342. *The Solubility of Barium Iodate in Salt Solutions.*

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THE measurements here reported concern the solubility of barium iodate monohydrate at 25° in dilute solutions of calcium chloride, and the chloride, nitrate, chlorate, and perchlorate of potassium. In addition, the conductivity of barium iodate solutions was measured in order to estimate the extent of ionic association in the saturated solution.

The results are of interest in two connexions. The solubility of a salt has usually been found to be markedly dependent on the individual nature of added salts and not merely, as simple theory would predict, on the ionic strength. In previous papers (J., 1930, 949, 2410, 2421) this has been attributed to ionic association, and it is here shown that for the bi-univalent salt now studied the specific effects appearing in dilute solutions can be quantitatively accounted for in the same way. Secondly, the results have been used to test the Debye–Hückel limiting equation $\log f = -0.505z^2\sqrt{\mu}$, where f is the activity coefficient of an ion of valency z, and μ is the ionic strength. When this work was under-

taken in 1930 there were grounds for doubting the correctness of the numerical factor in the equation, but several papers since published have demonstrated its validity, in agreement with the earlier results of Brönsted and LaMer (*J. Amer. Chem. Soc.*, 1924, **46**, 560); our results, after allowance is made for ionic association, are in complete harmony with the limiting theoretical equation.

<p style="text-align:center">EXPERIMENTAL.</p>

Materials.—The barium iodate monohydrate was prepared from A.R. barium hydroxide and iodic acid, solutions of the two being allowed to drop, with the acid in slight excess, into conductivity water in an apparatus protected from the atmosphere, and the crystalline precipitate being washed until its solubility was constant. It was analysed by the method
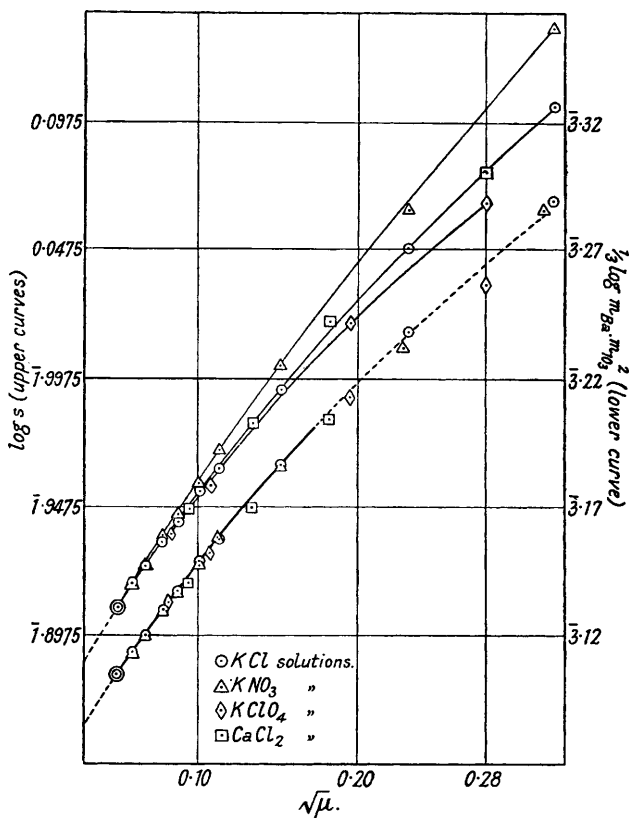
described below. The calcium chloride solutions were prepared from a stock solution standardised with silver nitrate. The potassium perchlorate was twice recrystallised from conductivity water, and the other salts were " A.R." chemicals which had been powdered, and dried in a vacuum.

Conductivity Measurements.—Water of measured specific conductivity (about 0·4 gemmho) was saturated with the pure salt in a conductivity cell of the Hartley and Barrett type. After periodic agitation for several days a constant conductivity was reached, and was measured on a bridge of conventional type; some of the solution was then withdrawn and analysed. The equivalent concentration was 0·001620, and the equivalent conductivity at 24·93° (after subtraction of the conductivity of the solvent) was 96·77. The equivalent conductivity at infinite dilution was calculated as follows : Shedlovsky's measurements give 63·63 for the mobility of barium ion, and 349·72 for that of hydrogen ion (MacInnes, Shedlovsky, and Longsworth, *Chem. Reviews*, 1933, **13**, 29; Shedlovsky and Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 1066), based on Parker's cell-constant data; on the Kohlrausch standard these become 63·75 and 350·22 respectively (cf. Davies, " Conductivity of Solutions," 1933, p. 206). Kraus and Parker's measurements (*J. Amer. Chem. Soc.*, 1922, **44**, 2429) give $\Lambda_0 = 391·15$ for iodic acid (Davies, *J.*, 1933,

