the value at infinite dilution (Λ_0) according to the expressions:-

$\Lambda = \Lambda_0 - (0.2274\,\Lambda_0 + 59.79)\sqrt{N}$, at 25°(1)

and $\Lambda = \Lambda_0 - (0.2238\,\Lambda_0 + 50.49)\sqrt{N}$, at 18°(2).

The straight lines in Figure 5 result from these equations, when Λ_0 is put = 383.0 at 25°, and = 343.5 at 18°. It will be seen that most of the experimental points lie within 0.5 mho of the theoretical line up to N = 0.010 ($\sqrt{N}$ = 0.10) at least.

The data obtained in the case of the most reliable previous work, namely that of Wegscheider and Lux(3), are also plotted in Figure 5. These results are based upon the values obtained by Kohlrausch, Holborn and Diesselhorst(4) for the specific conductivity of 0.02N potassium chloride at 25°. Jones and Prendergast(5) have furnished good evidence that the values obtained by these workers in the cases of 1.0N, 0.1N, and 0.01N

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(1) This is the equation usually given in the literature. Calculation from the data quoted by Falkenhagen (2) leads to $\Lambda = \Lambda_0 - (0.2271\,\Lambda_0 + 59.78)\sqrt{N}$. The difference is of no importance in the present connection.

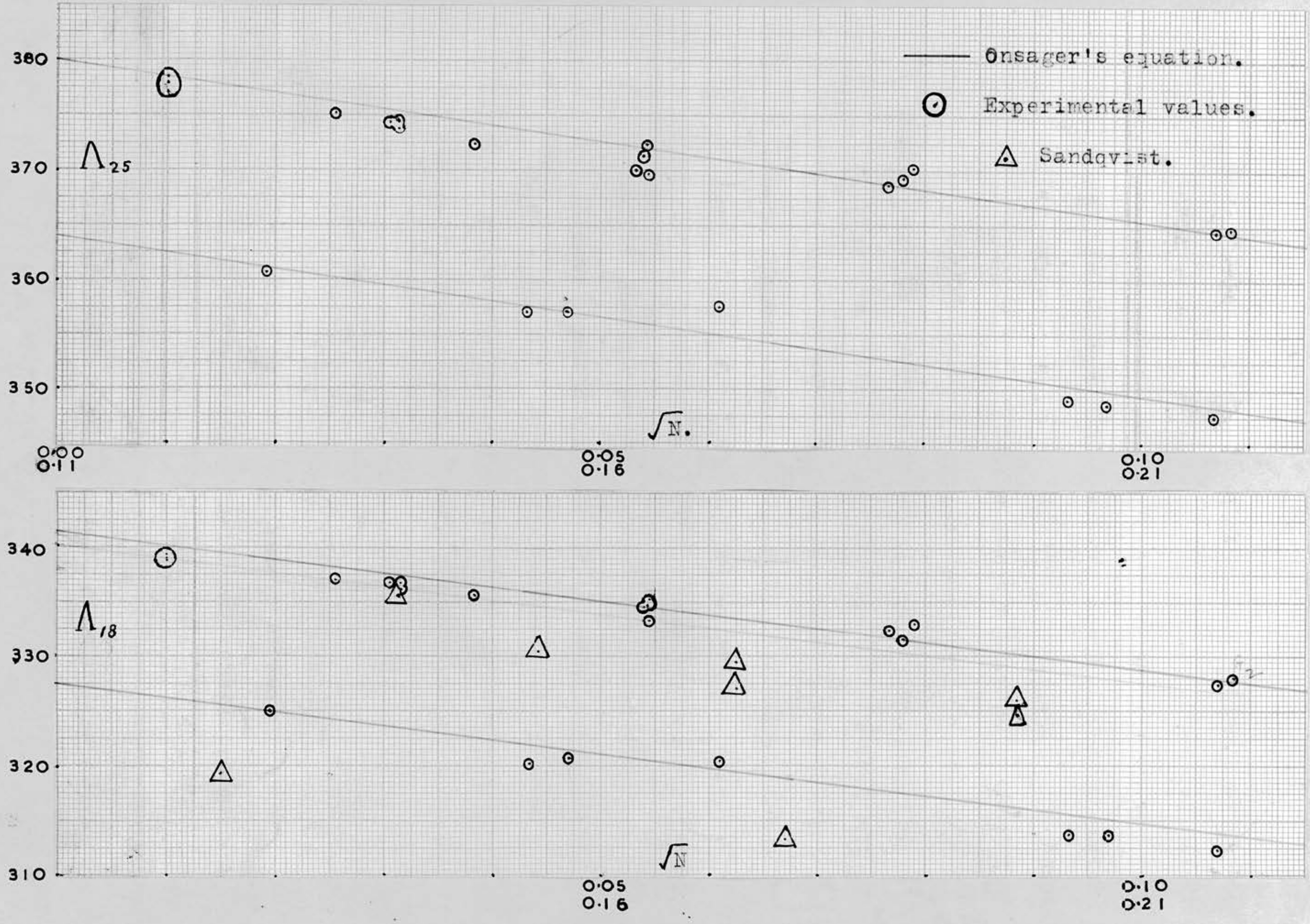
(2) Falkenhagen, "Electrolytes", (1934) page 193.

(3) Wegscheider and Lux, Monats., 30 (1909) 411. (Cf. da Monte and Zoso, Gazz. Chim. Ital., 27II (1897) 467; Wightman and Jones, J.A.C.S., 46 (1911) 56; Dawson and Crann, J.C.S., 109 (1916) 1262. 97?

(4) Kohlrausch, Holborn and Diesselhorst, Wied.Ann., 64 (1898) 417.

(5) Jones and Prendergast, J.A.C.S., 59 (1937) 731. See also Davies, J.C.S., 1937, 1326.

FIGURE 6.



CONDUCTIVITY OF PHENANTHRENE-3-SULPHONIC ACID AT 18° AND 25°C.

potassium chloride are in error by +0.060, -0.048, and +0.110 per cent. respectively. It would thus appear that the data of Wegscheider and Lux are probably correct to within ±0.10 per cent. at least. As they stand, the data agree quite well with the Onsager curve in Figure 5 up to N = about 0.0256 ($\sqrt{N} = 0.16$).

In view of the foregoing, it is reasonable to conclude that the present results and those of Wegscheider and Lux indicate (1) that Onsager's theory accounts, in the main, for the behaviour of p-toluene sulphonic acid up to a concentration of 0.01N at least, and (2) that the value of Λ_0 is probably 38~~0~~.0 ± 0.5 at 25°, and 3
343.5 ± 0.5 at 18°.

It is evident from Figure 5 that between 0.01N ($\sqrt{N} = 0.1$) and 0.04N ($\sqrt{N} = 0.2$), the experimental points commence definitely to diverge from the Onsager curve, the conductivity falling *less* rapidly, with increase in concentration, than at concentrations below 0.01N.

Phenanthrene-3-Sulphonic Acid.

The measurements of the conductivity of solutions of phenanthrene-3-sulphonic acid are recorded in Tables III and IV. In Figure 6 (page 83) the equivalent conductivity is plotted against the square-root of the normality for concentrations up to about 0.0484N ($\sqrt{N} = 0.22$), as in Figure 5 . The straight lines are the curves for Onsager's equations, with Λ_0 = 341.5 at 18°, and = 380.0 at 25°. Although the agreement between the experimental points and the theoretical curves is not so good as in the case of the toluene sulphonic acid, the straight lines may be said to represent fairly the results up to about 0.0225 ($\sqrt{N}$ = 0.15) at least.

Sandqvist's data$^{(1)}$ for phenanthrene-3-sulphonic acid, at 18°, are also plotted in Figure 6 . It will be seen that, with one exception, the points lie approximately on a straight line parallel to, but much below, that shown in the figure. All of Sandqvist's data appear to be based on Kohlrausch and Holborn's$^{(2)}$ value for the specific conductivity, at 18°, of 0.10N potassium chloride. Jones and Prendergast$^{(3)}$ have shown that this value is probably too low, but by only 0.017 per cent, which is quite inadequate to account for the above-mentioned discrepancy between Sandqvist's and the present data.

There is some indication in Figure 6 that at about 0.04N ($\sqrt{N}$ = 0.2) the experimental points are tending definitely to lie below the Onsager line, i.e., the conductivity is commencing to fall, with increase in concentration, <u>more</u> rapidly than at concentrations

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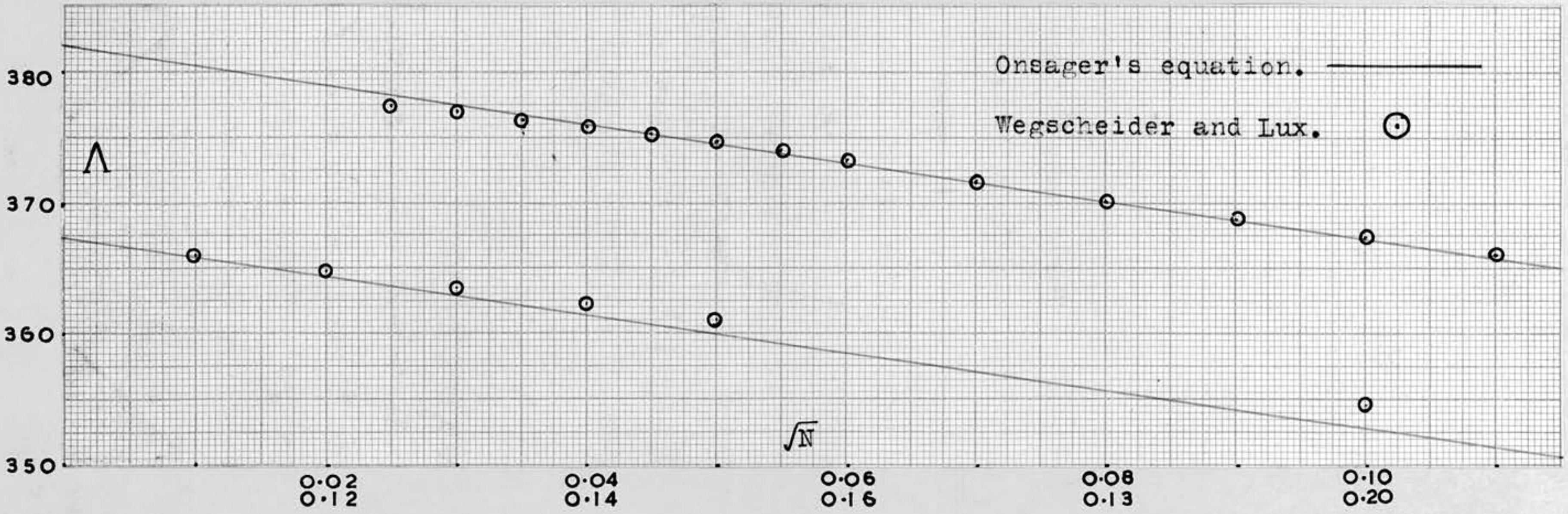
(1) Sandqvist, Ann., 369 (1909) 104; Arkiv. f. Kemi, etc., 4 (1911-1913) No. 33, pp.23 and 24.

(2) Kohlrausch and Holborn, "Leitvermögen der Elektrolyte" (1898) p.77; Measurements by Kohlrausch, Holborn and Diesselhorst, Wied. Ann., 64 (1898) 417.

(3) Jones and Prendergast, J.A.C.S., 59 (1937) 731.

FIGURE 7.

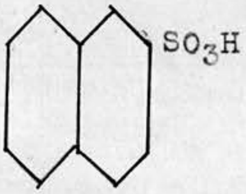


CONDUCTIVITY OF β-NAPHTHALENE SULPHONIC ACID AT 25°C.

below 0.0225N.

β-Naphthalene Sulphonic Acid.

Wegscheider and Lux(1) have measured the conductivity, at 25°, of β-naphthalene sulphonic acid,



up to the concentration 0.1169N. Their data(2) are shown in Figure 7 (page 86), the conductivity being plotted against $\sqrt{N}$ in the upper part of the Figure, and against the normality itself in the lower. It will be seen that up to 0.0121N ($\sqrt{N} = 0.11$) at least, the experimental points lie close to the Onsager line obtained by taking $\Lambda_0 = 382.0$. Thereafter the slope of the experimental curve decreases with increase in concentration, as in the case of p-toluene sulphonic acid.

Mobility of Sulphonate Ions.

According to MacInnes, Shedlovsky and Longsworth(3), the limiting equivalent conductivity (mobility) of the hydrogen ion is 349.7 mhos at 25°. Assuming this value, which is in all probability the most reliable

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(1) Wegscheider and Lux, Monats., 30 (1909) 411. The early work of Ostwald (Z. phys. Chem., 2 (1888) 845) must be regarded as approximate.

(2) These values are possibly subject to a correction of less than ±0.1 per cent., as in the case of Wegscheider and Lux's values for p-toluene sulphonic acid (see page 84).

(3) MacInnes, Shedlovsky, and Longsworth, J.A.C.S., 54 (1932)2758. Quoted by Dole, "Electrochemistry" (1935)158.

published so far, the following values are obtained for the mobilities of the anions of the three sulphonic acids discussed above.

Acid	p-toluene	β-naphthalene	phenanthrene-3-
Λ_0 at 25°	383.0	382.0	~~381.5~~ 380.0
Mobility H^+ at 25°	349.7	349.7	349.7
Mobility Sulphonate ion at 25°	33.3	32.3	~~31.8~~ 30.3

Wegscheider and Lux$^{(1)}$ also report measurements of the conductivity, at 25°, of dilute solutions of the sodium and potassium salts of p-toluene and β-naphthalene sulphonic acids. In all cases the plots of Λ against $\sqrt{N}$ give good straight lines, from which the following valuesof the limiting conductivities of the salts themselves and of the sulphonate anions have been deduced. The accurate valuesof MacInnes, Shedlovsky and Longsworth$^{(2)}$ for the mobilities of the sodium and potassium ions at 25° have been adopted for the latter purpose.

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(1) Wegscheider and Lux, Monats., 30 (1909) 411.
(2) MacInnes, Shedlovsky and Longsworth, J.A.C.S., 54 (1932) 2758. Quoted by Dole, "Electrochemistry" (1935) 158.

