

LXXXV.—*The Solubility of Iodine in Solutions of Halides.*

By JOHN STANLEY CARTER and CHARLES RANDALL HOSKINS.

MEASUREMENTS of the solubilities of certain non-electrolytes in solutions of electrolytes have shown that, in the absence of interaction between the two, the relation between the solubility  $s$  and the electrolyte concentration  $C$  is represented by the exponential equation  $s = s_0 e^{aC}$ , where  $s_0$  has a value equal to or approximating to the solubility in the pure solvent and  $a$  is a constant which measures the salting-out effect of the electrolyte. When the non-electrolyte and the electrolyte react to form a soluble complex, the salting-out effect is opposed by a tendency towards increased solubility, and the solubility actually observed will depend on the relative magnitudes of the two opposing effects. If the equilibrium involved in the formation of the complex is known, it should be possible, by making allowance for the salting-out effect, to obtain constancy of the mass-law expression concerned.

Such a case has already been investigated in connexion with the solubility of iodine in solutions of sodium chloride [Dawson and Carter, *Proc. Leeds Phil. Soc.*, 1925, **1**, (i), 14; Carter, *J.*, 1925, **127**, 2861]. Iodine dissolved in solutions of sodium chloride exists in part as free iodine and in part as the complex polyhalide  $\text{NaClI}_2$ , the influence of polyhalide formation being such that the solubility passes through a maximum as the concentration of sodium chloride increases. It was found possible to distinguish between the two opposing effects and to show that polyhalide formation was superimposed on the normal salting-out process.

The more comprehensive examination of this type of equilibrium now described includes measurements, not only of the solubility of iodine at  $25^\circ$  in solutions of simple halides, but also of the influence of certain inert salts. Bell and Buckley (*J. Amer. Chem. Soc.*, 1912, **34**, 10) determined the solubility of iodine in solutions of sodium and potassium bromides but did not attempt a quantitative interpretation; a representative selection from their data has therefore been recalculated on a weight-concentration basis and incorporated with the present measurements.

The equilibrium involved is  $X' + I_2 \rightleftharpoons XI_2'$ , where  $X = Cl, Br,$  or  $I$ . In the above equation, therefore,  $s$  is the concentration of free iodine,  $s_0$  is its solubility in pure water, and  $a$  is at present unknown. If  $S$  is the observed solubility, the concentrations of the participants in the equilibrium involved are  $[X'] = C - (S - s)$ ;  $[I_2] = s$ ;  $[XI_2'] = S - s$ , and according to the mass-action law,

$$K = [C - (S - s)]s/(S - s) \dots (1)$$

By plotting against  $C$  the values of  $K$  obtained from the simple mass-law relation (ignoring the salting-out effect) and extrapolating to  $C = 0$ , we obtain a value  $K_0$  which may be regarded as the true equilibrium constant. Now, from equation (1), if we assume that  $S - s$  is small compared with  $C$ , we see that  $S = s(1 + C/K)$ ; and putting the exponential relation in the form  $\log_e s = \log_e s_0 - aC$  and eliminating  $s$  between these two expressions, we obtain as an approximation

$$a = 1/C \cdot \log_e s_0(1 + C/K)/S,$$

the extrapolated value  $K_0$  being assumed to be equal to  $K$ .

This approximation is permissible for chlorides and bromides, but not for iodides. The solutions of iodides used were, however, very dilute, and in view of the known low salting-out power of the iodide ion, the data for solutions containing iodides have been considered without reference to this effect; the experimental data show that the procedure is justified.

Having thus obtained the value of  $a$ , the value of  $s$  for any particular concentration may be determined from the exponential relation. Actually it was more convenient to convert this relation to its equivalent in Briggsian logarithms, *viz.*,  $\log s = \log s_0 - a'C$ , where  $a' = a/2.3$ .

