

694. Solutions in Selenic Acid. Part II.¹ Transport-number Measurements in Selenic Acid Solutions

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The measurement of the apparent transport numbers of the ammonium and nitronium ions was attempted in approximately 98% selenic acid solutions. Only the ammonium ions gave reproducible results, which are reported. The small transport-number values indicate that conduction is carried out by an abnormal mechanism. The nature of conduction in selenic acid is discussed and compared with what is known about chain conduction in other solvents.

THE transport number of the ammonium ion shows that it conducts about 1% of the current, leaving about 99% to be conducted by other ions; the nature of these is not yet known with certainty, and a complete cryoscopic survey will be needed to elucidate it. The specific conductance of selenic acid was found to be quite high when compared to that of water and of sulphuric acid at the same temperature (Table 1).

TABLE I

Specific conductances ($\text{ohm}^{-1} \text{cm.}^{-1}$) of H_2SO_4 , H_2SeO_4 , and H_2O at 35° *

H_2SO_4	H_2SeO_4	H_2O
1.299×10^{-2}	1.82×10^{-1}	Approx. 10^{-7}

* The values are calculated from those for sulphuric acid ² and for selenic acid.¹

The high conductance of a solvent may be taken as an indication of its degree of autoprotolysis,³ and the presence of ions such as HSeO_4^- and H_3SeO_4^+ would be expected in a highly conducting liquid as selenic acid, whose specific conductivity is much greater than that of sulphuric acid. The relative mobilities of these ions are not yet known, but we may in this Paper consider that both ions contribute equally to the overall process of conduction. This assumption does not seem unreasonable, when we compare such solutions with solutions of sulphuric acid, where the HSO_4^- and H_3SO_4^+ ions have very high mobilities in sulphuric acid and oleum.⁴ Solutions of sulphuric acid (for which abnormal conduction is now fully established) and solutions of selenic acid have the following similarities:

(a) X-Ray analysis of the structures of sulphuric and selenic acids show that both are heavily hydrogen-bonded, even in the liquid state.^{5,6} The selenate group is surrounded by two hydrogen bonds of 2.61 Å and two of 2.68 Å. In sulphuric acid, the hydrogen bonds round the sulphate group have a length of 2.85 Å. A study of the density and viscosity of sulphuric acid⁷ and selenic acid³ solutions showed that both represent a compact three-dimensional structure, which favours abnormal conduction,⁸ and, since it has been shown that abnormal conduction occurs in sulphuric acid, it is to be expected that it would also occur in solutions of selenic acid.

(b) The viscosity of selenic acid was found to be 21.5 c.p. at 35° , while that of sulphuric acid is 17.6 c.p. at the same temperature;¹ the two systems are thus highly viscous, which is not a favourable condition for normal conduction by ionic diffusion. The viscosity of water at 35° is about 0.7 c.p., which means that selenic acid is about 30.7 times more viscous than water at the same temperature. Now, if the ionic conductance of an ion such as K^+ is about $70 \text{ ohm}^{-1} \text{cm.}^2$ in water at low concentrations (approx. 0.05N); in

¹ Part I, S. Wasif, *J.*, 1964, 1324.

² S. Wasif, Ph.D. Thesis, University of London, 1951.

³ S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941.

⁴ S. Wasif, *J.*, 1955, 372.

⁵ M. Bailey and A. F. Wells, *J.*, 1951, 968.

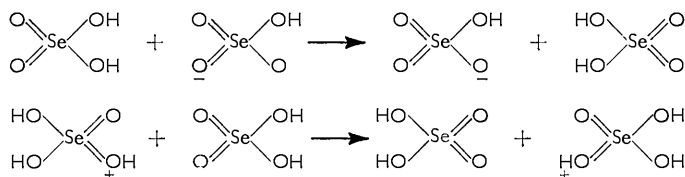
⁶ Finbach, Rouning, and Vier, *Tidsskr. Kjem. Berguesen Met.*, 1944, 426.

⁷ R. J. Gillespie and S. Wasif, *J.*, 1953, 215.

⁸ R. J. Gillespie and S. Wasif, *J.*, 1953, 209.

selenic acid solution the same ion would have a conductance of approximately $2.3 \text{ ohm}^{-1} \text{ cm}^2$. The equivalent conductance of KHSeO_4 in selenic acid is approximately $188 \text{ ohm}^{-1} \text{ cm}^2$ at a similar concentration ($0.05N$), and this leaves about $185.7 \text{ ohm}^{-1} \text{ cm}^2$ for other ions in solution (possibly HSeO_4^- and H_3SeO_4^+). Such high conductances of ions in a highly viscous solution can only take place by the proton-jump mechanism.