Acid	p-toluene		β-naphthalene	
Salt	Na	K	Na	K
Λ_o of salt at 25°	84.7	109.1	82.8	105.6
Mobility of cation at 25°	50.1	73.5	50.1	73.5
Mobility of sulphonate ion at 25°	34.6	35.6	32.7	32.1
MEAN	35.1		32.4	

The mobilities of the anions of the toluene and phenanthrene acids at 18° were deduced from the present data as follows. Shedlovsky and MacInnes(1) have measured the equivalent conductivity of 0.001N hydrochloric acid at 0°, 15°, 25°, and 38°. On plotting their results, it was evident that the values at 18° could be obtained with sufficient accuracy by interpolating on the straight line joining the values at 15° and 25°. This value proved to be 377.4, which, by application of Onsager's equation, leads to $\Lambda_o = 381.7$ for hydrochloric acid at 18°. From this the mobility of the hydrogen ion was derived in the following manner. The transport number at infinite dilution of the potassium ion is 0.4906 at 25°, according to Longsworth(2) and 0.4913 at 40°, according to Samis(3). Hence the value at 18° must be in the neighbourhood of 0.4902

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(1) Shedlovsky and MacInnes, J.A.C.S., 57 (1935) 1705.
(2) Longsworth, J.A.C.S., 54 (1932) 2741.
(3) Samis, Trans. Faraday Soc., 33 (1937) 469.

Now Davies(1) has obtained Λ_0 = 129.67 for potassium chloride at 18°. Thus the mobility of the potassium ion = 129.67 × 0.4902, = 63.36, that of the chlorine ion = 129.67 - 63.36 = 66.3, and that of the hydrogen ion = 381.7 - 66.3 = 315.4. On the basis of this value the mobilities of the sulphonate are as follows.

Acid	p-toluene	phenanthrene-3
Λ_0 at 18°	343.5	341.5
Mobility H^+ at 18°.	315.4	315.4
Mobility sulphonate ion at 18°	28.1	26.1

Reference should be made to the work of Jeffery and Vogel(2), who have determined the conductivity, at 25°, of benzene sulphonic acid up to 0.01047N, and that of sodium benzene sulphonate up to 0.01129N. The data(3) are fairly well represented by Onsager's equation, taking Λ_0 = 386.4 for the acid, and Λ_0 = 86.9 for the salt. The mobility of the sulphonate ion is, accordingly, 386.4 - 349.7 = 36.7, or 86.9 - 50.1 = 36.8(4).

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(1) Davies, J.C.S., <u>1937</u>, 432.
(2) Jeffery and Vogel, J.C.S., <u>1932</u>, 400.
(3) Based on the values obtained by Kohlrausch and Maltby ("Gesammelte Abhandl.", 2 (1911) 826) for the specific conductivity of potassium chloride at 18°. According to Parker and Parker (J.A.C.S., 46 (1924) 312) these values are too high by 0.145 per cent. This correction has therefore been applied to the data of Jeffery and Vogel to bring them in line with the present results.
(4) Somewhat smaller values are obtained by employing the empirical formula, $\Lambda = \Lambda_0 - bN^n$, where b and n are constants, and n is not necessarily equal to 0.5. This formula was advocated by Vogel, but is open to considerable criticism, as described by Davies ("The Conductivity of Solutions", 2nd ed. (1933) 99).

Summarising, we have:-

Anion	Mobility (l_0)			
	Author		Wegscheider and Lux	Jeffery and Vogel
	18°	25°	25°	25°
Benzene sulphonate	-	-	-	36.7 : 36.8
p-Toluene sulphonate	28.1	33.3	33.3 : 35.1	-
β-naphthalene sulphonate	-	-	32.3 : 32.4	-
phenanthrene-3-sulphonate	26.1	~~31.8~~ 30.3	-	-

It is of interest to compare the values of l_0 for these aromatic sulphonate ions with those for similar paraffin-chain ions. The only available data suitable for such comparison are due to Laing-McBain, Dye, and Johnston(1), who have determined the conductivity, at 25°, of some straight-chain sulphonic compounds of the general formula $C_nH_{n+1}SO_3H$ (or K). Onsager's equation was found to hold, for the C_2 and C_9(nonyl) acids, up to at least 0.0064N ($\sqrt{N} = 0.08$), and extrapolation of the theoretical curve gave $\Lambda_0 = 385$ and 374 respectively. From this l_0 for $C_2H_5SO_3^-$ = 385 - 349.7 = 35.3, and l_0 for $C_9H_{19}SO_3^-$ = 374 - 349.7 = 24.3. Measurements with $C_2H_5SO_3K$ gave $\Lambda_0 = 109$, from which l_0 for $C_2H_5SO_3^-$ = 109 - 73.5 = 35.5. It will

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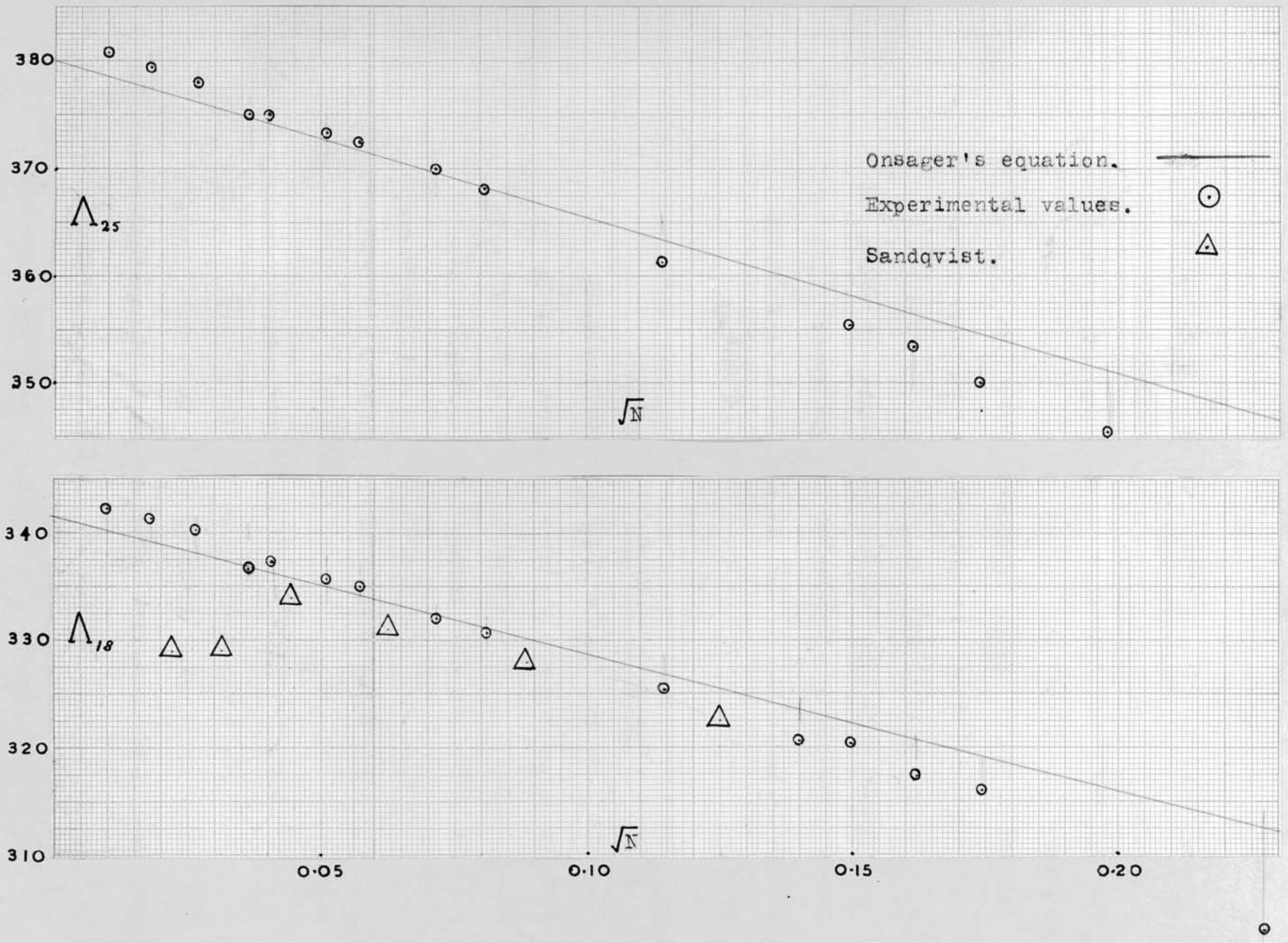
(1) McBain, Dye and Johnston, J.A.C.S., 61 (1939) 3210.

FIGURE 8.



CONDUCTIVITY OF PHENANTHRENE-2-SULPHONIC ACID AT 18° AND 25°C.

be seen that l_0 for the phenanthrene sulphonate ion ($C_{14}H_9SO_3^-$), containing 27 atoms, lies nearer to l_0 for $C_2H_5SO_3^-$ (11 atoms), although its atomic content is very much closer to that of the nonyl sulphonate ion (32 atoms). Hence it would appear highly probable that the mobility of the phenanthrene sulphonate ion will be markedly greater than that of the straight-chain sulphonate ion with the same number of atoms. A possible factor is the greater lack of symmetry in the aliphatic compound$^{(1)}$, but the available data are too limited to make further discussion profitable.

Phenanthrene-2-Sulphonic Acid.

The data for dilute solutions of this acid (Tables V and VI) are plotted in Figure 8 (page92), up to 0.05233N ($\sqrt{N}$ = 0.2287). Some of Sandqvist's$^{(2)}$ results (18°) are also shown. His conductivities varied widely, and only the highest of his values are given. Even these lie considerably below the present values.

The straight line at 18° is Onsager's curve with Λ_0 = 341.5, i.e., the same as for the 3-acid. Over the range $\sqrt{N}$ = about 0.035 to $\sqrt{N}$ = about 0.10 there is fairly good agreement between theory and experiment.

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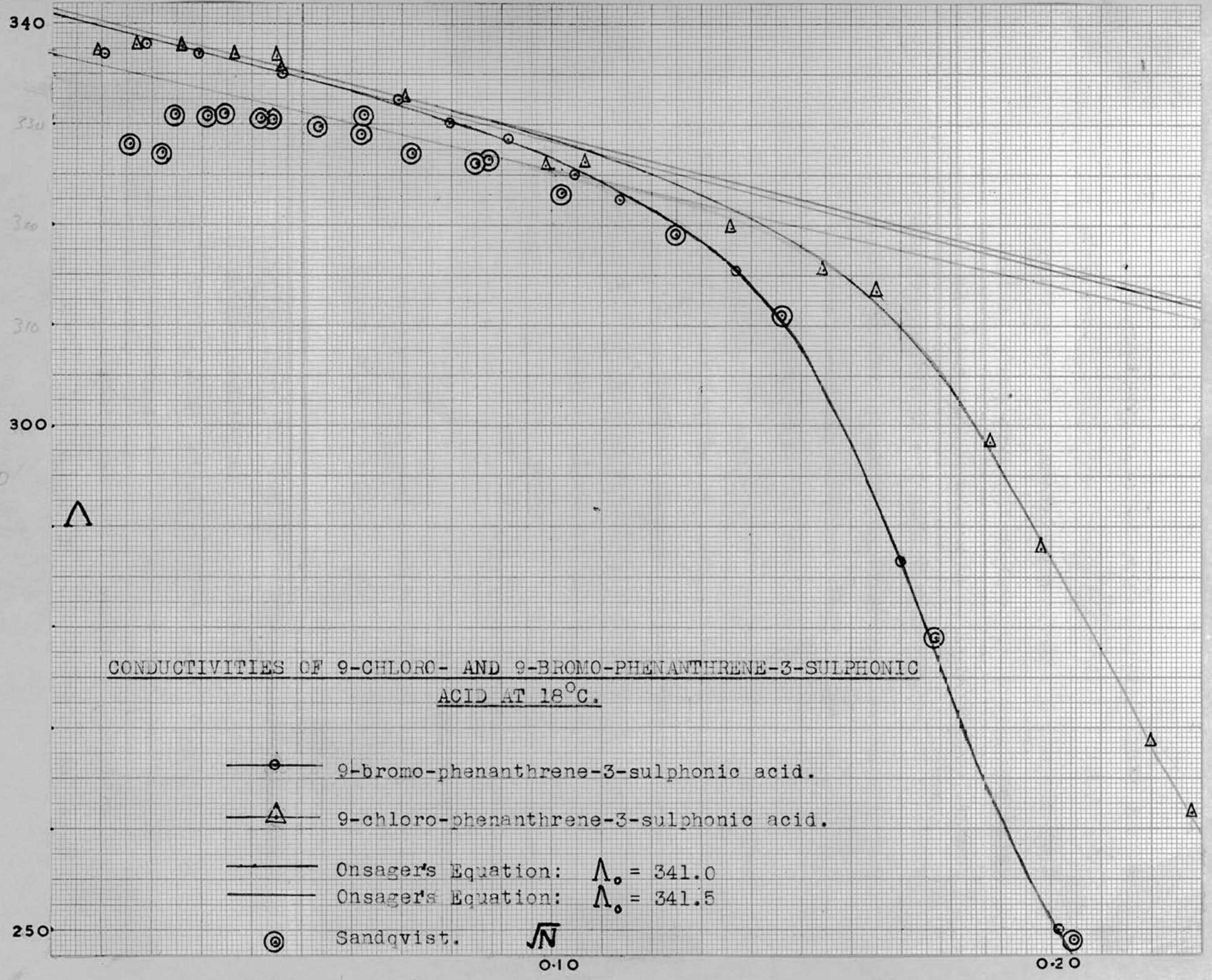
(1) See Ward, J.C.S., 1939, 522.
(2) Sandqvist, Arkiv. f. Kemi etc., 4, No. 33 (1911-1913) p. 55. Lieb. Ann., 379 (1911) 79.

FIGURE 9.



CONDUCTIVITIES OF 9-CHLORO- AND 9-BROMO-PHENANTHRENE-3-SULPHONIC ACID AT 18°C.

At the three lowest concentrations, however, the experimental points lie above the line by much more than the usual experimental error. Nevertheless, it seems preferable to ascribe the divergence to this source, rather than to assume a higher value for Λ_0, since it is hardly likely that the difference in the position of the sulphonic group would influence the mobility of the sulphonate ion to any great extent.

There is no doubt that thre experimental curve commences to <u>fall</u> <u>below</u> the Onsager line much earlier than in the case of the 3-acid, actually at $\sqrt{N}$ = about 0.1, as against $\sqrt{N} = 0.2$. Thus at 0.05233 ($\sqrt{N} = 0.2287$) the observed conductivity is 303.3 mhos, which is 9.2 less than the theoretical, whereas in the case of the 3-acid, $\Lambda = 308.7$ for $N = 0.05380$ (TableIII). The final measurements were made after the acids had been carefully repurified, so that the difference in behaviour appears to be genuine. Its possible significance will be considered at a later stage.

<u>9-Bromo- and 9-Chloro-phenanthrene Sulphonic Acids.</u>

In Figure 9 (page 94) the equivalent conductivity of 9-bromo-phenanthrene-3-sulphonic acid at 18° (Table VII) is plotted against $\sqrt{N}$, up to $\sqrt{N}$ = about 0.2 ($N = 0.04$).