4 z

645); combination of these figures gives $\Lambda_0 = 104\cdot65$ for barium iodate at $25°$, or $104\cdot50$ at $24\cdot93°$, whence the Onsager slope for barium iodate is 166, and the theoretical value for the equivalent conductivity of the saturated solution is $97\cdot82$. If the discrepancy, $1\cdot05$ units, is attributed to ionic association, it can be calculated by methods previously described (Righellato and Davies, *Trans. Faraday Soc.*, 1930, **26**, 592) that the dissociation constant for the second-stage dissociation, $BaIO_3{}^{\bullet} \rightleftharpoons Ba^{\bullet\bullet} + IO_3{}'$, is $0\cdot076$. Some further conductivity measurements were made on more dilute solutions, prepared by siphoning known amounts of stock solution into water of known conductivity in a second cell. For these solutions the solvent correction had to be obtained by calculation, and this was done by assuming that the only impurity in both samples of water was carbon dioxide. The uncertainty thus introduced is small, but in view of the relatively high magnitude of the solvent's conductivity in highly dilute solutions these measurements must be considered less accurate. Four such determinations gave on extrapolation a Λ_0 value $0\cdot7\%$ higher than that calculated above, and led (using this value) to a mean dissociation constant $K = 0\cdot083$. The value $K = 0\cdot08$ is used in the solubility calculations.

Solubility Measurements.—The apparatus was similar to that described by Money and Davies (*J.*, 1934, 400), and was immersed in a thermostat maintained at $24\cdot93° \pm 0\cdot01°$. The results recorded are each the mean of two determinations agreeing to within at least $0\cdot3\%$; that saturation was actually attained under the conditions of the experiments was ensured by passing a portion of the solution through the saturating column a second time. The analyses were effected by withdrawing 100 c.c. of the saturated solution in a calibrated pipette, and running it into an acid potassium iodide solution; the liberated iodine was titrated by weight against

c.	s.	$\sqrt{\mu}$.	$\frac{1}{3}\log m_{Ba^{\bullet\bullet}}\cdot m_{IO_3}{}'^{2}$.	$10^4\Delta$.
		Potassium chloride solutions.		
0	0·810	0·0491	$\bar{3}$·1048	+ 8
0·001	0·827	0·0588	$\bar{3}$·1132	+ 5
0·002	0·840	0·0670	$\bar{3}$·1202	+ 3
0·0035	0·859	0·0777	$\bar{3}$·1297	+ 5
0·005	0·874	0·0871	$\bar{3}$·1372	+ 1
0·0075	0·899	0·1008	$\bar{3}$·1489	+ 6
0·01	0·918	0·1128	$\bar{3}$·1579	0
0·02	0·985	0·1513	$\bar{3}$·1868	+ 2
0·05	1·117	0·2308	$\bar{3}$·2383	+ 18
0·1	1·269	0·3220	$\bar{3}$·2887	+104
		Potassium nitrate solutions.		
0·001	0·826	0·0587	$\bar{3}$·1124	− 2
0·002	0·841	0·0669	$\bar{3}$·1194	− 4
0·0035	0·863	0·0776	$\bar{3}$·1291	0
0·005	0·880	0·0869	$\bar{3}$·1367	− 2
0·0075	0·906	0·1004	$\bar{3}$·1474	− 6
0·01	0·932	0·1123	$\bar{3}$·1582	+ 7
0·02	1·006	0·1506	$\bar{3}$·1852	− 10
0·05	1·156	0·2279	$\bar{3}$·2321	− 29
0·1	1·361	0·3164	$\bar{3}$·2859	+ 98
		Potassium perchlorate solutions.		
0·004	0·866	0·0811	$\bar{3}$·1333	+ 13
0·008845	0·905	0·1074	$\bar{3}$·1523	− 14
0·035	1·045	0·1951	$\bar{3}$·2128	− 29
0·075	1·164	0·2800	$\bar{3}$·2568	− 43
		Calcium chloride solutions.		
0·002061	0·884	0·0937	$\bar{3}$·1398	− 26
0·004961	0·955	0·1328	$\bar{3}$·1698	− 34
0·009928	1·046	0·1809	$\bar{3}$·2046	− 21
		Potassium chlorate solutions.		
0·005	0·880			
0·01	0·924			
0·02854	1·031			
0·075	1·184			

