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Abstract

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Electrotransport of Ions in Absolute Sulfuric Acid

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A study of solutions of a number of substances in absolute sulfuric acid ([1]) led to the conclusion that a series of autoprotolytic processes exists, as a result of which the anion HSO_4^- ($HS_2O_7^-$) and the cation $H_3SO_4^+$ ([2]) are formed:

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-, \qquad \text{(I)}$$

$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^-$$

or the cation HSO_3^+:

$$3H_2SO_4 \rightleftharpoons HSO_3^+ + H_3O^+ + 2HSO_4^-. \qquad \text{(II)}$$

(All other ionization processes may be assigned to the type of ionic dehydration.) None of the schemes given, as far as we know, has found confirmation in studies of ion transport, except for data from the study of various substances in sulfuric acid ([3–10]), from which the transport of the solvent itself can be judged only indirectly.

It therefore seemed advisable to study the electromigration of ions in absolute sulfuric acid by the radioisotope variant of the Hittorf method previously proposed by us ([11]). (Analogous studies, carried out by another method, were performed in molten salts ([12,13]).) The experiments were carried out in a glass cell thermostatted at 25°, divided into three parts by sealed-in porous partitions. Sulfuric acid prepared, according to conductivity data ([14]), from chemically pure oleum and concentrated sulfuric acid was introduced into the side compartments. The same acid, labeled with S^{35}, was introduced into the middle compartment. The radiochemical purity of the preparation was monitored by determining the half-life. Smooth platinum electrodes placed in the side compartments of the electrolyzer were used for electrolysis. The duration of electrolysis in each experiment was 6–7 hours.

Table 1

Ion transport in absolute sulfuric acid

No.	Weight of acid before the experiment, g	Weight of acid before the experiment, g	Relative activity, disintegrations/min	Relative activity, disintegrations/min	Relative activity, disintegrations/min	Transported to the catholyte, mg-mol	Amount of electricity, $(q \cdot 10^3)/F$	g-mol/F
	catholyte	anolyte	middle compartment	catholyte	anolyte			
1	6.68	6.34	6160	146	—	1.62	4.15	0.39
2	12.67	13.25	5000	96	—	2.54	7.45	0.34
3	7.03	7.03	7937	250	—	2.33	5.57	0.42
4	13.42	12.90	5500	141	5	2.80	6.25	0.45

Control experiments (without passing current) showed that during such a time no appreciable transfer of activity from the middle compartment of the electrolyzer into the side compartments occurs as a result of diffusion. The current strength was 20–25 mA. The methods of meas—

changes in activity and the corresponding calculations are described in the papers cited above [10,11].

A quantitative characteristic of electromigration in the present case is the excess number of gram-moles of sulfuric acid transported into the near-electrode space and referred to 1 F (Faraday' s number) of electricity passed.

Table 1 gives the experimental results on the study of electromigration in absolute sulfuric acid.

In considering the data on ion transport in absolute sulfuric acid, attention is drawn to the practical absence of anodic transport, combined with a very considerable cathodic transport of sulfur.

The absence of anodic transport of sulfur indicates a relay mechanism of current transfer by the ion HSO_4^-. The existence of this mechanism for the bisulfate ion was proposed by Hammett and Gillespie [7,8] on the basis of the anomalously high mobility of this ion in absolute sulfuric acid. As we found [10], the relay mechanism for bisulfate is also retained in concentrated solutions of sulfuric acid. Thus, in a radioisotope study of transport numbers in the binary system sulfuric acid—acetic acid, it was established that in solutions containing more than a 0.85 mole fraction of H_2SO_4, there is no anodic transport of sulfur.

From the data of Table 1 it is seen that, when current is passed, activity corresponding to approximately 0.4 mole of H_2SO_4 per 1 F of electricity passes into the cathodic part. This indicates that sulfur-containing cations (formed as a result of processes I or II) either are incapable of the relay mechanism of current transfer, or exhibit this capacity to a much lesser extent than the bisulfate ion. To determine the nature of the phenomenon of cathodic transport of sulfur in sulfuric acid, we carried out a series of experiments clarifying the influence of various factors on the magnitude of the transport. It was found that, under the experimental conditions we selected, the various electrochemical processes taking place in the near-electrode regions cannot cause radioactive sulfur to diffuse to the cathode.