Sandqvist's values(1) for the bromo-acid are also reproduced in Figure 9. The agreement is fair down

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(1) Sandqvist, Arkiv. f. Kemi, etc., <u>6</u> (1916-1917) No.9, pp. 34 and 35. Kolloid Zeitschr., <u>19</u> (1916) 113. An earlier series of measurements (Arkiv, etc., <u>5</u> (1913-1915) No. 17, pp.39 and 40) gave even lower values.

to $\sqrt{N} = 0.15$, but beyond this, with decreasing concentration, Sandqvist's figures increasingly diverge from the present data, and indicate a much lower value for Λ_0.

The Figure shows that up to N = about 0.0025 ($\sqrt{N} = 0.05$) the present data (with the exception of the lowest concentration) agree quite well with Onsager's equation, if Λ_0 is taken as 341.0, as compared with 341.5 for the unsubstituted acid. At higher concentrations, however, the experimental curve diverges from the theoretical line with increasing rapidity, so that at 0.04N the observed conductivity is almost 27 per cent. less than the calculated value. Since the experimental curve for the unsubstituted phenanthrene-3-sulphonic acid lies only slightly below the Onsager line at 0.04N (see Figure 6), it is evident that the introduction of a bromine atom markedly affects the behaviour of the compound.

In some instances, negative divergence from the Onsager line has been satisfactorily interpreted in terms of the association of oppositely charged ions to form ion-pairs, as the result of the electrical attraction (Coulomb forces)(1) . From this point of view it would follow that the bromo-acid exhibits a greater tendency to form ion-pairs than does the

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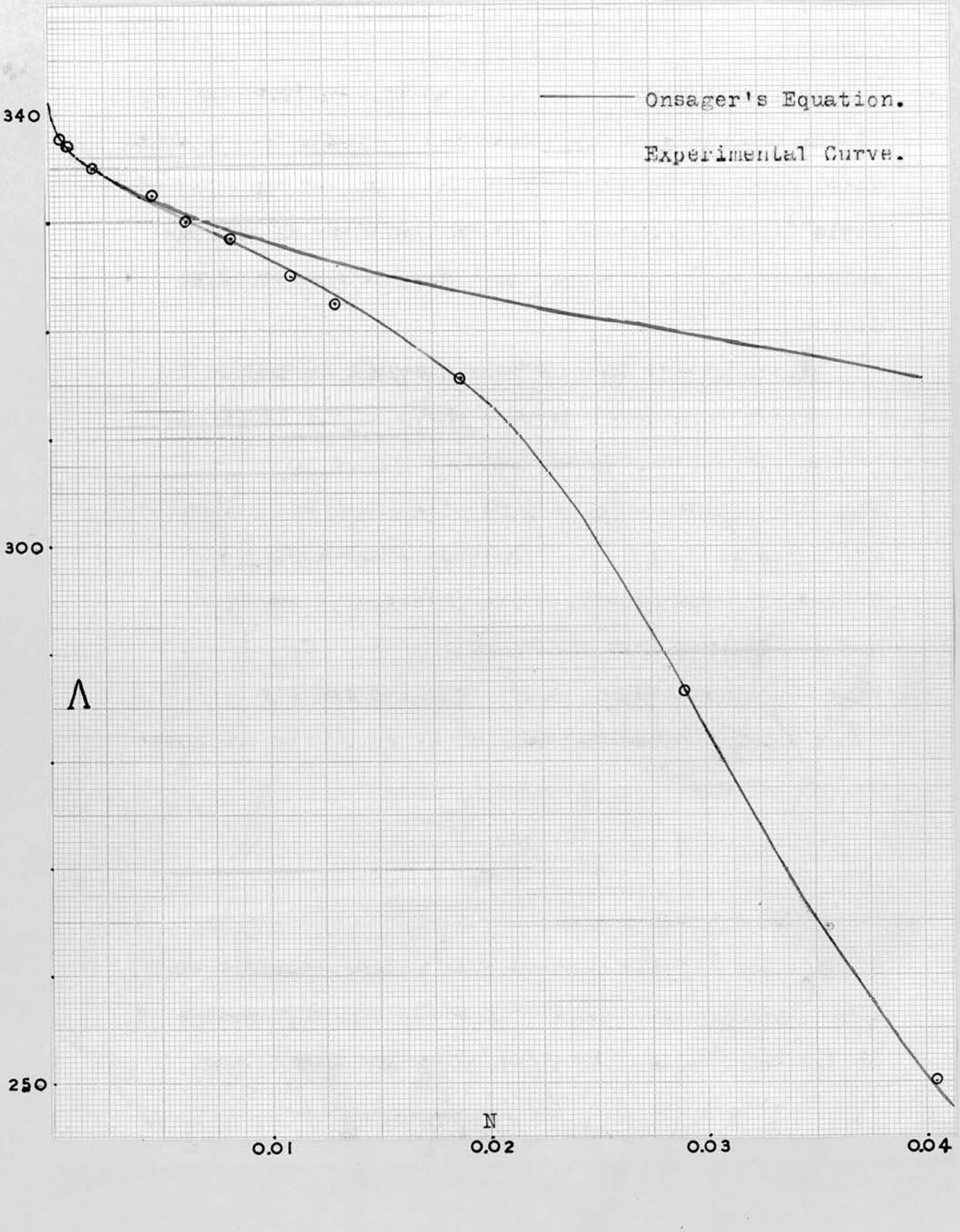
(1) Fuoss and Kraus, J.A.C.S., 55 (1933) 476; ibid 1019. Mead, Fuoss and Kraus, Trans. Faraday Soc., 32 (1936) 594. Robinson and Davies, J.C.S., 1937, 574.

FIGURE 10.



CONDUCTIVITY OF 9-BROMO-PHENANTHRENE-3-SULPHONIC ACID AT 18°C.

unsubstituted acid. In other words, the introduction of the bromine atom decreases the strength of the acid. This, however, is unlikely in the light of the work of Boyle$^{(1)}$, who has shown that halogenation of aniline sulphonic acid increases the strength to a striking degree.

That, in any case, simple ion-pair formation is inadequate to account for the whole of the behaviour of the bromo-phenanthrene sulphonic acid is evident when the conductivity is plotted against the normality, as in Figure 10 (p. 97). Between about 0.011N and 0.026N the conductivity curve undergoes a marked inflection away from the Onsager line. This means that a constant value is not obtained for the "dissociation constant" (K), as derived from the mass action formula$^{(2)}$:-

$$K = \frac{\alpha^2 N\, f_K f_A}{(1 - \alpha) f_{KA}} ,$$

where f_K, f_A, and f_{KA} are the respective activity coefficients of the unassociated kation, unassociated anion, and simple ion-pair (K + A), and α = degree of dissociation (i.e., fraction of unassociated ions)

$$= \frac{\Lambda}{\Lambda_0 - (0.2238\, \Lambda_0 + 59.79)\sqrt{\alpha N}} .$$

An approximate calculation showed that K actually

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(1) Boyle, J.C.S., 115 (1919) 1505
(2) See Falkenhagen, "Electrolytes", (1934) pp. 301-307.

decreases several fold between the above concentration limits.(1)

An inflection of the type discussed in the foregoing is uniformly observed in the case of long paraffin-chain sulphonic acids,(2) sulphonates,(3) sulphates,(4) and pyridinium salts,(5) and the ordinary soaps (when hydrolysis is suppressed).(6) Actually, the behaviour of the bromo-phenanthrene acid in this respect is intermediate between that of nonyl (C_2) sulphonic acid and undecyl (C_{11}) sulphonic acid. The study of various properties of the paraffin-chain compounds has led to the conclusion, now generally accepted, that the more or less sudden decrease in conductivity at low concentrations, is related to the appearance in the solution of aggregates or micelles. These are formed by the association of the organic radicles as the result of the operation of the van der Waals forces exerted by them. Opinion, however, differs in regard to the composition and structure of the

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(1) This result may be contrasted with that for iodic acid (in aqueous solution) obtained by Fuoss and Kraus (J.A.C.S., 55 (1933) 476). These workers derived values for K which up to a concentration of about 0.065N fell within the limits 0.163 and 0.177, with very few exceptions.

(2) Hartley, J.A.C.S., 58 (1936) 2347. Laing-McBain, Dye and Johnston, J.A.C.S., 61 (1939) 3210.

(3) Murray and Hartley, Trans. Faraday Soc., 31 (1935). Wright, Abbott, Sivertz and Tartar, J.A.C.S., 61 (1939)549.

(4) Lottermoser and Püschel, Koll. Zeitschr., 63 (1933)175. Howell & Robinson, Proc. Royal Soc., A 155 (1936) 386.

(5) Malsch and Hartley, Zeit. phys. Chem., 170 A (1934) 321. Hartley, Collie and Samis, Trans. Faraday Soc., 32 (1936) 795. Hartley, Ref. (1). Lottermoser and Frötscher, Koll. Beih., 45 (1937) 304.

(6) Bury, Chem. and Ind., 58 (1938) 1168.

(7) See for example, Hess and Suranyi, Zeitschr. phys. Chem. 184 (1939) 321.

micelles. McBain(1) considers that there are two types of aggregate, the poorly-conducting "neutral" micelle, composed mainly of ion-pairs or neutral molecules, and the highly-conducting "ionic micelle", composed mainly of paraffin-chain ions. In contrast with this, Hartley(2) maintains that the micelles are all of one kind, being made up of paraffin-chain ions associated with a smaller number of ion-pairs, and possessing a conductivity intermediate between those of the two types postulated by McBain. Hartley is of the opinion that the drop in conductivity is due partly to the formation of ion-pairs, and partly to enhanced interionic action of the Debye-Hückel description, whereas McBain considers that the second factor is of negligible importance. On either view the decrease in conductivity must be regarded as a consequence of the aggregation, and Hartley has advanced the interesting suggestion that ion-pair formation might be expected to accompany association of the paraffin chains, since the boundary region of the micelle may function as a medium of lower dielectric constant than that of water.

The shape of the conductivity curve at low concentrations is thus consonant with the view that 9-bromo-phenanthrene-3-sulphonic acid is a colloidal electrolyte. It would appear, however, that the tendency to form micelles is less pronounced than in

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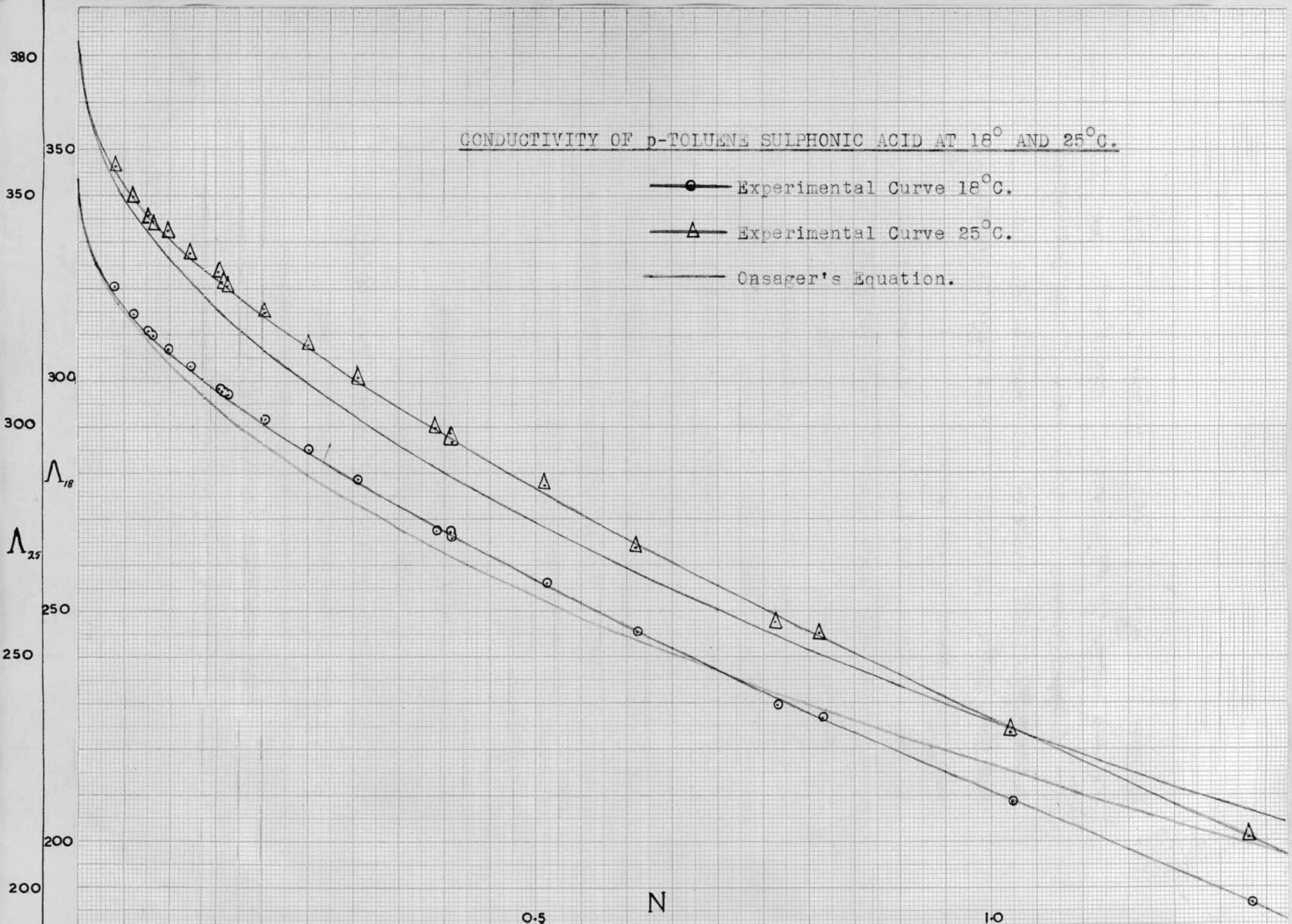
(1) See Laing-McBain, Dye and Johnston, J.A.C.S., 61 (1939) 3210.

(2) Hartley, Koll. Zeitschr., 88 (1939) 22.

FIGURE 11.



CONDUCTIVITY OF p-TOLUENE SULPHONIC ACID AT 18° AND 25°C.

the case of a paraffin-chain electrolyte containing the same number of carbon atoms. According to the data of Laing-McBain, Dye and Johnston,(1) the inflection in the conductivity curve of myristic acid (C_{14}) is much more sudden and occurs at a much lower concentration, viz., about 0.002N (at 25°).

