XVIII.—*The Salting-out Effect. Influence of Electrolytes on the Solubility of* m-*Cresol in Water.*

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MEASUREMENTS of the solubilities of certain non-electrolytes in solutions of various salts have shown that, provided interaction between non-electrolyte and salt be excluded, the relation between the solubility s and the salt concentration c is represented by the exponential equation $s = s_0 e^{-kc}$, where s_0 has a value equal to, or approximating to, the solubility in the pure solvent, and k is a constant which measures the salting-out effect of the salt (Setschenow, *Z. physikal. Chem.*, 1889, **4**, 117; Dawson, *J. Soc. Chem. Ind.*, 1920, **39**, 151T; Thorne, J., 1921, **119**, 262; Linderström-Lang, *Compt. rend. Trav. Lab. Carlsberg*, 1924, **15**, 4; Carter, J., 1925, **127**, 2861). When the salts are replaced by the corresponding acids, the above relationship is no longer valid, the solubility of the non-electrolyte often varying in a very complex manner with increasing concentration of acid (Manchot, Jahrstorper, and Zepter, *Z. anorg. Chem.*, 1924, **141**, 45; Carter, *loc. cit.*).

The measurements now recorded relate to the effects produced by the chlorides and sulphates of sodium and magnesium, the corresponding acids, and mixtures of phosphoric acid and sodium phosphate on the solubility of *m*-cresol in water at 25°. The *m*-cresol used had m. p. 9·5° and was obtained by distillation of a sample which had undergone a rigorous process of purification and in which the only impurity appeared to be water. Precautions were taken to ensure saturation and efficient filtration. *m*-Cresol was determined by the bromide–bromate method (Fox and Barker, *J. Soc. Chem. Ind.*, 1920, **39**, 169T). Electrolytes were determined by standard methods. The solubility of *m*-cresol in water at 25° was found to be 2·27 g./100 g. of solution, or 3·87 mols. per 1000 mols. of water, duplicate experiments giving exactly the same figure.

In the two following tables c represents the number of equivalents of electrolyte per 1000 mols. of water. The solubility of *m*-cresol is expressed in the same way, s being the measured value and s' the value calculated from the exponential equation, which was put into the form $\log s' = \log s_0 - k'c$, the value of the constant k' being given by the slope of the line on plotting $\log s$ as a function of c. On constructing such graphs from the data for the four salts investigated, it was found that the resulting lines did not cut the solubility axis at a point corresponding with the solubility of *m*-cresol in pure water, but at points corresponding with a somewhat lower

value.   Differences between the measured and extrapolated values for the solubility in the pure solvent were observed by Dawson with phenol and by Thorne with ether.   Extrapolated values s'_0 have been used in the calculation of the s' values given, which agree satisfactorily with the observed values (see Table I).

TABLE I.

$c.$	$s.$	$s'.$	$c.$	$s.$	$s'.$
		Sodium chloride, $s'_0 = 3{\cdot}61$, $k' = 0{\cdot}0101$.			
8·20	3·03	2·99	45·84	1·25	1·25
15·89	2·54	2·50	54·38	1·04	1·02
27·09	1·89	1·92	68·26	0·73	0·74
42·19	1·38	1·36	89·80	0·50	0·45
		Magnesium chloride, $s'_0 = 3{\cdot}61$, $k' = 0{\cdot}00815$.			
12·77	2·87	2·84	55·49	1·28	1·28
26·87	2·19	2·18	61·95	1·11	1·13
42·65	1·59	1·62	66·59	1·04	1·03
		Sodium sulphate, $s'_0 = 3{\cdot}80$, $k' = 0{\cdot}01405$.			
6·08	3·08	3·12	32·43	1·36	1·33
14·22	2·39	2·40	41·88	0·97	0·98
16·29	2·24	2·24	62·13	0·52	0·51
		Magnesium sulphate, $s'_0 = 3{\cdot}80$, $k' = 0{\cdot}0119$.			
6·86	3·13	3·15	29·97	1·69	1·67
14·22	2·58	2·58	47·74	1·00	1·03
24·23	1·97	1·96	80·44	0·37	0·42

Although the solubility of m-cresol in solutions of hydrochloric and of sulphuric acids (Table II) decreases in a regular manner with increasing concentration of acid, the exponential law is not obeyed ;

TABLE II.

Hydrochloric acid.

c	....	9·62	20·22	40·83	49·09	66·40	77·00
s	....	3·39	3·17	2·83	2·80	2·71	2·67

Sulphuric acid.

c	....	8·60	18·11	38·84	52·35	61·86	83·37
s	....	3·39	3·09	2·57	2·34	2·14	1·86

moreover, the solubility is greater than in solutions of the corresponding salts, and, as in the case of the salts, the salting-out efficiency of the sulphate ion is greater than that of the chloride ion.

In order to see how the magnitude of the solubility lowering produced by an acid electrolyte is altered by the progressive replacement of the dissociable hydrogen atoms by metal atoms, measurements were made of the solubility of m-cresol in phosphoric acid–sodium phosphate mixtures characterised by the approximate constancy of the concentration of phosphate ion.   Actually the concentrations c of these solutions varied between 0·997 and $1{\cdot}024N_w$. Assuming that over this small range of concentration-differences the

solubility lowering is proportional to concentration, the values of $l = 100(s_0 - s)/s_0 c$ were calculated. The value of l thus represents the percentage lowering of the solubility produced by an electrolyte which may be regarded as possessing the formula $H_{3-x}Na_xPO_4$ at a concentration of $1 \cdot 0 N_w$. The data are presented in Table III.

TABLE III.

Solution.	A.	B.	C.	D.	E.	F.
x	0·0	0·512	1·011	1·512	2·008	2·845
l	10·5	18·6	25·1	29·9	33·3	$-65\cdot4$

The greatly increased solubility of m-cresol in solution F is due to its reaction with the alkali present to form sodium m-tolyloxide. Solution E had a slightly alkaline reaction (p_H 9), but in view of the extremely small dissociation constant of m-cresol, there can have been practically no formation of tolyloxide. Neglecting the result for the most alkaline solution, a smooth curve is obtained on plotting l against x. The value of the ratio $\Delta l/\Delta x$ decreases as x increases.

The fact that the solubility lowerings produced by acids are much smaller than those produced by the corresponding salts shows that the salting-out powers of ions of the same valency do not necessarily increase with decreasing size of the ions, although this is usually the case, as Glasstone, Dimond, and Jones have pointed out in reference to the effect of various salts on the solubility of ethyl acetate (J., 1927, 2935).