Table 2

Effect of additives on the cathodic transport of sulfuric acid

Additive	Mole fraction of dissolved substance	Weight of electrolyte before the start of the experiment, g catholyte	Weight of electrolyte before the start of the experiment, g anolyte	Relative activity, counts/min middle compartment	Relative activity, counts/min catholyte	Relative activity, counts/min anolyte	Transferredity to catholyte, mg/mol	Amount of electricity ($q \cdot 10^3$), F	g-moles / F
H_2O	0.0012	6.75	6.39	6620	63.5	–	0.66	2.86	0.23
H_2O	0.005	6.18	6.86	5188	51.0	–	0.62	3.47	0.18
H_2O	0.0184	5.98	6.92	5934	51.4	–	0.53	3.79	0.14
H_2O	0.0426	6.45	6.32	5836	42.9	–	0.48	4.42	0.11
H_2O	0.0734	6.60	5.65	5365	10.7	–	0.113	3.58	0.03
CH_3COOH	0.0166	6.43	6.16	7975	114.6	–	0.932	7.11	0.13
CH_3COOH	0.0116	6.28	6.05	7500	60.2	–	0.500	6.48	0.078
CH_3COOH	0.0459	6.45	6.11	7430	40.0	–	0.344	6.58	0.052
CH_3COOH	0.0629	6.56	6.20	7030	9.4	–	0.086	6.61	0.013
$H_2S_2O_7$	0.0041	7.34	6.28	5190	74.8	–	1.08	4.20	0.26
$H_2S_2O_7$	0.0314	6.38	6.02	5222	53.6	–	0.67	4.86	0.14
$H_2S_2O_7$	0.0504	6.62	6.98	4786	36.4	–	0.52	3.93	0.13
HNO_3	0.0432	7.51	7.36	7134	2.0	1.0	–	6.18	–
CF_3COOH	0.0179	7.39	7.36	6905	382.0	–	4.06	7.19	0.56
CCl_3COOH	0.0582	14.74	13.52	4333	67.0	2.0	2.14	4.70	0.45

Various additives soluble in sulfuric acid exert a considerable influence on the cathodic transport of sulfur. All substances tested as additives can be divided into three groups according to their relation to sulfuric acid: bases–H_2O, CH_3COOH, HNO_3, acid–$H_2S_2O_7$, and weakly···

electrolytes–CF_3COOH, CCl_3COOH. Such a division follows from the studies of Gillespie ([16,17]), undertaken to determine the nature and magnitude of the ionization of a number of substances in sulfuric acid.

Table 2 gives the results of experiments on the influence of additives on the magnitude of the cathodic transport of sulfuric acid.

From the data in Table 2 it is seen that bases, with increasing concentration, very rapidly reduce the magnitude of cathodic transport. Thus, at a water concentration equal to 0.07 mole fraction, the phenomenon of cathodic transport practically disappears. Pyrosulfuric acid also lowers the cathodic transport of sulfuric acid, but more slowly than in the case of bases. Additives that are nonelectrolytes in sulfuric acid have practically no effect on cathodic transport.

The data on the influence of additives on the magnitude of cathodic transport can be explained by the fact that the introduction of electrolytes into absolute sulfuric acid decreases the concentration of sulfur-containing cations formed by one of processes (I) or (II). It is interesting that this decrease occurs more slowly than might have been expected from the value of the autoprotolysis constant of absolute sulfuric acid ([15]). The absence of the capacity for a relay mechanism of current transport for the sulfur-containing cations of sulfuric acid may be connected with the symmetry of these cations and the resulting difficulties in proton transfer ([18]). Apparently, an anomalously high value of the mobility of an ion alone cannot serve as a sufficient basis for judging that this ion conducts current by a relay mechanism.

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Note: Figure translations are in progress. See original paper for figures.