As is evident from Figure 9 , the behaviour of 9-chloro-phenanthrene-3-sulphonic acid (Table IX) is not identical with, though similar to, that of the bromine derivative. The limiting (Onsager) curve appears to lie slightly higher, giving Λ_0 = 341.5, and with increase in concentration the conductivity falls considerably less rapidly than that of the bromo-acid. Thus at 0.04N, the valuesof Λ differ by as much as 37 mhos. The significance of the difference in behaviour of the two acids will be discussed at a later stage.

THE COMPLETE CONDUCTIVITY CURVE.

p-Toluene Sulphonic Acid.

The complete conductivity curves from the data in Tables I and II are shown in Figure 11 (page 101), together with the theoretical curves obtained by applying Onsager's theory to the whole range of concentrations studied. In this and succeeding figures

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(1) Ref. (1), preceding page.

the equivalent conductivity is plotted against the normality itself.

The positive divergence of the experimental from the theoretical curve, which becomes evident between 0.01N and 0.02N, as already mentioned, continues up to approximately 0.25N for 18°, and 0.35N for 25°, where the differences between the experimental and theoretical values of Λ are 5 and 8 mhos respectively. After this the curves approach and eventually cross at about 0.75N for 18°, and 1.0N for 25°. Up to the highest concentration examined, i.e., about 1.275N, the curves undergo no inflection in the direction opposite to that of the inflection at low concentrations.

As a first step in the interpretation of the conductivity curve for p-toluene sulphonic acid, we may compare it with the somewhat similar curve for hydrochloric acid. According to Shedlovsky(1), it is highly probable that the experimental curve for hydrochloric acid shows positive divergence from the Onsager line at even the lowest concentrations, the theoretical curve representing only the limiting behaviour of this acid. With increase in concentration the divergence continuously increases, so that at 1.0N the value of Λ at 25° is 23 per cent greater than the theoretical value.(2) There is thus a considerable difference

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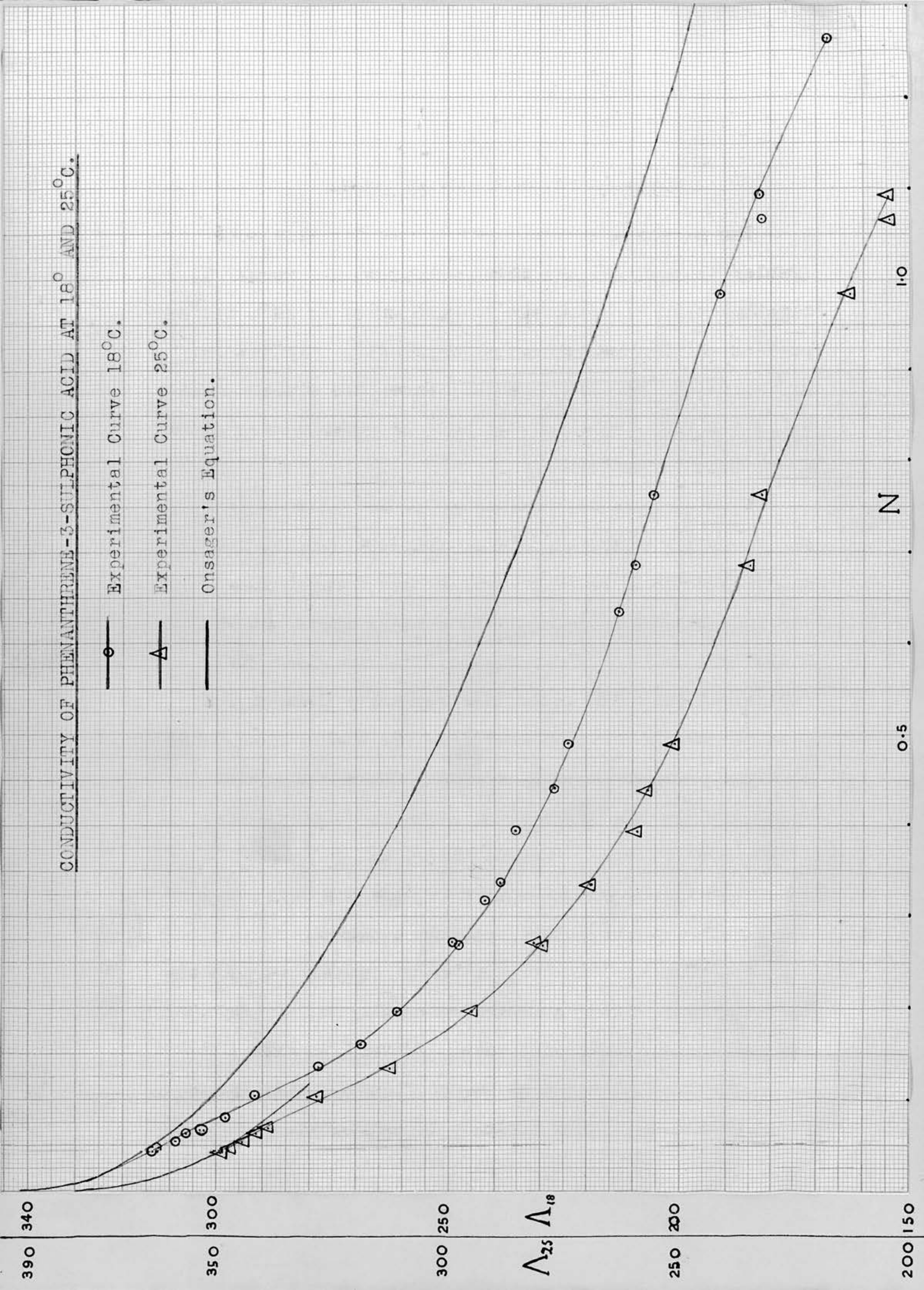
(1) Shedlovsky, J.A.C.S., 54 (1932) 1411.
(2) See MacInnes and Shedlovsky, International Crit. Tables, VI, p. 242.

between the behaviour of hydrochloric acid and that of the sulphonic acid, the conductivity of the latter being always less than would be the case of the two acids behaved in exactly the same way.

It is usual to regard hydrochloric acid as being an electrolyte of the strongest type, that is to say, one in which the dissociation is complete. From this point of view it follows that p-toluene sulphonic acid, though undoubtedly a strong acid, must be somewhat less than 100 per cent dissociated. In the absence of definite evidence to the contrary, it is reasonable to attribute the behaviour of this acid, in the main, to the formation of simple (unaggregated) ion-pairs.

FIGURE 12.



CONDUCTIVITY OF PHENANTHRENE-3-SULPHONIC ACID AT 18° AND 25°C.

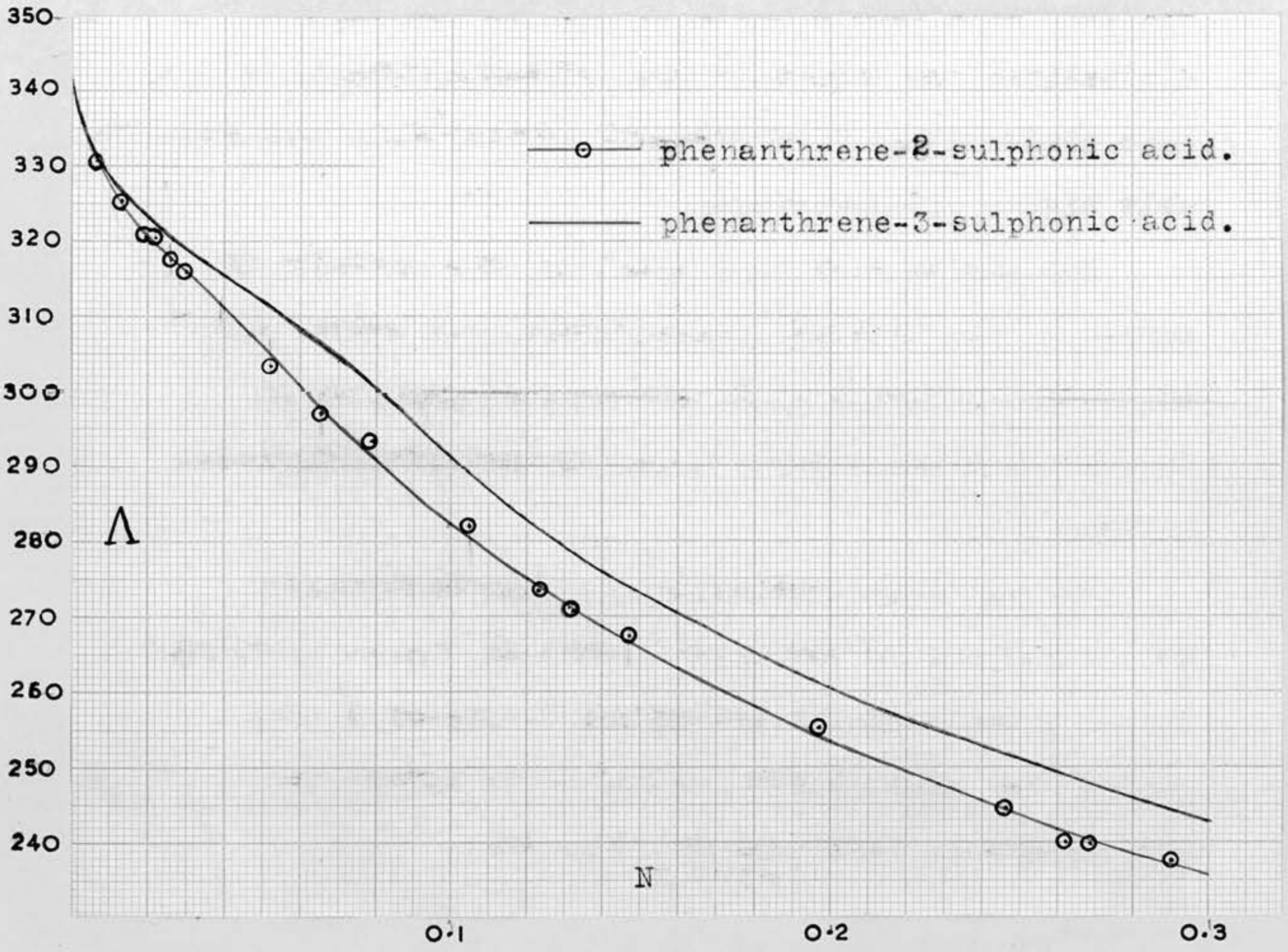
Phenanthrene-3-Sulphonic Acid.

The complete conductivity curves for this acid (Tables III and IV) are shown in Figure 12 (page105), together with the complete Onsager curve at 18°, and a portion of the theoretical curve at 25°. In the case of this acid, the experimental values lie either on or below the theoretical curve, and the experimental curve shows four inflections.

We will consider the curve for 18° in some detail. As previously remarked, the experimental points for dilute solutions at first fall on the Onsager line, but indications of negative divergence appear at about 0.04N (Figure 6). From Figure 12 it is clear that between about 0.04N and 0.125N the curve undergoes a considerable inflection away from the theoretical curve. At higher concentrations, however, the curve gradually bends towards the theoretical curve up to about 1.0N, after which it again changes direction. It will be seen that in the neighbourhood of 0.4N the experimental and Onsager values differ by about 29 mhos.

Applying the arguments already advanced to explain the behaviour of the halogenated acids, it follows that the inflection observed between 0.04N and 0.125N indicates that micelles are being formed by the unsubstituted acid also. The tendency to aggregation is,

FIGURE 13.



CONDUCTIVITY OF PHENANTHRENE-2-SULPHONIC ACID AT 18°C.

however, much less pronounced than in the halogen derivatives, as judged by the inflection, which is much more gradual, and first becomes evident at a considerably higher concentration.

For convenience in comparison, the conductivity curves of the toluene, phenanthrene, and bromo- and chloro-phenanthrene acids are plotted together in Figure 14, which clearly shows the marked differences between them.

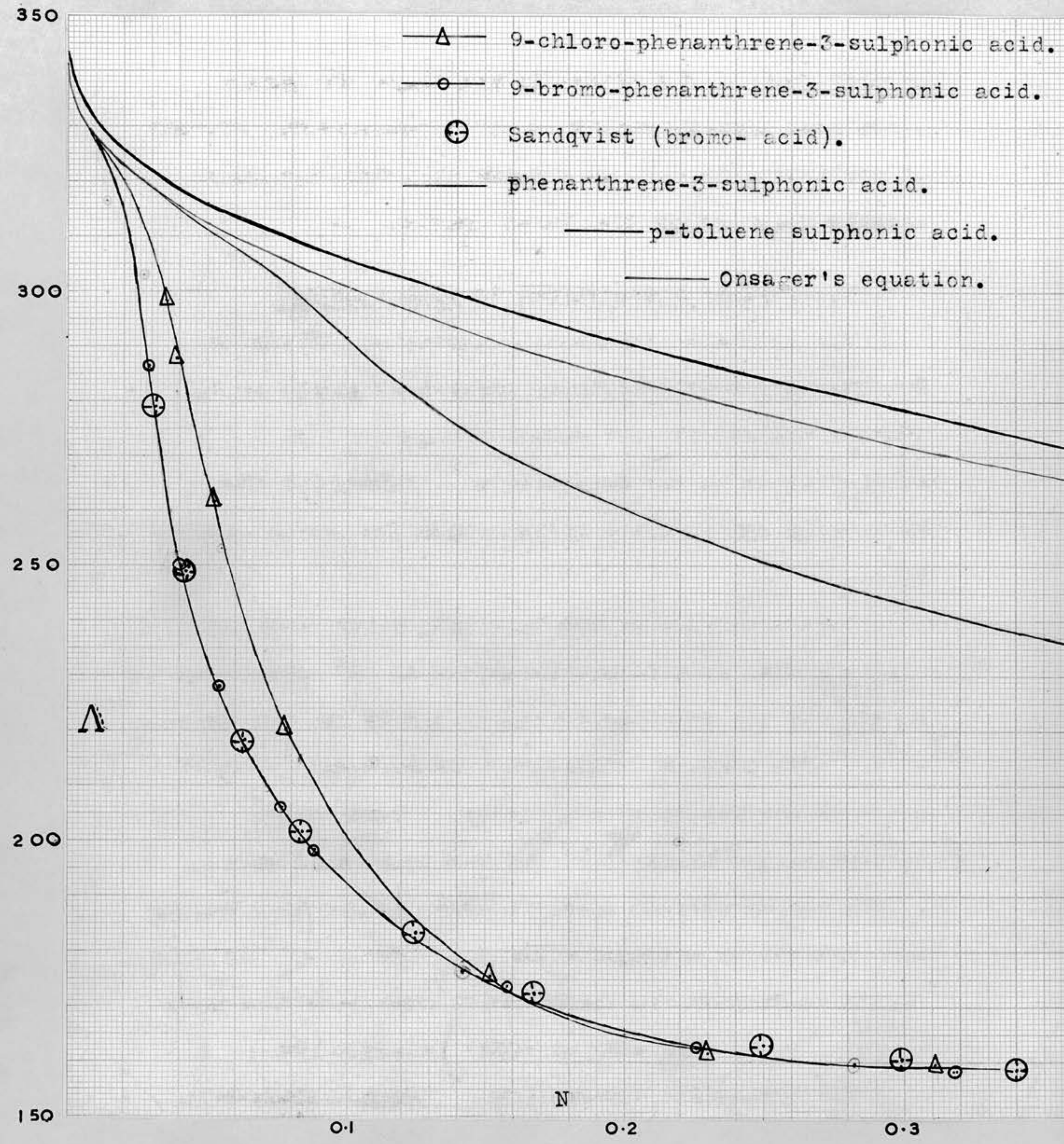
It may be pointed out that since Sandqvist's determinations of the conductivity of the unsubstituted phenanthrene acid did not extend to concentrations higher than about 0.03N, he failed to detect the characteristic behaviour of this acid.

