

CCCXCVI.—*The Salting-out Effect. The Influence of Electrolytes on the Solubility of Iodine in Water.*

By JOHN STANLEY CARTER.

THE fact that the solubility of non-electrolytes in water is lowered by addition of electrolytes has attracted considerable attention, and various empirical or semi-empirical equations have been put forward to express the relation between the change in the solubility and the concentration of the electrolyte. In most of the earlier work, the latter rarely exceeded one gram-equivalent per litre, and over this range the solubility lowering is approximately proportional to the concentration of the electrolyte. Experiments in which the electrolyte concentration was varied over a wider range show, however, that this proportionality by no means holds.

Measurements of the solubility of phenol in sodium sulphate solutions (Dawson, *J. Soc. Chem. Ind.*, 1920, **39**, 151r), of the solubility of ethyl ether in sodium chloride solutions (Thorne, *J.*, 1921, **119**, 262) and of quinol and quinone in various salt solutions (Linderstrom-Lang, *Compt. rend. Trav. Lab. Carlsberg*, 1924, **15**, 4) show that, over a considerable concentration range, the influence of electrolytes on the solubility of non-electrolytes can be expressed by the exponential formula  $s = s_0 e^{-kc}$ , first suggested by Setschenov (*Z. physikal. Chem.*, 1889, **4**, 117), where  $s_0$  and  $s$  denote respectively the solubilities of the non-electrolyte in water and in a salt solution, the concentration of which, expressed in terms of the volume of the solution, is represented by  $c$ , and  $k$  is a constant characteristic of the dissolved electrolyte.

In the present investigation, the validity of the exponential formula has been tested by measurements of the solubility of iodine in aqueous solutions, the concentration of which ranged up to saturation at the temperature of observation. In previous measurements (Jakowkin, *Z. physikal. Chem.*, 1896, **20**, 19; Dawson, *ibid.*, 1906, **56**, 606), in which the salting-out effect was examined by determining the partition of iodine between carbon disulphide and aqueous salt solutions, the concentration of the electrolytes was varied only between comparatively narrow limits. The numbers thus obtained are consequently of little use for the present purpose.

The experimental data now recorded have reference to the effects produced by sodium nitrate, sulphate, and dihydrogen phosphate and by nitric and sulphuric acids. These are all readily soluble in water and do not react with iodine. The salts of weak acids are generally inadmissible on account of hydrolysis, and the halogen

salts are unsuitable because of the readiness with which they form perhalogen compounds. Various other salts had to be rejected on account of their oxidising properties, which introduce difficulties in the estimation of the iodine by means of thiosulphate. Measurements were also made with sodium chloride, allowance for the effect of perhalide formation being made in a manner which will be described later.

#### EXPERIMENTAL.

Iodine and the salts employed were purified by the customary methods. Since Bray (*J. Amer. Chem. Soc.*, 1910, **32**, 932) has shown that the hydrolysis of iodine is repressed in faintly acid solution, the values of  $p_H$  for the solutions of sodium nitrate, sulphate and chloride were adjusted to 5–5.5 by the addition of small quantities of the corresponding acids.

In the determinations of solubility, every precaution was taken to ensure complete saturation, efficient filtration, and to prevent loss of iodine by volatilisation. In the experiments with nitric and sulphuric acids, the dissolved iodine was extracted from a known weight of the saturated solution by repeated shaking with carbon tetrachloride; the latter was then freed from mineral acid by shaking with dilute aqueous sodium acetate. Freshly prepared 0.01*N*-sodium thiosulphate was used for the titrations. In order to obtain solutions of sufficiently high salt concentration, the first experiments (with sodium sulphate) were made at 35°, but subsequent measurements were made at 25° and 10°.

Determinations of the solubility of iodine in water with a slight acid reaction ( $p_H$  5) gave the following results (millimoles per litre) :

At 10°	.....	0.835	0.837	
At 25°	.....	1.319	1.321	1.322
At 35°	.....	1.808	1.809	

The values at 25° agree with the value, 1.320, recorded by Bray (*loc. cit.*), but are lower than that, 1.334, given by Hartley and Campbell (*J.*, 1908, **93**, 741), which is considered by Bray to be a little too high.

In Table I the solubilities experimentally determined are compared with those calculated from the exponential equation, which was put into logarithmic form,

$$\log s = \log s_0 - k'c \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the value of the constant  $k'$  being given by the slope of the line in the graph of  $\log s$ -concentration.