an approx. $0.15N$-solution thiosulphate solution, $0.01N$-iodine solution being used for the back titration. The thiosulphate was periodically standardised against potassium iodate.

The results are shown in the figure (upper curves), and below : col. 1 gives the concentration of the solvent salt (in g.-mol./l.), and col. 2 the solubility of the barium iodate in millimol./l. If all the salts used are completely dissociated, the results should be in keeping with the limiting equation of the Debye–Hückel theory, *viz.*, $\log s = \log s_0 + 1.01\sqrt{\mu}$, where s_0 is a constant. It will be seen from the upper curves of the figure that the results are indeed compatible with the theoretical limiting slope, which is shown by a broken line, but that at the higher concentrations each solvent salt leads to a separate line; even for ionic strengths much below 0.01, the specific deviations are beyond the limits of experimental error. When allowance is made for ionic association, the results lead to the lower series of points in the figure, which show $\frac{1}{3} \log m_{Ba} \cdot m^2_{IO_3'}$ plotted against the square root of the corrected ionic strength. The ionic concentrations for this purpose were calculated by successive approximations as previously described (J., 1930, 949, 2410), employing equations of the form $\log m_A m_B/m_{AB} = \log K + a\sqrt{\mu} - b\mu$. K was given the following values : KIO_3, 2.0; KNO_3, 1.4; $BaNO_3^{\cdot}$, 0.12; $BaIO_3^{\cdot}$, 0.08; $BaCl^{\cdot}$, 1.35; $CaIO_3^{\cdot}$, 0.13; these have been previously published except that for $BaCl^{\cdot}$, which is derived from the data given in an earlier paper (*Trans. Faraday Soc.*, 1930, **26**, 593, Table 1), and that for $CaIO_3^{\cdot}$, which is obtained from conductivity measurements shortly to be published. a and b were both given the value unity for the uni-univalent salts, and the value 2 for the intermediate ions of uni-bivalent salts. These empirical values satisfy the conductivity figures, and considerable alterations in them have no significant effect on the small corrections they are used to calculate. Potassium and barium perchlorates, as well as potassium chloride, were assumed to be completely dissociated.

Col. 3 of the foregoing table shows the square root of the corrected ionic strength, col. 4 gives values of $\frac{1}{3} \log m_{Ba} \cdot m^2_{IO_3'}$, and col. 5 gives the difference (Δ) between these values and those calculated from the equation $\frac{1}{3} \log m_{Ba} \cdot m^2_{IO_3'} = -2.9433 + 1.01\sqrt{\mu} - \mu$. This equation is in harmony with the Debye–Hückel limiting law, and except for the calcium chloride results, which seem to be affected by a small constant error, the corrected figures are in good agreement with this common equation up to an ionic strength of approximately 0.03; an error of 0.3% in the analyses would lead to a value $10^4\Delta = \pm 10$, approximately. At the higher concentrations, individual differences begin to appear, but it will be evident from the figure that these are very much smaller than with the uncorrected results.

With potassium chlorate as solvent salt the treatment outlined above was impossible, as the extent of association between barium and chlorate ions was unknown. A reversal of the method of calculation for the two most dilute solutions of potassium chlorate gave an approximate value $K = 0.2$ for the process $BaClO_3^{\cdot} \rightleftharpoons Ba^{\cdot\cdot} + ClO_3'$.

SUMMARY.

The solubility of barium iodate monohydrate in a number of aqueous salt solutions at $25°$ is reported. Corrections for ionic association remove the specific deviations found in dilute solutions, and the results are in agreement with the Debye–Hückel limiting formula. The dissociation constant of the $BaIO_3^{\cdot}$ ion is 0.08, and that of $BaClO_3^{\cdot}$ is approximately 0.2.

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