XXXII.—*The Solubility of Ethyl Ether in Solutions of Sodium Chloride.*

By PERCY CYRIL LESLEY THORNE.

THE lowering of the solubility of ether in water by the presence of dissolved substances in the water has been known for a very long time.   In particular, the addition of sodium chloride to aqueous liquids which are to be extracted with ether is commonly adopted as a measure of economy in the laboratory.   Quantitative experiments on the precise effect of the addition of sodium chloride to the aqueous layer are, however, only occasionally met with in the literature (Euler, *Zeitsch. physikal. Chem.*, 1904, **49**, 303; Bennett, *Pharm. J.*, 1912, [iv], **35**, 146; Thorin, *Zeitsch. physikal. Chem.*, 1915, **89**, 685; Linde, *Arkiv. Kem. Min. Geol.*, 1917, **6**, No. 20, 1).   It seemed desirable, therefore, in view of the practical importance of this particular system and of its possible theoretical interest, to determine the solubility of ether in salt solutions for a complete range of concentrations of sodium chloride.

Experimental.

Determinations of solubility were made at 15° and at 25° for a number of concentrations of sodium chloride.

The ether used was distilled, washed with a solution of potassium permanganate and then with water, dried for a week over powdered calcium chloride, and finally over sodium. It was then redistilled and kept over sodium. It was obviously more essential to exclude alcohol than water from the ether used, which gave no iodoform reaction and no hydrogen with sodium.

Twice-distilled water was used. The purest sodium chloride obtainable was recrystallised from water, and found to be neutral and free from calcium and magnesium, sulphates, etc.; a concentrated solution was made, and diluted as required.

About 150 c.c. of the salt solution were covered with an excess of ether in a stout, wide-mouthed bottle, which was then vigorously shaken mechanically in the thermostat. Equilibrium was found to be rapidly established under these conditions, but in all cases the shaking was continued for three and a-half to four hours. The temperature remained constant to 0·1°.

A sample was removed from the aqueous layer in the bottle by the following method. The stopper was replaced by a rubber bung fitted with two glass tubes, one passing just through the bung, the other, of narrower bore, reaching to the bottom of the bottle. The end of the longer tube was drawn out to a fine point and sealed, whilst outside the bottle this tube was bent twice at right angles. On inserting the bung, the fine point was broken by contact with the bottom of the bottle, thus admitting the aqueous layer uncontaminated by the ethereal layer. By blowing into the shorter tube, a quantity of the aqueous layer was forced over into the analysis apparatus.

The ether dissolved by the salt solution was estimated by transferring the sample to a small distillation flask containing about 10 c.c. of water, and attached at the side-tube to two U-tubes in series filled with calcium chloride. The whole apparatus was weighed before and after the addition of the sample, then dry air free from carbon dioxide was bubbled through the diluted sample by means of a long tube passing to the bottom of the flask. In this apparatus, the sample was thus immediately diluted to reduce the loss of ether, and the ether estimated by the loss in weight of the whole apparatus, when, after the passage of air for three to six hours, it had become constant.

The sodium chloride was estimated by diluting the liquid remaining in the flask and titrating a suitable volume with silver nitrate.

At least two samples were taken for analysis from each equilibrium mixture, generally on successive days. The results of the duplicate estimation did not vary by more than 2 per cent. of the weight of the ether. The mean is given in each case in the following tables, I at 15°, II at 25°. Both sets of results are plotted in Fig. 1. It can be seen that even small additions of sodium chloride to water decrease the solubility of ether in a

Fig. 1.

Grams of ether dissolved in 100 *grams of solution.*
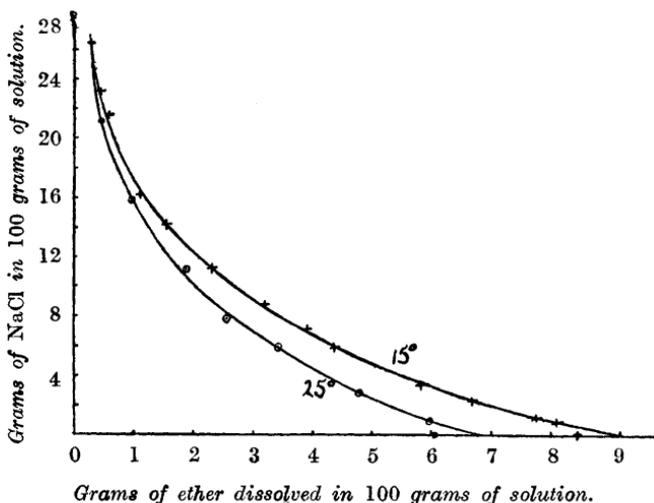
remarkable manner, the value being halved by the presence of 6 per cent. of the chloride.

TABLE I.

15°.