In the application of this formula to the results obtained for the more concentrated solutions, the mode of expressing the concen-

tration of the dissolved electrolyte is a matter of great importance. The range of validity of the logarithmic formula is very much greater when the concentration of the electrolyte is referred to a fixed weight of water than it is when the concentration is expressed in terms of a fixed volume of solution. In the latter case, deviations appear when the concentration of the electrolyte reaches 2—3 gram-equivalents per litre, and the magnitude of these deviations increases continuously with the concentration of the dissolved salt.

For this reason, the concentrations of the electrolytes,  $c$ , represent the number of moles (equivalents in the case of sodium sulphate) per 1000 moles of water. The solubility of iodine is expressed in the same way,  $s'$  being the measured value and  $s$  the value calculated from equation (1). The values of  $s_0$  at 25° and 35°, respectively, are 0.0238 and 0.0327. The ordinary weight percentage composition of the various solutions is given under " $w\%$ ."

TABLE I.

Sodium Nitrate at 25°.  $k' = 0.00296$ .

$w\%$	$s' \times 10^3$	$s \times 10^3$	$w\%$	$s' \times 10^3$	$s \times 10^3$	$w\%$	$s' \times 10^3$	$s \times 10^3$
5.89	22.2	21.8	25.67	14.5	14.5	39.83	9.11	9.16
11.10	20.2	19.9	29.75	12.5	12.9	44.16	7.53	7.60
15.31	18.5	18.4	35.43	10.8	10.8			

Sodium Nitrate at 35°.  $k' = 0.00243$ .

1.98	32.7	32.3	15.89	26.8	26.2	50.1	10.0	9.94
3.48	32.0	31.4	29.06	20.1	20.1			
6.85	30.2	30.0	40.17	14.3	14.7			

Sodium Sulphate at 25°.  $k' = 0.0090$ .

5.66	17.3	17.4	16.24	8.55	8.60	19.66	6.56	6.59
8.64	14.4	14.5						

Sodium Sulphate at 35°.  $k' = 0.0087$ .

1.05	31.8	31.1	9.13	20.2	19.8	25.31	5.78	5.85
2.31	29.3	29.0	14.79	13.3	13.5	31.80	3.05	3.06
4.93	25.2	25.2	21.10	8.39	8.42	33.1	2.58	2.66

Sodium Dihydrogen Phosphate at 25°.  $k' = 0.0062$ .

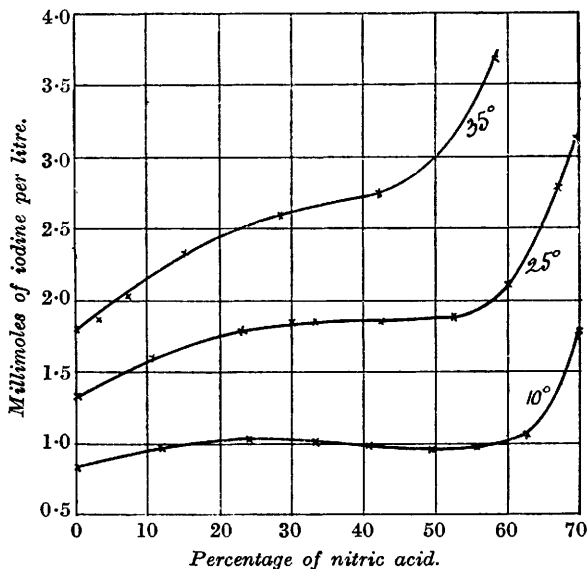
7.53	19.4	20.0	26.40	11.1	11.1	45.26	[1.8]	3.98
14.40	16.1	16.6	31.66	8.93	8.85			
20.64	13.5	13.7	41.06	[4.3]	5.35			

Comparison of the observed and the calculated solubilities of iodine shows that there is close agreement over the entire range of possible salt solutions in the case of sodium nitrate and sulphate; and also in the case of sodium dihydrogen phosphate, excepting the two most concentrated solutions, for which the measured solubilities are smaller than the calculated values. This divergence

suggests the operation of some factor other than that responsible for the normal salting-out effect. An explanation may possibly be found in the acid character of the electrolyte in this case, for, as will be seen later, the behaviour of nitric and sulphuric acids is quite different from that of the corresponding salts.

Iodine dissolved in a solution of sodium chloride exists in part as free iodine and partly in the form of a complex polyhalide. The influence of polyhalide formation is such that the solubility of iodine passes through a maximum when the concentration of the sodium chloride increases (Table II, column 2).

FIG. 1.



