Properties of Sulphuric Acid Solutions. Part I. Transport-number Measurements in Sulphuric Acid and Oleum Solutions.

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[Reprint Order No. 5314.]

The transport numbers of certain ionic species in 100% sulphuric acid and in approx. 35% oleum have been determined. The probable ionisations involved are discussed, ammonium sulphate being taken as a typical solute.

The purpose of this work is to extend the study of electrical conductivity in absolute sulphuric acid and in oleum solutions (Gillespie and Wasif, *J.*, 1953, 204, 209, 215, 221, 964). The transport numbers of some new ions, chiefly ammonium sulphate, acetic acid, and benzoic acid, have been measured in absolute sulphuric acid. Another series of transport-number measurements of these solutes and of alkali and alkaline-earth cations was carried out in oleum solutions (~35% SO_3).

Experimental

All the measurements were carried out by Hittorf's method at 25°, solutions of known concentrations of the different solutes being prepared and analysed before electrolysis.

Ammonium sulphate was determined by adding excess of ~30% sodium hydroxide solution to the solution in sulphuric acid, and estimation of the evolved ammonia in the usual manner.

For determination of acetic acid, the sulphuric acid was titrated by sodium carbonate until the solution contained only sodium hydrogen sulphate and acetic acid. Acetic acid was distilled off under a partial vacuum (~26 mm.) into a known volume of standard alkali, the excess of which was then titrated by standard hydrochloric acid. The following Table * contains the transport numbers found for some ions in sulphuric acid (A) and in 15% oleum (B).

Discussion

The foregoing results show that the general nature of ionic transport and electrical conductivity was somewhat similar in sulphuric acid and in oleum. However, owing to certain differences in the nature and composition of such solutions, they are discussed separately.

Ion	m	Amount of electricity passing (c)	10^5 × Increase in cathode concn.	10^5 × Decrease in anode concn.	Transport number :	
					cation	anion
$CH_3{\cdot}CO_2H_2^+$	0·5723 (A)	6523	150	151·6	0·022	0·0224
NH_4^+	0·4766 (A)	5910	189·7	183·6	0·031	0·030
	0·7836 (A)	5423	202·3	174·2	0·036	0·031
	0·9780 (A)	5885	207·4	244	0·034	0·040
Na^+	0·2240 (B)	2355	42	42	0·017	0·017
$\frac{1}{2}Sr^{++}$	0·2546 (B)	3416	77·8	42·5	0·022	0·012
$\frac{1}{2}Ba^{++}$	0·5060 (B)	4834	60·1	50·1	0·012	0·01
$CH_3{\cdot}CO_2H_2^+$	0·3521 (B)	3917	251	250	0·061	0·061
NH_4^+	0·5629 (B)	5790	21	186	0·035	0·031
K^+	0·4600 (B)	3860	116	132	0·029	0·033

* m = Molality of solute (mole per kg. of sulphuric acid or oleum); other concentrations are given in g.-equiv. per kg. of solvent.

(1) *Conductivities in Absolute Sulphuric Acid Solutions.*—The transport-number data of acetic acid, benzoic acid, and ammonium sulphate suggest that the hydrogen sulphate ion

conducts most of the current (97—99%) and most probably by the abnormal mechanism suggested earlier (*J.*, 1953, 209). It is noteworthy, however, that the transport numbers of the NH_4^+ ion did not change much with concentration. This is not in accord with the results obtained from Ba^{++} and Sr^{++} which were explained by the assumption that the high viscosity of their solutions made ionic diffusion more difficult (*loc. cit.*).

(2) *Conductivities in Oleum Solutions* (*Conduction of the Ion*, $H_3SO_4^+$, *in Oleum*).—The Table contains the results of the transport-number measurements of some solutes in oleum solutions of nearly the same sulphur trioxide concentration (~15%). In such solutions solutes are ionised according to a scheme for which we may take ammonium sulphate as an example :

