237. *The Electrolytic Dissociation of Strontium Iodate and of Strontium Hydroxide.*

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The conductivities of dilute aqueous solutions of strontium iodate at 25° have been measured. From the results, a value of $K = 0{\cdot}10$ is obtained for the dissociation constant of the intermediate ion $Sr(IO_3)^+$. The solubility of the salt in water and in sodium hydroxide solutions at 25° has also been measured and used to derive the dissociation constant of $Sr(OH)^+$. The average value of 0·11 agrees closely with that calculated from an equation given by Davies for the strong hydroxides which assumes that interaction occurs with the unhydrated cations.

THE sparingly soluble iodates of calcium and barium have been used by Davies (*e.g.*, *J.*, 1951, 233; *Trans. Faraday Soc.*, 1949, **45**, 770) for quantitative studies of ion association between these cations and various anions. Some general trends have been noticed in the results obtained; for instance, the dissociation constants of their hydroxides (as well as those of other cations which form " strong " hydroxides) are related to the crystallographic radii of the cations (Davies, *J.*, 1951, 1256). Similar trends are found with organic anions such as malonate (Stock and Davies, *J.*, 1949, 1371), but with simple inorganic anions such as the iodates and nitrates, the trends are in the reverse direction, namely, in the order of size of the hydrated cations. These factors, together with the effect of increasing valency forces, have been discussed previously (Jones, Monk, and Davies, *J.*, 1949, 2693). The intermediate size of the strontium ion, in both its hydrated and its unhydrated form, between calcium and barium should prove of some value in providing further information on the nature of these factors which influence ion-pair formation.

In order to obtain dissociation constants of strontium salts by the solubility method, we have prepared strontium iodate crystals in a suitable form, and have obtained the second dissociation constant of this from some conductivity measurements on its aqueous solutions. The solubility in sodium hydroxide solutions has also been used to derive the second dissociation constant of strontium hydroxide.

EXPERIMENTAL

Suitably sized crystals of strontium iodate were formed by allowing approximately 0·1N-solutions of " AnalaR " strontium chloride and of " AnalaR " potassium iodate to drip very slowly into 1 l. of distilled water at room temperature. Heating a sample of the crystals (dried by washing with acetone) to 150° showed these to be the monohydrate $Sr(IO_3)_2,H_2O$. Crystals prepared by allowing the parent solutions to drip into water kept at 80° proved to be unsatisfactory; they had a lower solubility which showed considerable variation, and tended to break up.

The solubility of the hydrated crystals in water at 25° was measured by packing the crystals in the type of saturator described by Money and Davies (*J.*, 1934, **401**) and titrating 20-ml. samples of the saturated solution against 0·06N-sodium thiosulphate that had been standardised with potassium iodate. The solubility of the salt in sodium hydroxide solutions was determined similarly. For the latter solutions a stock solution of " AnalaR " carbonate-free alkali was standardised with potassium hydrogen phthalate. Before samples were taken for titration, three separate portions were allowed to percolate through the iodate column, and the pipette was washed and dried to remove any carbonate formed.

The conductivity measurements were made with the apparatus described previously (Davies and Monk, *J.*, 1949, **413**). Conductivity water was passed through the saturator; the first washings were rejected and a quantity was collected in a flask containing sufficient water to ensure that crystals would not separate out at room temperature. The concentration of this stock solution was found by titration against sodium thiosulphate standardised with potassium iodate, both the strontium and the potassium solutions being weighed. Two separate stock solutions were made.

The conductivity data are reported in Table 1, where C is the concentration in g.-equiv. per l., and Λ is the equivalent conductivity. The solubility measurements and resultant calculations are given in Table 2.

TABLE 1. *The conductivity of strontium iodate solutions at 25°.*

10^4C	Λ	$10^3\alpha$	K	10^4C	Λ	$10^3\alpha$	K
2·3419	97·57	2·37	0·09$_0$	7·3866	95·38	6·63	0·09$_5$
5·2187	96·28	3·85	0·11	9·4788	94·76	7·33	0·11
7·3603	94·52	6·15	0·10				

TABLE 2. *The solubility of strontium iodate in sodium hydroxide solutions*
(concns. in m.-mols. or mg.-ions per l.).