Phenanthrene-2-Sulphonic Acid.

The complete conductivity curve at 18° for this acid (data in Table V) is plotted in Figure 13 (p.107), along with the corresponding portion of the curve for the 3-isomer. Owing to the insolubility of the 2-acid, it was not possible to extend the measurements beyond about 0.3N.

In the light of previous remarks, the natural assumption is that the 2-acid possesses a greater tendency to form micelles than does the 3-acid, since the negative divergence from the Onsager line occurs at a considerably lower concentration (compare Figures 6 and 8). It is therefore surprising that over the

FIGURE 14.



CONDUCTIVITY
of
9-BROMO- AND 9-CHLORO-PHENANTHRENE-3-SULPHONIC ACIDS AT 18°C.

greater part of the concentration range the 2-acid curve runs almost parallel to the 3-acid curve, instead of continuing to fall more rapidly. This apparent anomaly requires further investigation.

Halogenated Phenanthrene Sulphonic Acids.

The complete conductivity curves at 18° for the 9-bromo- and 9-chloro-phenanthrene-3-sulphonic acids (Tables VII and IX) are given in Figure 14 (p. 109). As the figure shows, Sandqvist's (1) values for the bromo-acid agree fairly closely with the new determinations.

Determinations of the turbidity-point (see page 51) indicate that anisotropic behaviour at 18° sets in at 0.425N for the bromo-acid, and at 0.315N for the chloro-acid. The present conductivity measurements thus stop short of the region of anisotropy. Sandqvist (2) determined the conductivity of the bromo-acid at a single concentration, namely 0.508N, within this region and obtained an average value of 181 for Λ. If this figure is correct the conductivity must pass through a minimum, since the value at 0.34N is about 159.

Many colloidal electrolytes (3) show a minimum in the conductivity curve. The rise in the conductivity of soap solutions at high concentrations was, in fact,

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(1) See footnote 1 on page 95.
(2) Sandqvist, Arkiv. etc., 6, No. 9 (1916-17) 29, 34.
(3) See references on pages 99 and 100.

one of the considerations which McBain(1) originally advanced as evidence of the formation of ionic micelles. He pointed out that if Stokes' law was applicable under the given conditions, it followed that an aggregate of similarly-charged ions should have a mobility higher than that of the constituent ions when moving separately. McBain interpreted, and still interprets,(2) the rise in conductivity in concentrated solutions as the result of the formation of these highly-conducting aggregates (ionic micelles), which are considered to appear first in significant amounts in the region of the conductivity minimum. On the other hand, Hartley,(3) in conformity with his view that there is only one type of micelle, the formation of which produces a decrease in the conductivity when the solution is dilute, has attempted to account for the rise in conductivity at high concentrations in a quite different manner from McBain. Hartley's(3) most recent suggestion is that the mobility of those ions of opposite charge which are not incorporated in the micelles increases with increase in concentration because the potential gradient in the solution becomes more uniform as the concentration increases.

It should be pointed out that Hartley agrees that aggregation tends to increase the mobility, but maintains

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(1) McBain and Salmon, J.A.C.S., 42 (1920) 450.
(2) See, for example, McBain, Dye and Johnston, J.A.C.S., 61 (1939) 3215.
(3) Hartley, Kolloid-Zeitschr., 88 (1939) 22.

that an increase in the conductivity will result only if some factor operates to effect the depressive effect of ionic interaction, or of the association of oppositely charged ions. Since the magnitude of the depressive factors decreases with dilution, it would be expected on this view that instances of increase in conductivity at very <u>low</u> concentrations could occur. Actually, Robinson and Moillet(1) have observed a maximum in the conductivity of certain colloidal dyes at high dilutions, which they ascribe to the formation of micelles. Apparently, in the case of the halogenated phenanthrene sulphonic acids, the tendency to ion-pair formation is great enough in dilute solution to offset any enhancement of the mobility due to aggregation of the organic ions. The behaviour of p-toluene sulphonic acid (see page104) indicates that ion-pair formation must occur.

It is evident that in a general way the conductivity curves of the halogenated phenanthrene sulphonic acids resemble those of the paraffin-chain colloidal electrolytes. There is, however, at least a certain amount of difference in that, as already mentioned, the rise in conductivity of the bromo-acid was reported by Sandqvist to occur in the anisotropic region, and the present data also indicate that if an increase does take

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(1) Robinson and Moillet, Proc. Roy. Soc., A143 (1934) 630.

place, it will be in this region. Thus the curve at 18° for the chloro-acid is still falling slightly at 0.3115N, which is very close to the turbidity point (= 0.315N), and first separates into two layers (see page 52). Sandqvist also records that the conductivity (as well as the viscosity) of the anisotropic solution of the bromo-acid could be varied by mechanical means. He states(1) "Wurde die Lösung zwischen den Messungen durchgemischt, bekam man bald höhere, bald niedrigere Werte, die sich bis 5 Prozent unterscheiden konnten und sich zudem anfangs mit der Zeit anderten", and values of the specific conductivity of 0.508N at 18° are given which vary between 0.0910 and 0.0960 mho.(2) In contrast with the foregoing, in the case of paraffin-chain electrolytes, the rise in conductivity occurs in solutions which, although concentrated, are stated to be homogeneous, clear and isotropic,(3) and the value of the conductivity depends upon the temperature and concentration alone. Thus it would appear that further investigation of the conductivity of the halogenated phenanthrene sulphonic acids in the anisotropic region might yield some interesting information.

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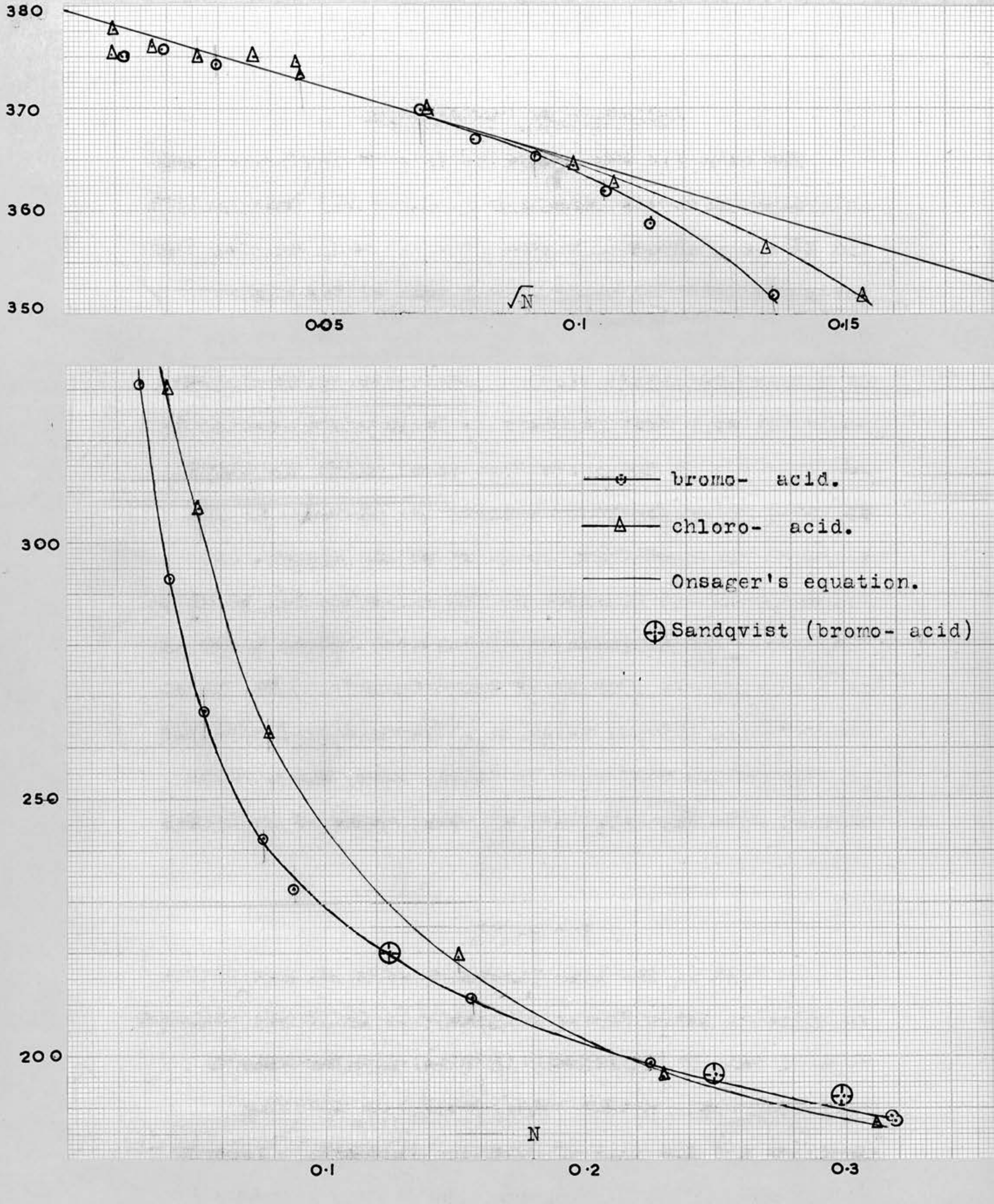
(1) Sandqvist, Arkiv. etc., 6 (1916-17) No. 9, pp. 33, 34.

(2) Sandqvist, ibid., p. 29.

(3) See, for example, Hartley, Kolloid-Zeitschr., 88 (1939) 22.

FIGURE 15.



CONDUCTIVITY
of
9-BROMO- AND 9-CHLORO-PHENANTHRENE-3-SULPHONIC ACIDS AT 25°C.

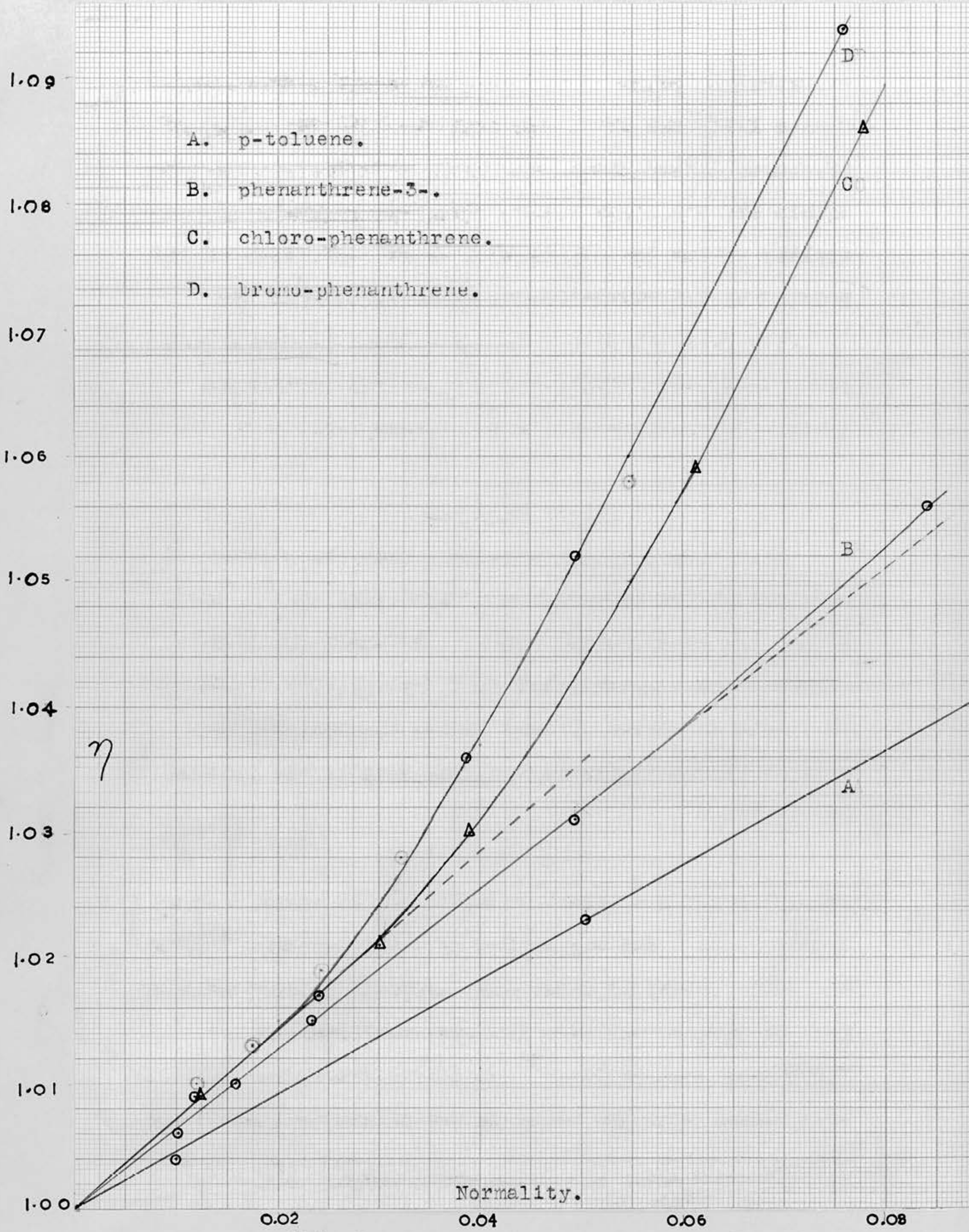
Influence of Temperature.