Grams of $NaCl$ (c) in 100 grams of solution.	Grams of ether (s) in 100 grams of solution.	(s) Calc.	Grams of $NaCl$ (c) in 100 grams of solution.	Grams of ether (s) in 100 grams of solution.	(s) Calc.
0·0	8·43 ($= s_0$)	9·16	8·750	3·20	2·99
*0·91	8·10	8·19	11·08	2·32	2·22
1·033	7·73	8·05	14·16	1·55	1·50
2·300	6·67	6·82	16·24	1·11	1·15
3·307	5·81	6·00	21·58	0·577	0·582
5·881	4·37	4·33	23·18	0·454	0·473
7·108	3·91	3·70	26·52	0·307	0·309

* Bennett (*loc. cit.*).

Fig. 2 is obtained by plotting the values of c and $\log_{10} s$ at both temperatures, and the fact that two straight lines are obtained

indicates a relation of the form $\log s = a - kc$, where s is the solubility of ether in brine of concentration c grams in 100 grams of solution, k is a constant depending on the temperature and the nature of the dissolved substance, a is a constant approximately equal to $\log_{10} s_0$, where s_0 is the solubility of ether in pure water. Replacing a by $\log_{10} s_0$, we have $\log s = \log s_0 - kc$, or

$$\frac{1}{c} \log \frac{s_0}{s} = k.$$

The constant k has the value $0 \cdot 0555$ at $15°$ and $0 \cdot 0536$ at $25°$ when logarithms to base 10 are used and concentrations expressed in grams per 100 grams of solution. The solubilities of ether

FIG. 2.
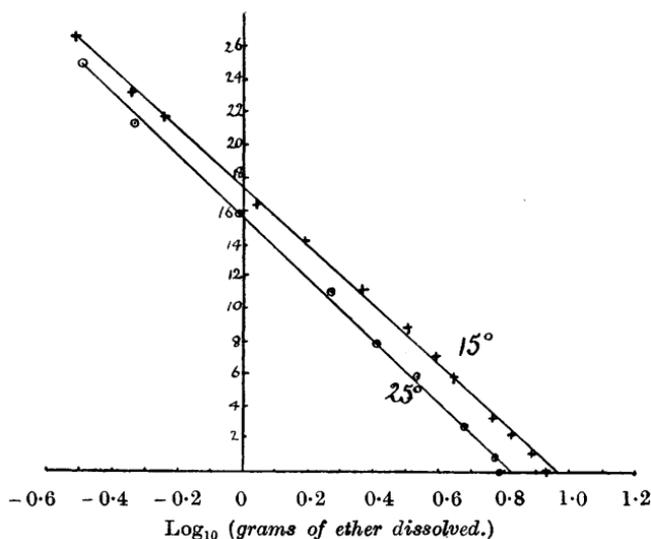
Grams of NaCl *in* 100 *grams of solution.*

Log$_{10}$ (*grams of ether dissolved.*)

TABLE II.

$25°$.

Grams of NaCl (c) in 100 grams of solution.	Grams of ether (s) in 100 grams of solution.	(s). Calc.	Grams of NaCl (c) in 100 grams of solution.	Grams of ether (s) in 100 grams of solution.	(s). Calc.
0·0	6·05	6·76	7·812	2·57	2·57
*0·91	5·96	6·04	11·08	1·88	1·72
2·837	4·78	4·76	15·79	0·979	0·963
5·970	3·41	3·24	21·18	0·463	0·495
			24·90	0·309	0·312

* Bennett (*loc. cit.*).

K*

calculated from the equation are given in column 3 of tables I and II, and the agreement with the observed results is good, except at concentrations below 1 per cent.

This relation has not hitherto been recorded in reference to the system ether–sodium chloride–water. The less extensive values of Linde (*loc. cit.*), when similarly plotted, also give a straight line, but he does not suggest such a relation. Equations of a similar nature have, however, been deduced by several investigators when working with similar systems, for example, Setschenov (*Zeitsch. physikal. Chem.*, 1899, **4**, 117; *Ann. Chim. Phys.*, 1892, [vi], **25**, 226), with various salts and carbon dioxide; Bodländer (*Zeitsch. physikal. Chem.*, 1891, **7**, 308), with alcohol and sucrose; Euler (*Arkiv. Kem. Min. Geol.*, 1903, **1**, 133), with various salts and aniline; Knopp (*Zeitsch. physikal. Chem.*, 1904, **48**, 97), with various salts and hydrogen or nitrous oxide; Dawson (*J. Soc. Chem. Ind.*, 1920, **39**, 151T), with sodium sulphate and phenol. In these systems (except in the case of sucrose–alcohol–water), a non-electrolyte, a gas or liquid of comparatively low solubility, is expelled from the solution by an electrolyte which is fairly soluble. The converse case, in which a slightly soluble electrolyte is made less soluble by the addition of a non-electrolyte of considerable solubility, has been studied for many systems by Rothmund (*Zeitsch. Elektrochem.*, 1908, **14**, 532; *Zeitsch. physikal. Chem.*, 1909, **69**, 523), who found that a similar relation existed. He gives in his second paper a theoretical deduction of the logarithmic law in the two cases, stating it in the general form

$$\frac{1}{c} \log_e \frac{\eta_1}{\eta'_1} = \frac{a}{RT}.$$

Hoffmann and Langbeck (*Zeitsch. physikal. Chem.*, 1905, **51** 385) give two logarithmic expressions of greater complexity to summarise the results of their work on the alteration in solubility in water suffered by benzoic, o-nitrobenzoic, and salicylic acids on the addition of electrolytes and non-electrolytes, respectively.