This procedure involves the assumption that halide and polyhalide have the same salting-out power. With both chlorides and bromides the proportion of polyhalides is extremely low and hence no appreciable error is thereby introduced. The data for the simple halides are collected in Table I. In accordance with previous practice all concentrations have been referred to a fixed weight of water and are expressed as mols. (equivs. in the case of magnesium and barium chlorides) per 1000 mols. of water. The value of  $s_0$  is  $2.38 \times 10^{-2}$ . The first column gives the concentration of halide, the second the observed solubility, the third the calculated concentration of free iodine, and the last the value of the mass-law constant calculated from equation (1).

The solubility data for hydrochloric acid are in excellent agreement with the solubility and partition measurements of Rây and Sarkar

TABLE I.

Hydrochloric acid, $a' = 0.0005$ .				Potassium chloride, $a' = 0.0032$ .			
<i>C.</i>	100 <i>S.</i>	100 <i>s.</i>	<i>K.</i>	<i>C.</i>	100 <i>S.</i>	100 <i>s.</i>	<i>K.</i>
8.48	4.31	2.36	10.3	6.15	3.49	2.27	11.4
17.9	6.55	2.33	9.9	12.3	4.38	2.17	12.1
25.1	7.93	2.31	10.3	24.6	5.89	1.99	12.6
31.5	9.51	2.29	10.0	36.3	7.11	1.82	12.5
65.3	17.0	2.21	9.8	48.2	8.22	1.67	12.3
79.5	19.7	2.17	9.8	60.6	9.05	1.52	12.2
109.2	25.2	2.10	9.9	73.9	9.75	1.38	12.2
141.0	29.9	2.02	10.2	86.8	10.03	1.26	12.5
Magnesium chloride, $a' = 0.0055$ .				Barium chloride, $a' = 0.0058$ .			
<i>C.</i>	100 <i>S.</i>	100 <i>s.</i>	<i>K.</i>	<i>C.</i>	100 <i>S.</i>	100 <i>s.</i>	<i>K.</i>
8.48	3.94	2.14	10.1	3.67	3.05	2.27	10.7
13.0	4.65	2.02	10.0	4.89	3.18	2.23	11.5
26.3	6.34	1.71	9.7	12.1	4.26	2.03	11.0
53.5	7.41	1.21	10.4	24.0	5.38	1.73	11.4
67.5	7.50	1.01	10.5	35.6	6.10	1.48	11.4
96.1	7.32	0.70	10.2	46.9	6.60	1.27	11.2
125.9	6.36	0.48	10.3	57.8	6.76	1.10	11.2
141.3	5.73	0.40	10.6	68.6	6.71	0.95	11.3
*Sodium bromide, $a' = 0.0042$ .				*Potassium bromide, $a' = 0.0015$ .			
<i>C.</i>	10 <i>S.</i>	100 <i>s.</i>	<i>K.</i>	<i>C.</i>	10 <i>S.</i>	100 <i>s.</i>	<i>K.</i>
16.9	2.449	2.02	1.49	16.8	2.598	2.25	1.57
34.5	4.009	1.70	1.51	37.8	5.165	2.09	1.57
68.6	5.955	1.23	1.44	65.2	8.155	1.90	1.54
83.0	6.491	1.07	1.38	82.9	10.06	1.79	1.47
Hydriodic acid, $a' = 0$ ; $s = s_0$ .							
10 <i>C.</i>	10 <i>S.</i>	100 <i>K.</i>	10 <i>C.</i>	10 <i>S.</i>	100 <i>K.</i>	10 <i>C.</i>	100 <i>K.</i>
2.117	1.326	2.25	13.21	2.908	2.33	2.117	2.33
5.284	2.956	2.25	17.63	9.228	2.29	5.284	2.29
8.810	4.715	2.30	49.64	27.84	1.90	8.810	1.90

\* Calculated from Bell and Buckley's values (see p. 580).

(*J.*, 1922, **121**, 1449) for dilute solutions, the value of *K* calculated from their data being 10.8.

Consideration of the data for the chlorides shows that when  $a'$  is very small the solubility increases almost linearly with the concentration of electrolyte. When the value of  $a'$  is considerable, the observed solubilities are smaller and show maximum values. Potassium chloride shows no maximum, but the curve is considerably flattened at high salt concentrations.