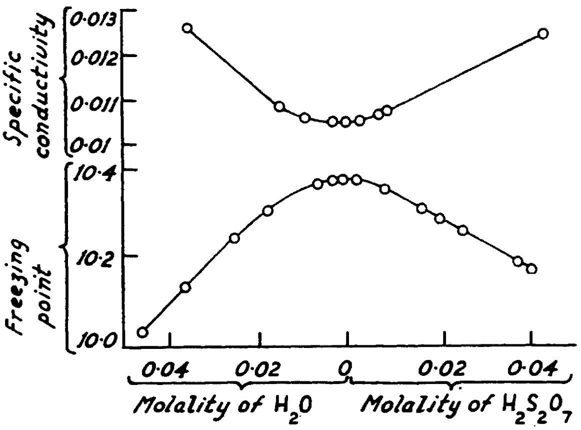
$$(NH_4)_2SO_4 + H_2SO_4 \longrightarrow 2NH_4^+ + 2HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$H_2S_2O_7 + H_2SO_4 \longrightarrow H_3SO_4^+ + HS_2O_7^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$H_3SO_4^+ + HSO_4^- \longrightarrow 2H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$HS_2O_7^- + H_2SO_4 \longrightarrow H_2S_2O_7 + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It gives rise to ammonium and hydrogen sulphate ions, and part of the disulphuric acid ionises in sulphuric acid according to equation (2) into hydrogen disulphate ions and $H_3SO_4^+$ ions. The latter ions react according to equation (3) (Gillespie, *J.*, 1950, 2542). Part of the hydrogen disulphate ions will, however, be solvolysed by sulphuric acid (4) to give rise to hydrogen sulphate ions. In such solutions we find that the NH_4^+ and $H_3SO_4^+$ ions are the only positive ions present and the $HS_2O_7^-$ and HSO_4^- ions are the corresponding negative ions. The amount of hydrogen sulphate ions could be calculated from a knowledge of the solvolysis constant of the hydrogen disulphate ion in sulphuric acid (*idem, ibid.*).



It should be pointed out that the amount of the hydrogen sulphate ions, however little it may be, will cause some error in the results in the Table, but this is not very serious because only about 30% of the disulphuric acid molecules are ionised, and only about 5—10% of the hydrogen disulphate ions are solvolysed according to equation (4) (*loc. cit.*). The amount of chain conduction due to the presence of hydrogen sulphate ions could not be more than 10% of the total chain conduction that would take place in such solutions. The results in the Table are therefore only approximate for these and other reasons. The other ions present are NH_4^+ and $HS_2O_7^-$, which have been shown (Gillespie and Wasif, *J.*, 1953, 209, 964) to carry only a small part of the current. The NH_4^+ ion in pure sulphuric acid was shown to carry only about 3% of the total current by the diffusion mechanism (see Table).

There is some doubt as to the nature of conduction of the hydrogen disulphate ion in these solutions. It is not certain that the chain mechanism would be the only way in which conduction takes place on account of the difficulty with which the proton would jump between the $HS_2O_7^-$ ion and H_2SO_4 molecules owing to the high potential barrier between the two entities (Glasstone, Laidler, and Eyring, " The Theory of Rate Processes," Van Nostrand, 1941). The conductivity of the hydrogen disulphate ion has been found not to exceed 5% of that of the hydrogen sulphate ion (Gillespie and Wasif, *J.*, 1953, 964).

The above considerations suggest that in such solutions the $H_3SO_4^+$ ion must be the one responsible for the process of chain conduction in oleum solutions in just the same way as the HSO_4^- ion conducts in pure sulphuric acid solutions. That such an ion conducts by an abnormal rather than the normal mechanism can be seen from the values of the transport numbers for the different ions measured in these solutions, and their comparison with those in absolute sulphuric acid. The mobility of the hydrogen ion was found to be comparable with that of the hydrogen sulphate ion from a consideration of the conductivity titration curve of the sulphur trioxide–water system and its comparison with the freezing-point curve for the same system (see Fig.). The maximum point on the f. p. curve, which was found to correspond to the composition of pure sulphuric acid, coincides with the minimum conductivity on the specific-conductivity curve. If the mobilities of the $H_3SO_4^+$ and the HSO_4^- ion were different, that would lead to a shift of the minimum point on the specific-conductivity curve towards the water side or towards the sulphur trioxide side according as the HSO_4^+ is the faster or the slower ion.

The author thanks Dr. R. J. Gillespie for his useful suggestions and continuous encouragement.

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[*Received, April 5th,* 1954.]