Soly.	NaOH	$[Sr(IO_3)^+]$	$[NaIO_3]$	$[Sr(OH)^+]$	10^3I	K
5·87	—	0·37	—	—	16·87	—
6·55	16·70	0·37	0·05	0·41	34·74	0·115
6·73	22·31	0·36	0·07	0·53	40·65	0·115
6·98	30·21	0·36	0·09	0·74	48·86	0·106
7·40	45·99	0·35	0·14	1·06	65·23	0·106

DISCUSSION

The Onsager limiting conductivity equation for strontium iodate in water at 25° is $\Lambda = 100{\cdot}21 - 132{\cdot}83\,I^{\frac{1}{2}}$, where Λ is the equivalent conductivity, and I the ionic strength. The equivalent conductivity of 100·21 at zero concentration is derived from 59·46 for the strontium ion (Shedlovsky and Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 1066) and 40·75 for the iodate ion (Monk, *ibid.*, 1948, **70**, 3281). Comparison with the experimental conductivities shows that the theoretical values are slightly higher, and this may be attributed to the presence of the ion-pair $Sr(IO_3)^+$. The dissociation constant of this ion may be calculated by the method of Righellato and Davies (*Trans. Faraday Soc.*, 1930, **26**, 592) for 2 : 1-valent types of electrolytes. The exact mobility of the ion-pair is not known, but comparison of similar types of ions of valencies 1 and 2 suggests that it has a value of 0·5—0·65 of that of the strontium ion. We have assumed that the $Sr(IO_3)^+$ ion has the lower value, *i.e.*, its conductivity at zero concentration is equal to half that of the strontium ion, so that the corresponding Onsager equation for the dissociation process $Sr(IO_3)^+ \rightleftharpoons Sr^{2+} + IO_3^-$ is $\Lambda = 70{\cdot}48 - 76{\cdot}38\,I^{\frac{1}{2}}$, and if in any particular solution we assume that α is the fraction of strontium ions which associate to form $Sr(IO_3)^+$ ions, combination of the two equations gives an expression from which α may be calculated, namely,

$$\Lambda\,(\text{obs.}) = 100{\cdot}21 - 132{\cdot}83\,I^{\frac{1}{2}} - \alpha(64{\cdot}97 - 94{\cdot}64\,I^{\frac{1}{2}})$$

The ionic strength is given by $I = C(1{\cdot}5 - \alpha)$. The values of α thereby obtained are given in Table 1 together with the dissociation constants for the equilibrium

$K = [Sr^{2+}][IO_3^-]f_1f_2/[Sr(IO_3)^+]f_3$, the limiting Debye–Hückel activity coefficient expression $-\log f_i = 0{\cdot}509z_i^2I^{\frac{1}{2}}$ being used (where z_i is the ion valency). The average of $K = 0{\cdot}10$ lies between those of 0·13 for calcium (Wise and Davies, *J.*, 1938, 273) and 0·08 for barium (MacDougall and Davies, *J.*, 1935, 1416). In all three cases the results are dependent to some extent on the assumption previously referred to concerning intermediate ion mobilities, and the absence of significant drifts in the K data over a range of concentrations probably supports the assumption. In any case, since all three constants have been calculated on the same basis, the results are at least qualitatively comparable. Broadly speaking, the general order of these constants is in the same direction as the radii of the hydrated cations if one takes the cation mobilities as a criterion. The comparison is only approximate, however, since the calcium and strontium mobilities are almost identical.

The batch of strontium iodate crystals used for the solubility measurements reported in Table 2 had a solubility of 5·87 m.-mol. per l. in water at 25°. This remained constant, although a second batch prepared in a similar fashion showed a solubility of 5·89. Account being taken of the presence of $Sr(IO_3)^+$ ions, the activity solubility product (*i.e.*, of the first batch) is $3{\cdot}289 \times 10^{-7}$. In calculating this, use has been made of the activity coefficient expression used by Davies for similar work (*J.*, 1938, 2093), namely, $-\log f_i = 0{\cdot}5z_i^2\{I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}2I\}$. On this basis, and with allowance for the slight association that occurs between sodium and iodate ions, for which $K = 3{\cdot}0$ (MacDougall and Davies, *loc. cit.*), the concentrations of $Sr(OH)^+$ ion pairs were calculated by successive approximations. From these, the dissociation constant of the equilibrium $Sr(OH)^+ = Sr^{2+} + OH^-$ has been derived. These results are shown in the last column of Table 2, and the average is 0·11.

Davies, in a discussion of the dissociation of the metal hydroxides (*J.*, 1951, 1256), has shown that the dissociation constants of those which are " strong " can be expressed by $pK = 0{\cdot}607z^2/r - 1{\cdot}150$, where r is the crystallographic radius of the cation in Å, and z is its valency. Pauling (" Nature of the Chemical Bond," 2nd edn., Cornell Univ. Press, p. 346) gives r as 1·13 Å for strontium, so Davies's relation predicts a K of 0·10, in good agreement with the experimental value. Accordingly, the dissociation constant of strontium hydroxide is also related to the size of the unhydrated cation.

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