Bell and Buckley have shown that the solubility in solutions of sodium bromide is maximal at a high salt concentration ( $C = 120$ ). Potassium bromide shows no maximum, nor is the solubility curve particularly flattened at high concentrations.

In view of the number and nature of the assumptions involved and the considerable range of electrolyte concentration, the agreement amongst the values in the last column of each section is satisfactory. The values of *K* indicate that the combining power of the halogen ion is not entirely independent of the associated kation. The

values of  $a'$  are in good agreement with those anticipated from considerations of the available data on the salting-out effect.

From the data for hydriodic acid, it is seen that  $K$  is approximately constant for dilute solutions, but, as the last determination shows, tends to decrease at higher concentrations, probably as the result of the formation of higher polyiodides. This behaviour is in agreement with the existing data on the solubility of iodine in solutions of iodides.

It is interesting to compare the  $a'$  and  $K$  values for the three halogens. Taking the sodium salt as representative, we find for  $K$ , chloride, 12.0; bromide, 1.45; iodide, 0.025, and for  $a'$ , chloride, 0.00575; bromide, 0.0042; iodide, nil. These values indicate that the tendency to form polyhalides increases and the salting-out power decreases with increasing atomic weight.

Attempts were made to determine the solubility of iodine in solutions of fluorides. It was found, however, that the solubility increased with the period of agitation, due to reaction between iodine and fluoride with production of iodide and development of acidity. The solubility measurements were therefore abandoned, but it is hoped to investigate this particular reaction in the future.

*Influence of Inert Salts.*—The following data refer to the changes in solubility at 25° due to the addition of inert salts when the concentration of halides remains fixed. The salts chosen were sodium nitrate and sulphate, the appropriate values of  $a'$  (*viz.*, 0.00296 and 0.0180 respectively) being taken from an earlier paper. Under the experimental conditions, the salting-out in the case of solutions containing iodides is entirely due to the added salt only; but with solutions containing bromide, this is in some degree responsible for the salting-out. To determine the magnitude of the latter effect, it was assumed that the bromide present had the same effect as an amount of sodium sulphate equal to the concentration of bromide multiplied by the ratio of the  $a'$  values concerned. Thus, 9.25 mols. of sodium bromide =  $9.25 \times 0.0042/0.0180 = 2.16$  mols. of sodium sulphate. The first column of Table II gives the concentration of added salt, the second the observed solubility, the third the calculated concentration of free iodine, and the last the value of  $K$  according to the mass-law expression. All concentrations are expressed as mols./1000 mols. of water.

A consideration of the data shows that the value of  $K$  is not constant: with bromide it decreases, and with iodide it passes through a maximum. The value undergoes no serious variation, however, and in view of the assumptions made and the high salt concentrations involved, the approximate constancy cannot be regarded as other than satisfactory. The numbers show that

TABLE II.

Sodium bromide-sodium sulphate. Sodium iodide-sodium nitrate.

[NaBr] = 9.245; log $s$ = log $s_0$ - 0.018([Na <sub>2</sub> SO <sub>4</sub> ] + 2.16).				[NaI] = 0.4938; log $s$ = log $s_0$ - 0.00296[NaNO <sub>3</sub> ].			
[Na <sub>2</sub> SO <sub>4</sub> ].	100 S.	100 s.	K.	[NaNO <sub>3</sub> ].	10 S.	100 s.	100 K.
0.00	16.02	2.18	1.43	0.0	2.670	2.38	2.45
6.42	12.48	1.67	1.41	12.0	2.526	2.19	2.50
12.84	9.82	1.28	1.37	24.0	2.383	2.02	2.55
19.26	7.60	0.979	1.36	36.0	2.230	1.86	2.63
25.68	5.97	0.751	1.32	48.0	2.087	1.72	2.71
				60.0	1.957	1.58	2.76
				120.0	1.480	1.05	2.72
				180.0	1.131	0.698	2.55

Sodium iodide-sodium sulphate.