The present values for the transport number of the ammonium ion are only apparently due to the presence in the solvent of small amounts of water, which would also contribute to the process of conduction, but this contribution would not be expected to be greater than that of the ammonium ion. This deduction is based on the behaviour of the same ions in sulphuric acid.⁹ The apparent values reported for the ammonium ion are lower than those for the same ion in sulphuric acid and oleum solutions.⁴ Such low values leave no doubt that conduction in selenic acid solutions takes place by an abnormal mechanism involving a proton jump and molecular rotation. By analogy with sulphuric acid, it is possible to represent schematically the way in which conduction takes place:



Whether proton transfer or molecular rotation is the rate-determining process in the abnormal conduction of selenic acid is not yet known.

Comparison of Abnormal Conductivities on Different Solvents.—It is of interest to compare the abnormal mobilities of the hydrogen and hydrogen selenate ions in selenic acid with the mobilities of analogous ions in other solvents. At first sight, the mobilities of the hydrogen and hydrogen selenate ions in selenic acid are 50–100 times greater than those of cations such as NH_4^+ and K^+ . This is primarily due to the high viscosity of selenic acid, which causes the mobilities of the ions that conduct by a diffusion mechanism to be very small.

In sulphuric acid, which is also highly viscous, the hydrogen and hydrogen sulphate ions have mobilities 50–100 times as great as those of other ions, and the former has a much greater mobility than the latter.¹⁰ In water, the hydrogen and hydroxyl ions have mobilities 4–5 times greater than those of other ions, the hydrogen ion having a greater mobility than the hydroxyl ion. In methanol and ethanol, the ions CH_3OH_2^+ and $\text{C}_2\text{H}_5\text{OH}_2^+$ have abnormal mobilities while the methoxide and ethoxide ions have normal mobilities. In acetic and formic acids, both acetate and formate ions have normal mobilities. No abnormal mobility has been noticed in hydrogen fluoride or hydrogen cyanide.³ In nitric acid, the nitrate ion appears to have normal mobility.¹¹ It has been suggested that abnormal mobilities are related to the autoprotolysis constant of the solvent and only occur in solvents in which this is high.³ This shows that selenic acid is probably highly self-dissociated, but further proof is needed to support this conclusion.

Experimental.—Selenic acid solutions from 97.5–98.5% were used as solvents for ammonium selenate and nitric acid. All measurements were made by the Hittorf method in a cell similar to that used by Gillespie and Wasif.⁸ The current used was restricted to 20–25 mA to prevent heating and convection. The quantity of electricity was measured by means of a copper coulometer, which was calibrated against a silver coulometer constructed by the method of Rosa and Vinal.¹² At the end of each experiment, the solutions in the three compartments were separated, removed, weighed, and analysed.

⁹ S. Wasif, unpublished work.

¹⁰ "Hydrogen Bonding," Pergamon Press, London, 1957, 415.

¹¹ W. H. Lee and D. J. Millen, *J.*, 1958, 2248.

¹² C. C. Rosa and G. W. Vinal, *Bur. Stand. Bull.*, 1936, **13**, 479.

Method of analysis. Weighed amounts of the solution were diluted with water, an excess of alkali was added, and the resulting ammonia was passed through a known volume of standard sulphuric acid, the excess of which was back-titrated against standard barium hydroxide. A number of samples were analysed from each compartment. The differences between the transport numbers calculated from the analyses were within $\pm 20\%$, which seems reasonable in view of the very low values.

In the experiments with nitric acid as solute, it was possible to show that the acid migrated from the anode compartment, but no attempt was made to determine its ionic transport number quantitatively. The method of analysis was based on the work by Bennett, Brand, and Williams.¹³ The difficulty here was that, when electrolysis lasted for few hours, very little nitric acid migrated from the anode compartment but, when the time of electrolysis was increased, electrode reactions introduced serious difficulties.

Table 2 contains some of the results for the transport numbers of the ammonium ion in selenic acid.

TABLE 2
Transport-number data of the NH_4^+ ion in selenic acid

Molality	Q Coulombs	Equivs. lost by anode	Equivs. gained by cathode	t_a	t_c
0.20	5983	6.46×10^{-4}	3.6×10^{-4}	1.06×10^{-2}	0.59×10^{-2}
0.20	5211	7.56 "	3.34 "	1.40 "	0.62 "
0.20	5420	6.16 "	6.16 "	1.10 "	0.60 "
0.30	5600	5.85 "	3.36 "	1.01 "	0.58 "

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¹³ G. H. Bennett, J. C. D. Brand, and G. Williams, *J.*, 1946, 875.