The data for the conductivities of the bromo- and chloro-phenanthrene sulphonic acids at 25° (Tables VIII and X) are plotted in Figure 15. It will be seen that Onsager's equation holds fairly well at the highest dilutions, taking $\Lambda_0 = 379.5$ (cf. $\Lambda_0 = 380.0$ in the case of the unsubstituted acid). Comparison with the data at 18° reveals that increase in temperature results in (a) increase in the concentration at which the rapid decrease in conductivity occurs, (b) increase in the slope of the conductivity curves at the highest concentrations, (c) increase in the concentration at which the bromo- and chloro-acid curves meet (about 0.22N at 25°, as compared with about 0.16N at 18°). The first two of these effects point to a decrease in the degree of aggregation with rise in temperature, which is in harmony with the behaviour of other types of colloidal electrolytes.

VISCOSITY.

In view of the high viscosity of solutions of the halogenated phenanthrene sulphonic acids it was necessary to ascertain by experiment if these systems behaved normally, i.e., whether the product of the total pressure and the time of flow was constant. Accordingly determinations of h, the mean hydrostatic pressure of the liquid in the viscometer, were carried out as

FIGURE 16.



VISCOSITY OF SULPHONIC ACIDS AT 18°C.

described on pages 46, 47 . The data are given in Tables XXIII and XXIV, and show that for the range of pressures investigated, the value of h was constant to within about 0.1 per cent. Thus Poisseulle's law applies to the two halogenated acids, and hence to the p-toluene, and unsubstituted phenanthrene-3-acids.

The final viscosity data are given in Tables XXV, XXVI, XXVII and XXVIII, and are plotted in Figures 16 (page 116), 17 (page 122), and 18 (page 124).

Dilute Solutions.

From Figure 16 it is evident that the initial portions of the curves of all four acids are linear within the experimental error. Grinnell Jones and others (1) have established that the relative viscosity of dilute solutions of many strong electrolytes are is related to the concentration according to the general expression:-

$$\eta = 1 + A\sqrt{c} \pm Bc ,$$

where A and B are constants and c is the concentration (normality). The suggestion of Jones and Dole (2) that the Debye theory of interionic attraction could account for the square-root term has been confirmed by Falkenhagen and others, (3) who have obtained by calculation values of A (in terms of the valency and mobility

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(1) For references see Jones and Stauffer, J.A.C.S., 62 (1940) 335.

(2) Jones and Dole, J.A.C.S., 51 (1929) 2950.

(3) For references see Dole "Electrochemistry", (1935) p. 100.

of the ions) which often agree closely with those found by experiment.

The theoretical value of A for hydrochloric and nitric acids at 18° is about 0.002,(1) and Joy and Wolfenden(2) have obtained 0.0023 for nitric acid by experiment. Hence it is highly probable that A will be of this order in the case of the sulphonic acids, whereas B (positive) is of the order 0.4 (see curve for p-toluene acid) or more. It follows that under the given conditions the square root term is comparable with the experimental error, so that the initial parts of the curves would appear as straight lines, if the acids were behaving as simple strong electrolytes, which is actually the case.

The values of B follow the sequence p-toluene $<$ unsubstituted phenanthrene $<$ chloro- or bromo-phenanthrene acid. At present it does not appear possible to offer any satisfactory interpretation of the variation of B with chemical constitution.

In the case of the p-toluene acid, the linear relation persists up to at least 0.1N, after which a slight tendency for the viscosity to increase more rapidly than the concentration can be detected. The unsubstituted phenanthrene acid, however, shows a more definite positive divergence at lower concentrations, viz., between 0.05N and 0.08N, while the halogenated

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(1) Falkenhagen, "Electrolytes", (1934) p. 248.
(2) Joy and Wolfenden, Proc. Royal Soc., 13A (1931)413.

acids give marked inflections in still more dilute solutions.

In the case of the bromine derivative the inflection becomes apparent at about 0.025N, and in that of the chlorine compound at about 0.03N. Reference to Figure 9 shows that these concentrations are in the neighbourhood of those at which the respective conductivity curves commence to fall rapidly. The abnormal fall in conductivity and rise in viscosity therefore appear to be due to the same change in the condition of the dissolved acid, that is to say to the formation of micelles. Similarly, as Figure 12 shows, the abnormal fall in conductivity of the unsubstituted acid begins at approximately 0.07N, which lies within the range of concentration (see above) where divergence of η from the linear relation first appears.

Tartar and Wright,(1) and Hess, Philippoff and Kiessig(2) have observed a marked inflection, similar to that found with the halogenated phenanthrene sulphonic acids, in the viscosity curve of sodium dodecyl sulphate in the neighbourhood of the concentration where aggregation commences. Hess and co-workers also report the existence of an inflection in the case of sodium laurate. None of these workers have attempted to account for an increase in viscosity as the result

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(1) Tartar and Wright, J.A.C.S., 61 (1939) 544.
(2) Hess, Philippoff and Kiessig, Kolloid-Zeitschr., 88 (1939) 40.

of the formation of micelles in dilute solutions of long paraffin-chain compounds.

Robinson and Morrell(1) found that the viscosity, measured at 25°, of a freshly boiled 0.5 per cent. solution of arsphenamine dihydrochloride was 1.012. After keeping the solution for a prolonged period at 15° the viscosity, again measured at 25°, increased to 1.087. It was further observed that under the same conditions the specific conductivity increased from 2845 to 2947×10^{-6}.

Robinson and Morrell consider that the increase in viscosity cannot be due to increase in hydration, as this would decrease the mobility of the ions, and, therefore, the conductivity. Further, structural viscosity, in the sense of a tendency to build up a network through the solution, cannot account for the increase in conductivity. On the other hand, following Staudinger,(2) if aggregation of the arsphenamine occurs and is accompanied by an increase in asymmetry of the solution units, the effective size of these will be greater than if they were symmetrical. Hence, according to Einstein's well-known equation, the viscosity should be enhanced by such aggregation. Since it is known that arsphenamine tends to form long-shaped particles under certain conditions,(3) Robinson and

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(1) Robinson and Morrell, Trans. Faraday Soc., <u>30</u>(1934) 339.
(2) Staudinger, Ber. 65B (1932) 267.
(3) Freundlich, Stern and Zocher, Biochem. Zeitschr., <u>138</u> (1923) 207.

Morrell suggest that the increase in viscosity may be due in part to an increase in asymmetry.

The most interesting suggestion put forward by Robinson and Morrell is, however, that the increase in viscosity may be connected with an increassin ionic interaction due to the formation of ionic micelles. They point out that the value of A in the equation of Jones, Dole and Falkenhagen increases rapidly with increasing valency of the ions, so that while the formula for A would presumably need modification in the case of a colloidal electrolyte, it is reasonable to postulate 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". This view would be in harmony with the increase in conductivity of the arsphenamine solution in so far that it is difficult to account for such an increase in any way other than as due to the formation of highly mobile polyvalent micelles by the aggregation of simple ions (see pages 111 and 112.

As previously stated (page 100), however, opinion differs with regard to the degree of importance to be assigned to the Debye-Hückel ionic interaction in the case of micelles. The chief experimental evidence of the view that such interaction is of considerable importance is provided by the work of Schmid and Larsen (1)

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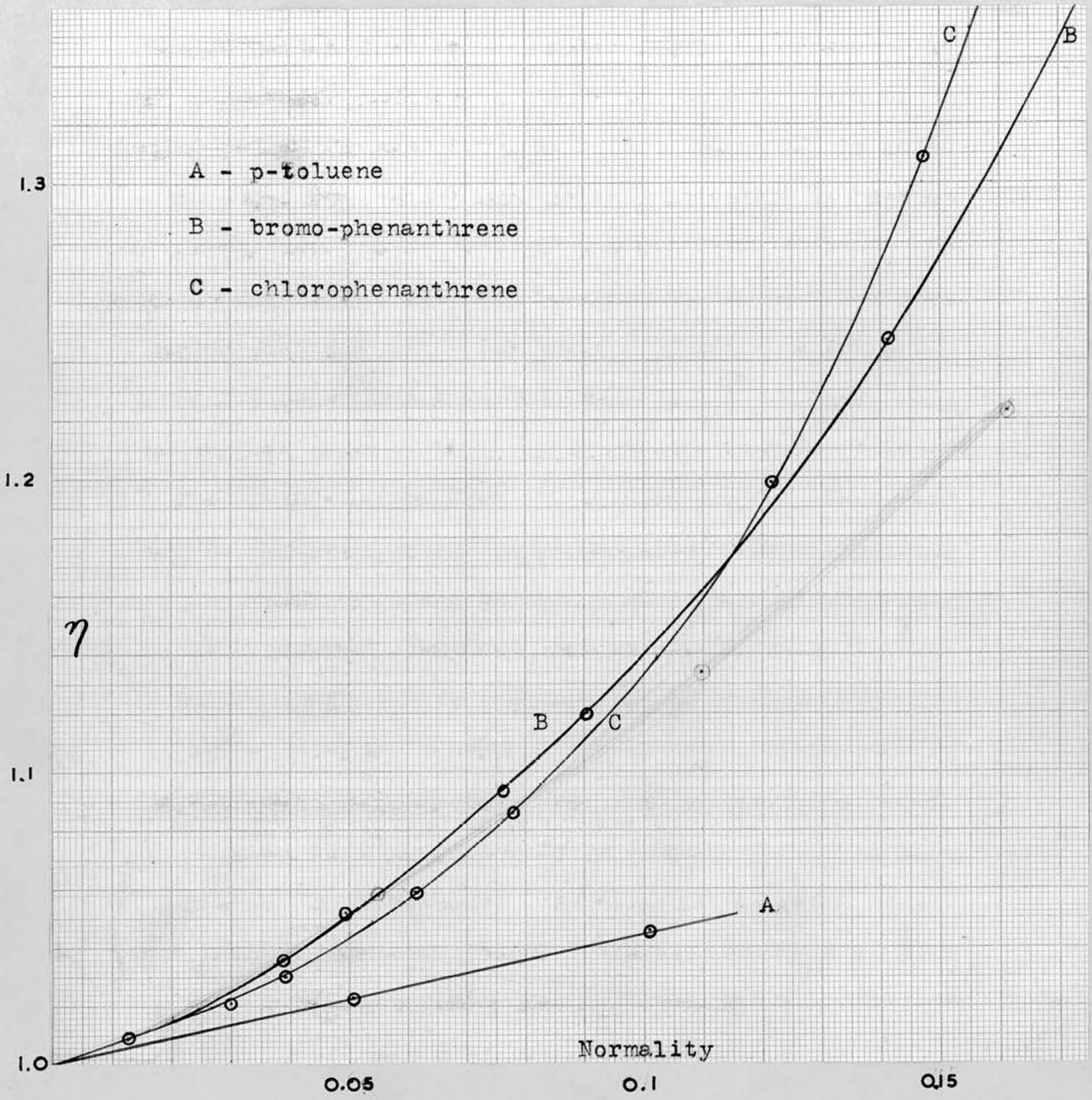
(1) Schmid and Larsen, Zeitschr. Elektrochem., <u>44</u> (1938) 651.

FIGURE 17.



VISCOSITY OF SULPHONIC ACIDS AT 18°C.

on the high-frequency conductivity of colloidal electrolytes. These workers found that in the region of concentration where micelle formation commences, the value of the conductivity obtained with a high-frequency current is abnormally higher than that obtained with the ordinary low-frequency current, i.e., the effect is abnormally great as compared with that shown by a simple, unaggregated, strong electrolyte. On the theoretical side, Hartley(1) has advanced arguments to show that if the Debye-Huckel theory is modified to take account of the radius of the micelle, it follows that the ionic interaction will be enhanced by the aggregation of the constituent ions. Up to the present, Hartley's theoretical conclusions have not been controverted.

With regard to the results for the viscosity of dilute solutions of the phenanthrene sulphonicacids, it can at least be said that they are not inconsistent with an interpretation on the lines of the theory of Jones, Dole and Falkenhagen. The question, however, will be further considered below in connection with the viscosity of the more concentrated solutions.

The Complete Viscosity Curve.

Figures 17 and 18, taken together, show the complete curves for the acids under consideration, as far as they have been examined. The curves are plotted from the data in Tables XXV to XXVIII.

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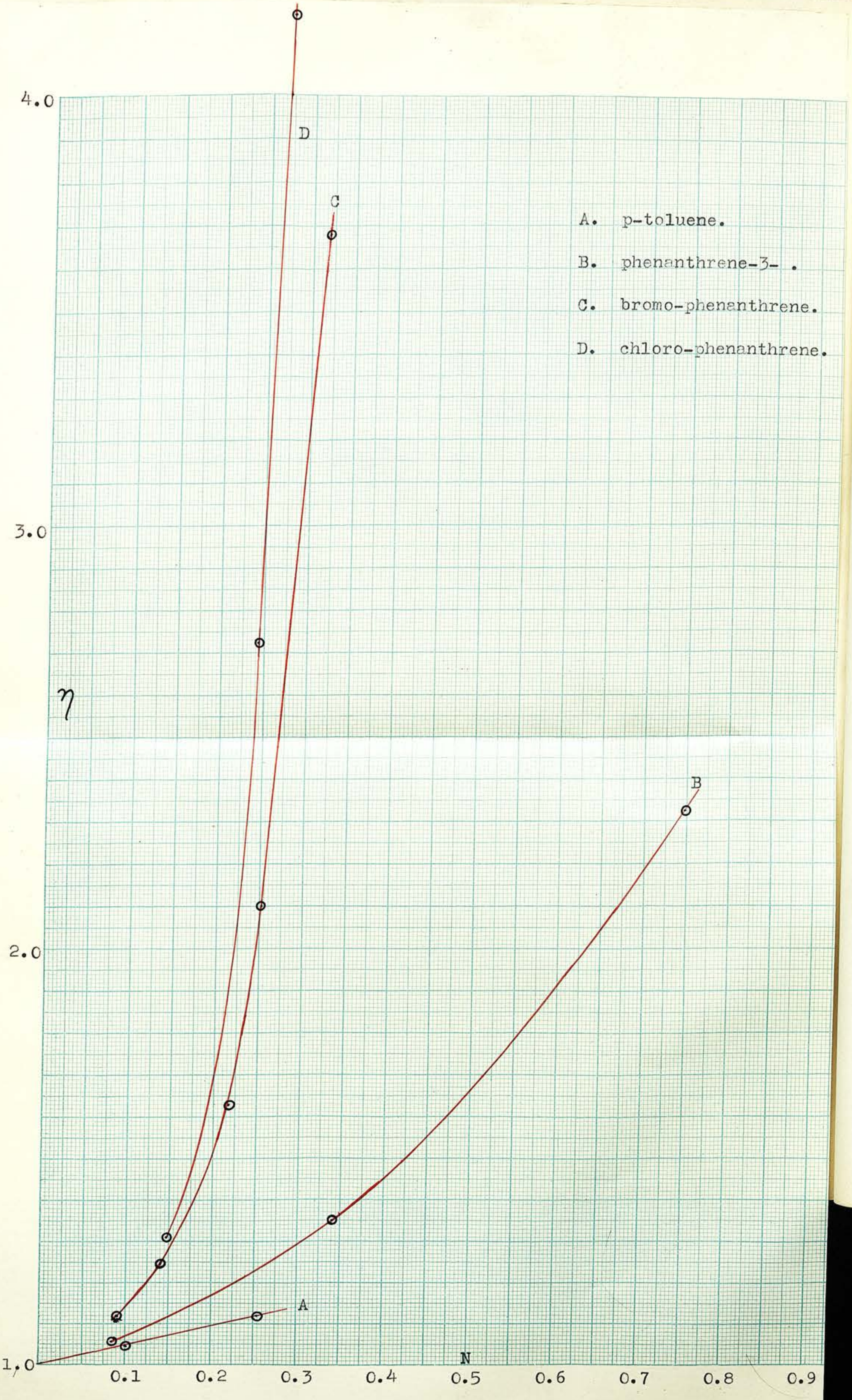
(1) Hartley, Kolloid Zeitschr., 88 (1939) 29.