[NaI] = 0.4938; log $s$ = log $s_0$ - 0.0180[Na <sub>2</sub> SO <sub>4</sub> ].							
[Na <sub>2</sub> SO <sub>4</sub> ].	10 S.	100 s.	100 K.	[Na <sub>2</sub> SO <sub>4</sub> ].	10 S.	100 s.	100 K.
6.0	2.290	1.86	2.50	24.0	1.411	0.880	2.40
12.0	1.938	1.45	2.54	30.0	1.179	0.686	2.37
18.0	1.630	1.13	2.55				

sodium sulphate is about five times as efficient as sodium nitrate in repressing the tendency to form tri-iodide.

It is interesting to compare some of our mean values of  $K$  for chloriodides with those for corresponding chlorobromides, obtained with relatively dilute solutions by partition measurements, and recalculated to our units of concentration (all the data relate to 25°, except that for HClBr<sub>2</sub> which relates to 30°):

	HClI <sub>2</sub> .	KClI <sub>2</sub> .	MgCl <sub>2</sub> I <sub>2</sub> .	BaCl <sub>2</sub> I <sub>2</sub> .	HClBr <sub>2</sub> .	KClBr <sub>2</sub> .	MgCl <sub>2</sub> Br <sub>2</sub> .	BaCl <sub>2</sub> Br <sub>2</sub> .
$K$	10.0	12.2	10.2	11.2	12.8*	13.1†	13.0‡	13.1‡

\* Rây and Sarkar, *loc. cit.* † Jakowkin, *Z. physikal. Chem.*, 1896, **20**, 19.  
‡ Lancaster, J., 1924, **125**, 2038.

From an examination of the above it is apparent that the chloro-dibromides and -di-iodides are dissociated to approximately the same extent, the latter being slightly more stable. The  $K$  value for HClBr<sub>2</sub> at 25° would be somewhat lower than that at 30°; it is thus seen that the  $K$  values for the acids are, in general, somewhat lower than those for the corresponding salts, indicative of the greater stability of the acid complexes. Similar behaviour is observed with the tri-iodides, the  $K$  values at corresponding concentrations being  $2.25 \times 10^{-2}$  for acid and  $2.45 \times 10^{-2}$  for the sodium salt. Jakowkin (*loc. cit.*) and Dawson (J., 1901, **79**, 238) obtained similar results by partition measurements.

*Experimental.*—Iodine was purified by customary methods and the electrolytes used were of good quality. The usual precautions were taken in determining solubilities.

*Conclusions.*

The data presented may be said to have established the fact that the solubility of iodine in solutions of halides is the result of two opposing effects—the tendency to form polyhalides and the simple salting-out effect. The observed solubility is dependent on the relative magnitude of these effects. With iodides the salting-out effect is negligible, but with bromides and especially with chlorides it is of considerable importance. These considerations do not apply to the halogen acids, which possess little or no salting-out action. It has, however, been shown in numerous investigations of the salting-out effect that the behaviour of acids is quite different from that of the corresponding salts, so the present anomaly is scarcely surprising.

Brönsted and Pedersen (*Z. physikal. Chem.*, 1923, **103**, 307) have made some measurements of the tri-iodide equilibrium by the solubility method, using as solvent a 1.65*N*-potassium chloride solution, and their value for the mass-law expression has been not infrequently quoted and used by others. These authors assumed that iodine dissolved in the aqueous solution of potassium chloride is entirely present as free iodine. Their *K* value is therefore considerably in error. When suitable corrections are made for the disturbing effect of polyhalide formation, it is found that the resulting value of *K* is approximately the same as when the solvent is water.

Our thanks are due to the Government Chemist, Sir Robert Robertson, F.R.S., for providing facilities for the work to be carried out and for permission to publish these results.

THE GOVERNMENT LABORATORY,  
LONDON, W. C. 2.

[Received, January 16th, 1929.]

---