A logarithmic relation of the type applicable to the salting out of ether appears, therefore, to express the equilibria in a large number of similar systems, and as it can be deduced thermodynamically, is preferable to merely empirical equations of more restricted utility.

The closely related results of some other workers have been plotted in similar fashion by the present author, and straight lines obtained in the following cases:

	Electrolyte.	Non-electrolyte.
Steiner (*Wied. Ann.*, 1894, (2), **52**, 275) ...	Sodium chloride	Hydrogen
Euler (*Zeitsch. physikal. Chem.*, 1904, **49**, 303)	Sulphuric acid	Ether
Kremann (*Monatsh.*, 1910, **31**, 275)	,, ,,	,,
Linde (*Arkiv Kem. Min. Geol.*, 1917, **6**,		
No. 20, 1)	Sodium chloride	Ether
	Sodium acetate	,,
	Sodium chloride	Ethyl acetate
	Sodium acetate	,, ,,

In no case does the straight line pass accurately through the point obtained for the solubility of the non-electrolyte in water, and the values for low concentrations, when given, do not lie on the line. Euler's values for the system ether–sulphuric acid–water are only given for three concentrations, and are therefore scarcely conclusive; those of Kremann for the same system at 0° range from 16·9 grams to 81·6 grams of sulphuric acid per 100 grams of dilute acid, and, with the exception of the solubility value for pure water, which is particularly distant from the theoretical point, and the value for 49·1 per cent. sulphuric acid, lie very near a straight line.

Without doubt, many other similar systems would give results in accordance with the general equation brought forward in this paper.

TABLE III.

Interpolated Values.

15°.			25°.		
Grams of NaCl (c) in 100 grams of solution.	Grams of ether (s) in 100 grams of solution.	Molecular hydration of NaCl (H).	Grams of NaCl (c) in 100 grams of solution.	Grams of ether (s) in 100 grams of solution.	Molecular hydration of NaCl (H).
0	8·43 (s_0)	—	0	6·05 (s_0)	—
1	8·06	[24·9]	1	5·98	[0·52]
2	7·09	[22·6]	2	5·28	[17·4]
4	5·49	25·1	4	4·13	22·6
5	4·84	24·4	5	3·65	22·6
6	4·26	24·1	6	3·22	22·1
8	3·30	21·5	8	2·52	20·5
10	2·55	19·4	10	1·97	18·7
15	1·35	15·0	15	1·11	14·4
20	0·71	11·6	20	0·57	11·5
25	0·37	9·2	25	0·31	9·1

In seeking for the cause of the lowering of solubility one comes, naturally, to the idea of hydration of the salt in solution. Taking as basis the suggestion of Philip (T., 1907, **91**, 711) that solvent thus attached to the solute is unavailable for the solution of a second solute, the molecular hydration of the sodium chloride has been calculated for the interpolated values given in table III. The water required to dissolve the observed quantity of ether was

K* 2

calculated in each case from the solubility of ether in water, and the remaining water actually present was assumed to be used in hydrating the sodium chloride.

The values of H are given as molecules of water per molecule of sodium chloride, and are obtained by substitution in the expression

$$H = \frac{58 \cdot 5}{18} \left(\frac{100}{c} \cdot \frac{s_0 - s}{s_0} - 1 \right).$$

The values obtained for the hydration at low concentrations of sodium chloride (below 4 per cent.) are obviously affected by other factors. For greater concentrations, the molecular hydration is considerably larger than that obtained by various methods by other workers. Thus Biltz (*Zeitsch. physikal. Chem.*, 1902, **40**, 220) obtained 19 and 25 as the hydrations of sodium chloride in $N/2$- and $N/10$-solutions, respectively, using the freezing-point method, and 14·5, 14·8, and 16·3 for $N/1$-, $N/2$-, and $N/4$-solutions, respectively, at 20° from the reduction in solubility of phenyl-thiocarbamide (*Zeitsch. physikal. Chem.*, 1903, **43**, 41).

The explanation may be that the ether is itself hydrated in aqueous solution.

It is hoped by wider application of the relations discussed in this paper to elucidate further the vexed problems of solution; work on the salting out of certain dyestuffs is now being carried on.

Summary.

(1) The solubility of ethyl ether in solutions of sodium chloride has been determined at 15° and at 25°. It decreases with increasing concentration of the salt.

(2) The logarithm of the weight of ether dissolved is found to vary directly with the concentration of sodium chloride, except in dilute solutions.

(3) The expression $\frac{1}{c} \log \frac{s_0}{s} = k$ holds, not only for this system, but for many other similar systems.

(4) The hydration of the sodium chloride has been calculated from these results.

THE SIR JOHN CASS TECHNICAL INSTITUTE,
    JEWRY STREET, ALDGATE, E.C.   [*Received, January* 13*th*, 1921.]