FIGURE 18.



VISCOSITY OF SULPHONIC ACIDS AT 18°C.

The viscosity curves show several interesting features. It will be seen that there is an enormous increase in the viscosity of solutions of the halogenated phenanthrene sulphonic acids at relatively high concentrations (Figure 18). Moreover, the concentrated solutions of the chloro-acid are much more viscous than corresponding solutions of the bromo-acid. Since this is the reverse of the state of affairs at low concentrations, the curves for the two acids intersect at a concentration of about 0.15N (Figure 17).

In spite of their high viscosity, concentrated solutions of the halogenated acids were found to conform to Poiseuille's law, that is to say, the time of flow was always inversely proportional to the pressure upon the liquid, as is shown by the constancy of the values of h in Tables XXIII and XXIV. Thus the present experiments give no evidence of the existence of so-called "structural viscosity" in these solutionx, in the sense that the micelles are linked together to form a network which resists rupture and hence gives rise to an apparent decrease in viscosity as the pressure is increased.

The reversal in viscous behaviour which occurs on passing from dilute to concentrated solutions is unusual and difficult to interpret. It seems probable that the phenomenon is connected with the fact that the concentration at which anisotropic behaviour commences is lower in the case of the chloro-acid than in that of the bromo-acid, as observed by Sandqvist and confirmed by the author (see page 52). The anisotropy is undoubtedly due to the formation of liquid crystals, and since these are also obtained, as Rinne(1) has shown, by bringing the solid acid in contact with water, it would appear that they contain water molecules as well as molecules of the acid. It may therefore be possible to account for the behaviour of the isotropic solutions by postulating the existence of two types of aggregate as follows. At low concentrations the aggregates, in the main, are composed of sulphonic ions only, and the abnormal increase in viscosity is largely due to Coulomb forces, as already discussed. At high concentrations, however, ultramicroscopic liquid crystals are formed, consisting of alternating layers of water molecules and organic ions or molecules. The inclusion of water in the aggregates increases the volume of the disperse phase, and hence, assuming Einstein's theory of the viscosity of colloidal systems, produces an increase in the viscosity. The first type of aggregate is formed more readily by the bromo-acid, and the second more readily by the chloro-acid, in harmony with its stronger tendency to give anisotropic systems.

It may be of significance in this connection that evidence is accumulating to show that two types of micelle exist in the case of paraffin-chain electrolytes.

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(1) Rinne, Zeitschr. Krystallogr. etc., 82 (1932) 379; Trans. Faraday Soc., 29 (1933) 1016.

The X-ray investigations of Stauff(1) and of Hess, Philippoff and Kiessig(2) have established the presence of units with crystalline structure in isotropic solutions of sodium soaps and alkyl sulphates. Moreover, Stauff's results indicate that on dilution the crystalline structure disappears at a concentration greater than that at which micelles first appear in the solution as shown by the sudden decrease in the conductivity and osmotic activity. There thus appear to be two types of micelle.

The Influence of Hydrochloric Acid.

Comparison of the data in Tables XXIX and XX with those in Tables XXVII and XXVIII shows that the addition of hydrochloric acid to solutions of the halogenated phenanthrene sulphonic acids produces a very striking increase in the apparent viscosity, even at quite low concentrations of the sulphonic acids. This phenomenon, as stated in the Introduction, was first observed by Sandqvist,(3) but the present data reveal the additional fact that the mixed solutions do not conform to Poiseuille's law. As will be seen, the value of $(h + p)t/h_0t_0$ is not constant, but decreases with increase in the rate of flow, i.e., the rate of shear. Thus the mixed solutions possess so-called "structural viscosity".

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(1) Stauff, Kolloid Zeitschr., 89 (1939) 224.
(2) Hess, Philippoff and Kiessig, Kolloid Zeitschr., 88 (1938) 40.
(3) Sandqvist, Kolloid Zeitschr., 19 (1916) 113; Arkiv. etc., 5 (1913-15) No. 17: Lieb. Ann.. 417 (1918) 17.

In agreement with Sandqvist it was found that the effect was much more pronounced in the case of the chloro-acid than in that of the bromo-acid. Thus an approximately 0.02N solution of the former acid was as effective as an approximately 0.05N solution of the latter, 0.41N hydrochloric acid being present in both cases. Quantitatively, however, the difference was less than that recorded by Sandqvist.

The mixed solutions were quite clear and examination of a thick layer in the polarising microscope provided no evidence of anisotropy.

DENSITY.

The densities of solutions of the p-toluene and phenanthrene-2- and -3-sulphonic acids are given in Tables XI to XVI. By trial and error it was found that over a considerable part of the concentration range, the data were best represented by linear expressions, as follows.

Toluene sulphonic acid, up to about 0.6N :-

$$d_4^{18} = 0.99863 + 0.052756N.$$

$$d_4^{25} = 0.99707 + 0.052248N.$$

Phenanthrene sulphonic acids, up to about 0.4N :-

$$d_4^{18} = 0.99863 + 0.082048N.$$

$$d_4^{25} = 0.99707 + 0.081154N.$$

($0.99863 = d_4^{18}$, and $0.99707 = d_4^{25}$ for water (1)).

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(1) Findlay, "Practical Physical Chemistry", (1935) 64.

FIGURE 19.

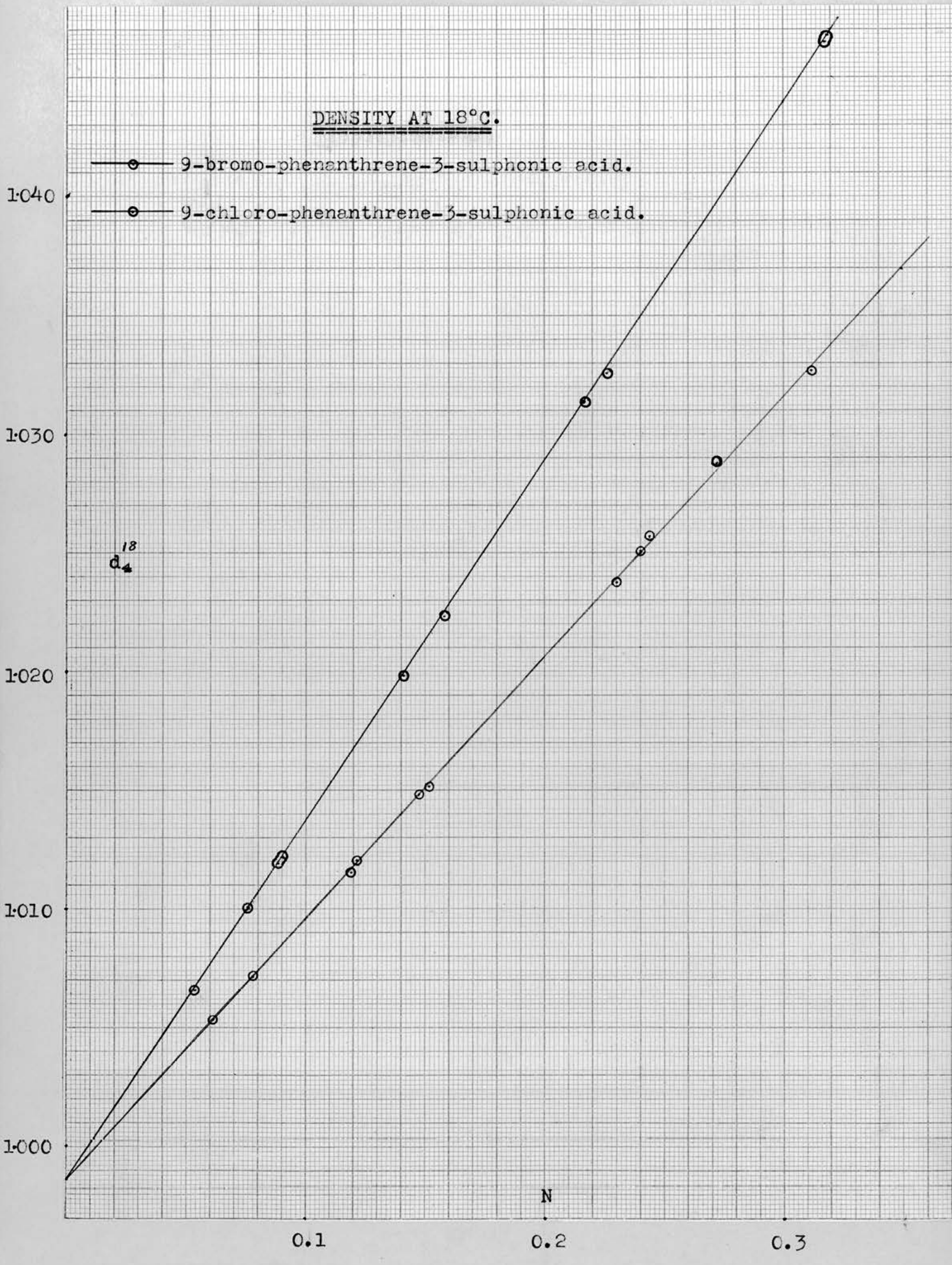
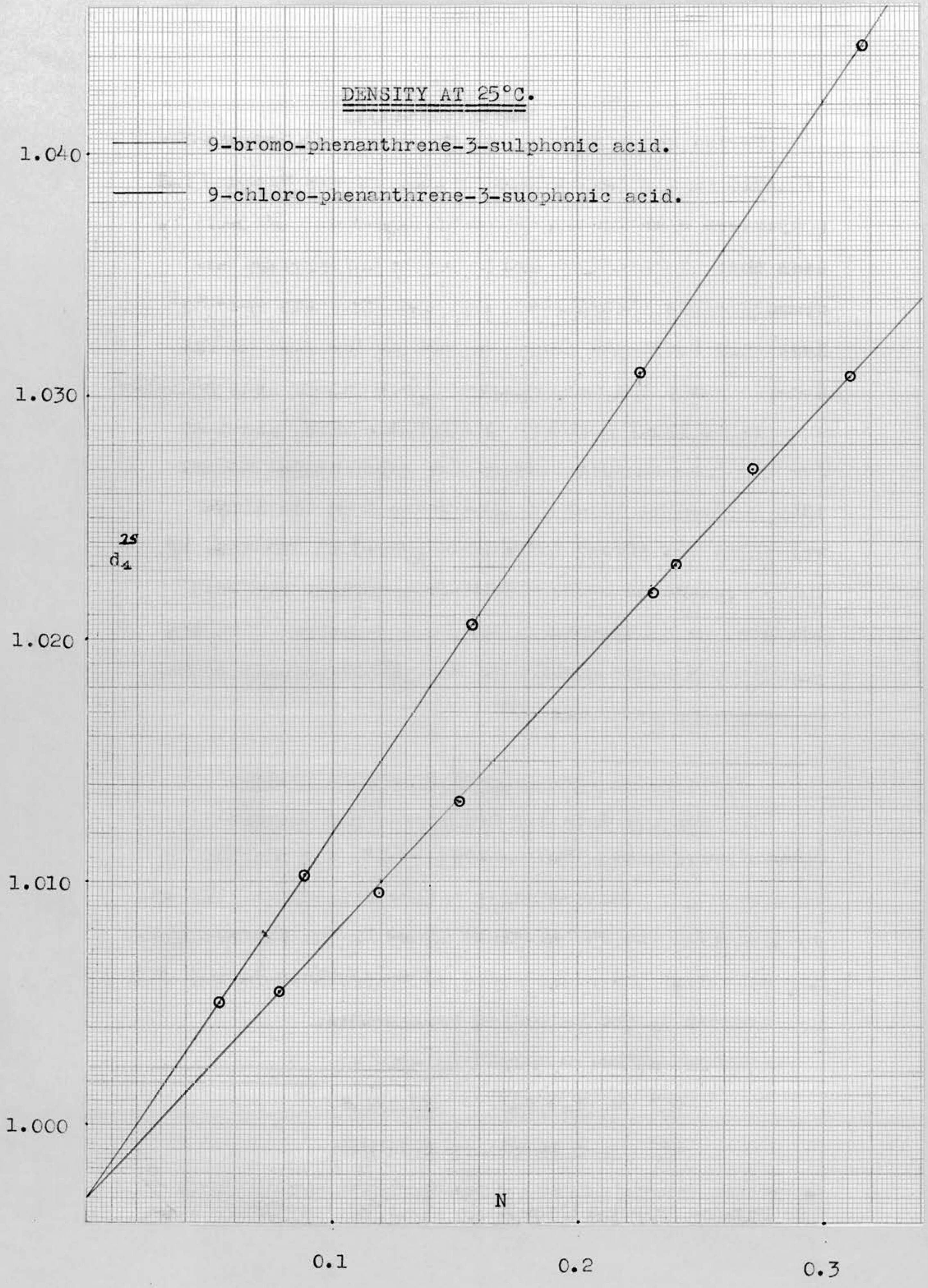

DENSITY AT 18°C.
9-bromo-phenanthrene-3-sulphonic acid.
9-chloro-phenanthrene-3-sulphonic acid.
1·040
1·030
1·020
1·010
1·000
d_4^{18}
N
0.1
0.2
0.3

FIGURE 20.


DENSITY AT 25°C.
9-bromo-phenanthrene-3-sulphonic acid.
9-chloro-phenanthrene-3-suophonic acid.
d_4^{25}
1.040
1.030
1.020
1.010
1.000
N
0.1
0.2
0.3

Values calculated by means of these formulae are recorded in the last column of each of the Tables, for comparison with the experimental figures. It will be seen that the positive and negative differences are symmetrically distributed, and that they are usually less than 0.005 per cent., except in the case of the 2-acid, where the measurements appear to be less reliable.