*Solubility of iodine in aqueous solutions of nitric acid.*

In order to obtain the value of  $k'$  in equation (1) for sodium chloride, it was assumed that the polyiodide equilibrium  $\text{NaCl} + \text{I}_2 \rightleftharpoons \text{NaClI}_2$  conforms to the requirements of the mass-law equation and that the variations in the value of the expression  $[\text{NaCl}][\text{I}_2]/[\text{NaClI}_2] = a$  are due to the salting-out effect of the sodium chloride on the iodine. By plotting these values against the sodium chloride concentration and extrapolating to zero salt content, a limiting value of  $a = 12.0$  was obtained, and this was assumed to be the true value of the mass-law constant. In calculating the concentrations of free and combined iodine from this number, advantage was taken of the fact that the total salt concentration may be

substituted for [NaCl] in the mass-law equation without introducing any serious error.

TABLE II.

Sodium Chloride at 25°.  $k' = 0.00575$ .

% NaCl.	Conc. of total dissolved iodine.	Conc. of combined iodine = $[\text{NaClI}_2]$ .	Conc. of free iodine = $s'$ .	$s$ .
4.52	0.04403	0.02405	0.0200	0.0197
7.43	0.05295	0.03560	0.0174	0.0172
14.14	0.06289	0.05085	0.0121	0.0122
20.31	0.06311	0.05475	0.00835	0.00843
23.15	0.06105	0.05405	0.00700	0.00698
25.95	0.05790	0.05210	0.00580	0.00571

The close agreement between the numbers in the last two columns of Table II affords clear evidence that the salting-out effect of sodium chloride is exactly similar to that of the other salts examined when due allowance is made for the disturbing influence of polyiodide formation.

Tables III and IV contain the data for solutions of nitric and sulphuric acid. As there is no simple relation between the solubility of the iodine and the concentration of the dissolved acid, the concentration of the iodine is expressed in millimoles per litre ( $b$ ).

TABLE III.

Solubility of Iodine in Nitric Acid Solutions.

10°.		25°.		35°.	
% HNO <sub>3</sub> .	$b$ .	% HNO <sub>3</sub> .	$b$ .	% HNO <sub>3</sub> .	$b$ .
11.80	0.969	10.91	1.60	3.31	1.87
23.88	1.035	23.16	1.79	6.50	2.04
32.35	1.020	30.05	1.85	15.50	2.33
40.82	0.985	33.62	1.86	28.72	2.60
49.57	0.952	42.28	1.85	42.63	2.75
55.82	0.962	52.77	1.89	43.13	2.73
64.30	1.08	60.36	2.10	58.34	3.68
70.00	1.78	63.81	2.36		
		67.41	2.78		
		69.65	3.12		
		72.60	3.94		

TABLE IV.

Solubility of Iodine in Sulphuric Acid Solutions at 25°.

% H <sub>2</sub> SO <sub>4</sub> .	$b$ .	Colour of sat. sol.	% H <sub>2</sub> SO <sub>4</sub> .	$b$ .	Colour of sat. sol.
11.87	1.02	Brown.	40.42	0.545	Brown with pink tinge.
22.72	0.820	Brown.	59.53	0.380	Pink with brown tinge.
33.25	0.615	Brown.	72.04	0.270	Pink.
			87.37	0.200	Pink.

The somewhat complicated relations exhibited by the data for solutions of nitric acid are more clearly represented in the diagram.

The curve for 35° shows that the solubility increases continuously with the concentration of the acid, but the rate of increase diminishes markedly in the middle portion of the curve. The factors which give rise to this diminution have obviously a much greater influence at lower temperatures, in that the curve for 10° shows a maximum and a minimum. At 25°, the relations are intermediate in character; the form of the curve corresponds with the behaviour expected from the results at 10° and 35°. In connexion with these results, it may be noted that solutions containing more than 60%  $\text{HNO}_3$ , although brown when viewed in bulk, have a distinctly pink shade. In sulphuric acid solutions, the solubility of iodine decreases continuously as the concentration of the acid increases from 0 to 87%, but the data do not conform at all to the requirements of the logarithmic formula which expresses the salt effects. The colour of the solutions changes gradually from brown to pink.

There is apparently no connexion between the effects observed with nitric and sulphuric acid solutions and those obtained for neutral salt solutions. If the mineral acids exert any action which is comparable with that of the salts, it is more or less completely masked by other effects which play no part in the case of the neutral salts. It seems probable that the solvent power of nitric acid for iodine is in part responsible for the complicated behaviour exhibited by nitric acid solutions.

Recent measurements (Manchot, Jahrstorper, and Zepfer, *Z. anorg. Chem.*, 1924, **141**, 45) of the solubility of nitrous oxide in aqueous solutions also have shown that the influence of the free mineral acids is totally different from that of the corresponding salts.

My thanks are due to Professor H. M. Dawson for suggesting the lines of this research and for his helpful criticism and advice.

UNIVERSITY OF LEEDS.

[Received, October 30th, 1925.]

---