CCLXXXIX.—*Polyiodide Equilibrium in Aqueous and Salt Solutions.*

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THERE is abundant evidence to show that the dissolution of iodine in solutions of iodides involves the formation of polyiodides, and that in dilute solutions the whole of the combined iodine is present as tri-iodide. Consequently, saturation of dilute solutions of iodides with iodine involves the establishment of the equilibrium $I' + I_2 \rightleftarrows I_3'$. When active masses are identified with actual concentrations the equilibrium expression is $K = [I'] \times [I_2]/[I_3']$. If the solutions are dilute, the concentration of free iodine may be assumed to be constant and equal to the solubility in the pure solvent.

The measurements now recorded have reference to the solubility of iodine at 25° in solutions of sodium iodide, the concentrations of which were varied between fairly wide limits, (*a*) pure water and (*b*) a $1{\cdot}698M_w$-sodium sulphate solution being used as solvents. The relevant data are in Tables I and II, all concentrations being expressed as mols. per 1000 g. of water, since this mode of expression has already been found satisfactory in correlating solubility measurements in aqueous and concentrated salt solutions (J., 1925, **127**, 2861). The solubility data have been utilised on the assumption that the only polyiodide present is the tri-iodide, and that the iodide and the tri-iodide have no influence on the solubility of iodine as such. The concentration of tri-iodide is then given by the difference between the observed solubility s and the solubility s_0 in the iodide-free solvent. The concentration of uncombined iodide is the difference between the initial concentration of iodide c and that of the tri-iodide. The last column gives the values of K. Iodide and polyiodide are assumed to be completely ionised in both media.

TABLE I.

Solvent, water; $s_0 = 1{\cdot}324 \times 10^{-3}$.

$c \times 10^3$.	$s \times 10^3$.	$K \times 10^3$.	$c \times 10^3$.	$s \times 10^3$.	$K \times 10^3$.
0·392	1·494	1·7	47·20	24·66	1·353
0·7838	1·676	1·63	97·88	50·04	1·336
1·959	2·260	1·447	221·9	116·1	1·235
3·918	3·199	1·442	358·0	192·9	1·150
7·838	5·126	1·403	604·4	349·1	0·977
19·59	10·96	1·366	1135	757·5	0·664

TABLE II.

Solvent, 1·698M_w-sodium sulphate; $s_0 = 3{\cdot}784 \times 10^{-4}$.

$c \times 10^3$.	$s \times 10^3$.	$K \times 10^3$.	$c \times 10^3$.	$s \times 10^3$.	$K \times 10^3$.
0·251	0·413	2·2	52·77	11·97	1·346
0·655	0·497	1·71	65·34	14·79	1·325
1·431	0·666	1·502	66·22	15·13	1·321
3·271	1·048	1·472	100·6	23·17	1·293
6·531	1·738	1·439	154·2	37·79	1·181
12·74	3·063	1·416	207·8	53·59	1·097
26·19	6·031	1·375	347·7	101·6	0·919
52·53	11·90	1·347	572·9	203·5	0·689

A consideration of the data shows that the value of K is not constant, the variation being such as to indicate that the tendency to form higher polyiodides (*e.g.*, pentaiodide) increases with increasing initial concentration of iodide. The value of K for the two series follows the same course, but changes relatively very slowly between $c = 0{\cdot}002$ and $0{\cdot}1$. It is in this region that the results are most suitable for correlating the two series of measurements, since in these dilute solutions practically the whole of the combined iodine may be assumed to be present as tri-iodide, and K should be constant. Actual constancy is, of course, not observed, but the magnitude of K is approximately the same in both series and the drift in the value is small. In view of the nature of the assumptions involved, this approximate agreement with the requirements of the mass-law equation is not unsatisfactory and supports the view that the relation between active masses and actual concentrations is much closer than would be anticipated from considerations of the theory of activities. The value of the ratio $[\mathrm{I}']/[\mathrm{I}_3']$ is about 1·05 for the sulphate-free solutions and about 3·5 for the sulphate solutions. Apart from the fact that it indicates that the extent of polyiodide formation is greatly depressed in presence of sulphate, the difference between these values is also of interest from the point of view of the theory of activities. Although, in the absence of values for the activity coefficients concerned, it is impossible to make a quantitative prediction, a consideration of the ideas associated with the theory of activities leads to the conclusion that within this concentration range the value of this ratio should be practically independent of the presence of added salts.

Results in extremely dilute solutions are considerably influenced by small errors in the actual determination of the dissolved iodine, but it is considered that the observed effects are real.

Jakowkin (*Z. physikal. Chem.*, 1896, **20**, 19), Dawson (J., 1901, **79**, 238), and Pearce and Eversole (*J. Physical Chem.*, 1924, **28**, 245) have investigated the partition of iodine between solutions of iodides and an organic solvent and found that K is approximately constant for dilute solutions, but not for concentrated solutions. This is clearly shown by the data presented in Table III, which refer to the equilibria established when iodine is distributed between carbon tetrachloride and fairly concentrated solutions of sodium iodide; under C and W are recorded the concentrations of iodine (mols./1000 g. of solvent) in the carbon tetrachloride and aqueous phases, respectively, and under $[\mathrm{I}_2]$ are tabulated the concentrations of the uncombined iodine in the aqueous layer, calculated from a knowledge of the distribution ratio. The last column contains the values of K computed on the assumption that the only polyiodide present is the tri-iodide.

The ratio in which iodine is distributed between water and carbon tetrachloride was first determined :

$C \times 10^3$ (approx.) ...	57	46	25	21	10
Partition ratio	54·8	54·2	53·5	53·6	53·2
				53·5	

A curve was then drawn from the data, the assumption being made that neither the iodide nor the polyiodide has any influence on the value of the distribution ratio : as the salting-out effect of the iodide ion is practically nil, this assumption is not unreasonable.

The values of K apparently tend towards constancy when the concentration of iodine is small. The data indicate the presence of polyiodides more complex than the tri-iodide in the more concentrated solutions.

TABLE III.

Sodium iodide = 0·9940M_w.				Sodium iodide = 0·4933M_w.			
$C \times 10^3$.	$W \times 10^2$.	$[I_2] \times 10^5$.	$K \times 10^3$.	$C \times 10^3$.	$W \times 10^2$.	$[I_2] \times 10^5$.	$K \times 10^3$.
0·356	0·444	0·665	1·49	0·663	0·414	1·240	1·47
0·840	1·047	1·570	1·478	3·684	2·258	6·885	1·440
1·875	2·331	3·503	1·462	8·083	4·853	15·13	1·390
3·510	4·318	6·533	1·440	9·067	5·430	16·94	1·375
3·592	4·452	6·713	1·434	20·39	11·31	38·12	1·287
7·236	8·872	13·52	1·382	36·42	17·34	67·82	1·259
16·86	20·12	31·56	1·247	47·42	21·24	87·50	1·168
21·61	25·81	40·41	1·154	49·82	21·99	91·75	1·150
33·05	36·56	61·39	1·055				
53·08	51·36	97·23	0·913				

Experimental.—Iodine, sodium sulphate, and carbon tetrachloride were purified by customary methods. The sodium iodide contained no impurity other than water. The usual precautions were taken in determining solubilities and distribution ratios.

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