Above about 0.6N for the toluene acid, and 0.4N for the phenanthrene-3-acid, the experimental values show increasing negative divergence from the linear relation, the effect being more marked in the case of the phenanthrene acid. Similar behaviour has been observed by Laing-McBain, Dye, and Johnston (1) in the case of the lower members of the paraffin-chain series of sulphonic compounds.

Halogenated Phenanthrene Sulphonic Acids.

The density data for the bromo- and chloro-phenanthrene acids (Tables XVII to XX) are plotted in Figures 19, 20 (concentrated solutions), and 21 (dilute solutions). As the straight lines in the Figures show, the data over the whole range of concentrations are well represented by the following expressions.

Bromo-phenanthrene sulphonic acid :-

$$d_4^{18} = 0.99863 + 0.15110N.$$

$$d_4^{25} = 0.99707 + 0.14993N.$$

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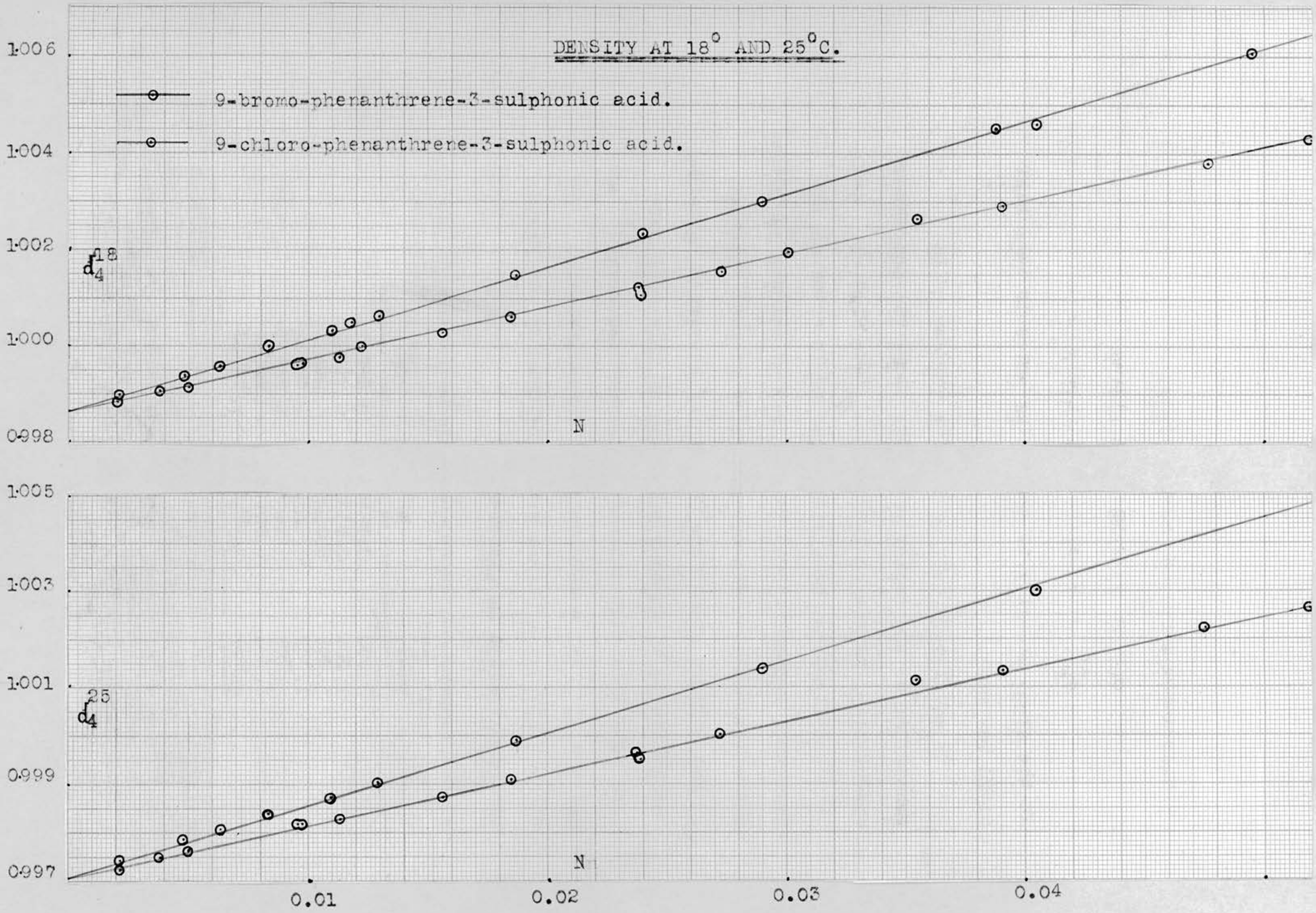
(1) McBain, Dye and Johnston, J.A.C.S., 61 (1939) 3210.

FIGURE 21.


DENSITY AT 18° AND 25°C.

Chloro-phenanthrene sulphonic acid :-

$$d_4^{18} = 0.99863 + 0.11013N.$$

$$d_4^{25} = 0.99707 + 0.10837N.$$

In the great majority of cases, the error is less than 0.005 per cent.

Of particular interest is the absence of an inflection in the region of 0.03N, where the equivalent conductivity begins to fall rapidly (see Figures 9 and 15 . Inflections have been reported to occur at the "critical concentration" in the case of certain paraffin-chain compounds. The example which is most relevant in the present connection is that of potassium laurate. The densities of aqueous solutions of this salt have been very carefully determined by Bury and Parry(1) at 25° and 35° over a wide range of concentrations. At 25° the following values were obtained for the region of concentration in question.(2)

Wt. per cent.	N	d_4^{25}
2.000	0.08385	0.99927
1.505	0.06306	0.99883
1.501	0.06291	0.99881
1.000	0.04190	0.99835
0.797	0.03338	0.99813
0.595	0.02492	0.99789
0.300	0.01256	0.99749

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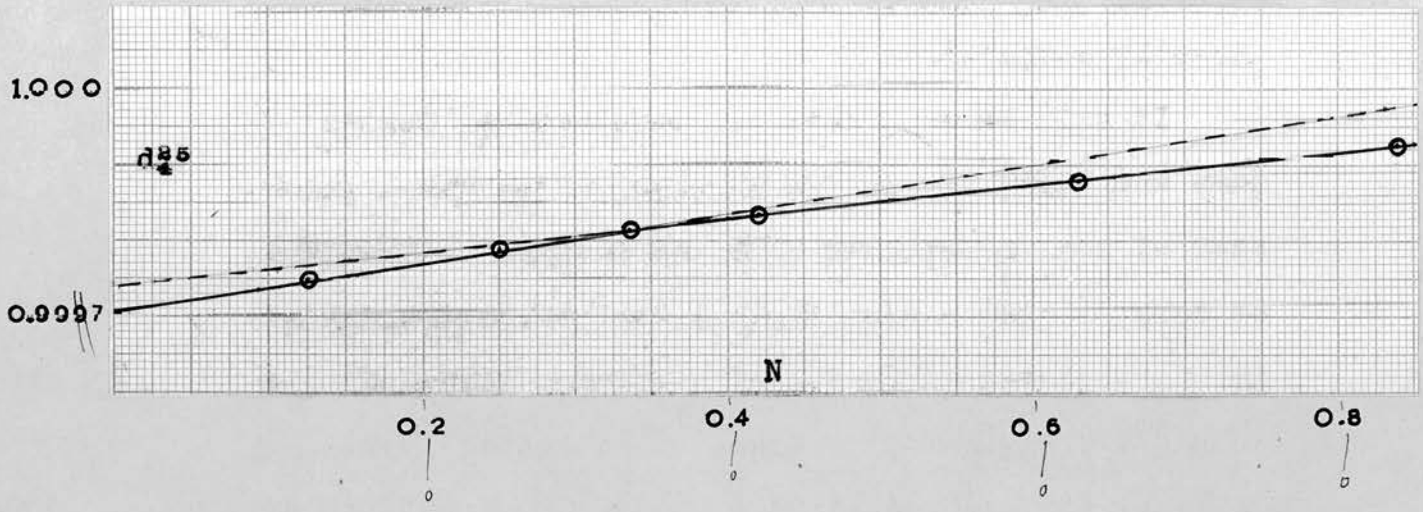
(1) Bury and Parry, J.C.S., <u>1935</u>, 626.

(2) Bury and Parry expressed concentrations in terms of weight percentage (grms. salt per 100 grms. solution), and their figures have been converted to volume normalities.

FIGURE 22.



DENSITY OF POTASSIUM LAURATE AT 25°C.

The data are plotted in Figure 22, on the same scale as that used in Figure 21, so that the two are directly comparable.

It will be seen that the experimental values of Bury and Parry lie on two straight lines which intersect at a point between 0.03 and 0.035N. According to Bury,(1) the conductivity at 25° of potassium laurate in the presence of excess of potassium hydroxide (to suppress hydrolysis) undergoes a relatively sudden decrease in this region of concentration, indicating the onset of micelle-formation. The break in the density curve would thus appear to be due to the aggregation of the paraffin-chain ions. It will be seen that no such break occurs in the density curves for the halogenated phenanthrene sulphonic acids, although the conductivity data indicate that micelle-formation first becomes prominent at about the same concentration as in the case of potassium laurate.

Breaks in the density curves of solutions of potassium n - octoate and sodium dodecyl sulphonate have also been reported,(2)(3) so that the phenomenon appears to be characteristic of long paraffin-chain electrolytes. Hartley(4) has suggested that the paraffin chains are not regularly arranged in the interior of the micelles,

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(1) Bury, General Discussion on "Aggregation of Ions in Paraffin-chain Salt Solutions", Chemistry and Industry, 57 (1938) 1167.
(2) Davies and Bury, J.C.S., 1930, 2263.
(3) Wright and Tartar, J.A.C.S., 61 (1939) 544.
(4) Hartley, Kolloid Zeitschr., 88 (1939) 25.

but approximate to the condition of a liquid hydrocarbon, which occupies a larger volume than the crystalline material. Thus the formation of the micelles produces an increase in the partial volume of the paraffin-chain electrolyte. This might also account for the different behaviour as compared with the phenanthrene compounds.

FORMATION OF MICELLES.

It appears reasonable to ascribe the formation of micelles in solutions of the unsubstituted phenanthrene sulphonic acids at least partly to the squeezing out from solution, as it were, of the organic ions by the mutual attraction of the water molecules, to which attention was called in the Introduction. On this view it would be expected that the larger the aromatic nucleus, the greater will be the tendency to aggregation, since a greater number of water-water links must be broken to bring a single separate organic ion into solution. In keeping with this, p-toluene sulphonic acid shows little, if any, tendency to form micelles. Norris(1) also concludes from her osmotic data that solutions of sodium anthraquinone-sulphonate are more colloidal than those of sodium naphthalene sulphonate.

It is obvious, however, that the water-water attraction is only one of a number of factors to be taken into consideration, and that the chemical

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(1) Norris, J.C.S., 121 (1922) 2161.

constitution of the organic ion may assume a predominant role. Thus the present work shows that (a) phenanthrene sulphonate ions possess much less tendency to aggregate than similar paraffin-chain ions with the same number of carbon atoms, (b) the tendency of phenanthrene sulphonate ions to form micelles is influenced by even small differences in the position of the sulphonic group (similarly Norris (loc. cit.) reports that β-sodium naphthalene sulphonate is more colloidal than the α-isomer), (c) substitution in the phenanthrene nucleus can markedly influence the degree of aggregation, (d) closely related substituents can influence the degree of aggregation to different extents.

SUMMARY.

1. The conductivities, densities and viscosities at at 18°C. and 25°C. of aqueous solutions of the following acids have been determined over a wide range of concentration:- p-toluene sulphonic acid, phenanthrene-2- and -3-sulphonic acids, 9-chloro- and 9-bromo-phenanthrene-3-sulphonic acids.

2. The conductivity data indicate that:
   (a) In sufficiently dilute solutions all the acids are present mainly as simple ions, with a small proportion of ion-pairs of the Bjerrum type.
   (b) The mobility of the phenanthrene sulphonate ion is considerably greater than that of a paraffin-chain sulphonate ion containing the same number of atoms.
   (c) p-toluene sulphonic acid behaves throughout the given concentration range as a simple strong electrolyte whose ions associate to some extent to form ion-pairs.
   (d) The phenanthrene sulphonic acids under consideration are colloidal electrolytes, their anions aggregating to form micelles to an extent dependent upon the concentration, the temperature, and the chemical constitution of the acid.

(e) The tendency to form micelles in dilute solution increases in the order:-
unsubstituted 3-acid < unsubstituted 2-acid ≪ chloro-acid < bromo-acid.

(f) Phenanthrene sulphonate ions show less tendency to form micelles than similar paraffin-chain ions with the same number of carbon atoms.

(g) No minimum occurs in the conductivity curve for clear (isotropic) solutions of the halogenated phenanthrene sulphonic acids.

3. The viscosity curves for dilute solutions of the phenanthrene sulphonic acids undergo inflection at concentrations in the neighbourhood of those at which micelle-formation becomes prominent, as indicated by the conductivity data. It is suggested that the observed enhancement of viscosity is due to an increase in the Coulomb attractive forces resulting from the ion-aggregation.

4. The viscosity data show that:-

(a) Concentrated isotropic solutions of the halogenated phenanthrene sulphonic acids are very much more viscous than corresponding solutions of the unsubstituted 3-acid.

(b) Despite their high viscosity, there is no evidence of "structural viscosity" in concentrated isotropic solutions of the halogenated phenanthrene sulphonic acids.

(c) Concentrated isotropic solutions of the chloro-phenanthrene sulphonic acid are more viscous than corresponding solutions of the bromo-acid.

5. The observation of Sandqvist that the region of anisotropic behaviour commences at a lower concentration in the case of the chloro-phenanthrene sulphonic acid than in that of the bromine derivative has been confirmed.

6. It is suggested that the high viscosity of concentrated isotropic solutions of the halogenated phenanthrene sulphonic acids is due to the presence of aggregates which take the form of ultramicroscopic liquid crystals. These differ from the micelles in dilute solutions in that they include water molecules.

7. Sandqvist's observation that the addition of hydrochloric acid to solutions of the halogenated phenanthrene sulphonic acids produces a remarkable increase in viscosity has been confirmed, the effect being greater for the chloro-acid. It is found that the mixed solutions possess "structural viscosity".

8. The density curves for solutions of the phenanthrene sulphonic acids show no breaks such as observed with paraffin-chain colloidal electrolytes, and which therefore appear to be characteristic of these compounds.

In conclusion I wish to express my appreciation of the unfailing help and guidance given by Dr. T. R. Bolam throughout the course of the work. My thanks are due also to the Moray Fund for a grant for the purchase of the silica conductivity cell.