CLIV.—*Selective Solvent Action. Part V. Salting in.*

By Robert Wright.

The mutual lowering of solubility which takes place when an electrolyte and an organic substance are dissolved together in water has been the subject of many investigations (Rothmund, "Löslichkeit und Löslichkeitsbeeinflussung"), and is the basis of the process of "salting out" when an organic compound is driven out of aqueous solution by the addition of a salt. What may be termed "salting in" is the reverse phenomenon, that is, a mutual increase in solubility of electrolyte and organic compound when added to the same solvent, which in this case is not pure water but aqueous alcohol.

In former papers (J., 1922, **121**, 2252; 1923, **123**, 2493; 1925, **127**, 2335) it was shown that the addition of a semi-solute to a mixed solvent raised both the vapour pressure and the freezing point of the constituent in which it was insoluble. Thus sodium chloride (or other salt) raised the alcohol vapour pressure of aqueous alcohol, whilst water raised the freezing-point of benzene in an alcohol–benzene mixture. It was pointed out that this might be explained on the solvate hypothesis : in the alcohol–benzene mixture, we have complexes formed between the two constituents; water, when added, competes with the benzene for the alcohol, forming water–alcohol solvates and decomposing some of the alcohol–benzene solvates, thus leaving the solution richer in free benzene and therefore with a higher freezing-point and benzene vapour pressure.

A corresponding effect might be expected in the case of solubility. The addition of salt to aqueous alcohol should form salt hydrates with a consequent increase in the free alcohol present and a corresponding increase in solvent power for benzene or other organic substances. Conversely, the presence of benzene should increase the solvent power of the mixed solvent for a water-soluble solute.

This effect can readily be demonstrated in a qualitative manner. To 100 c.c. of 50% alcohol, benzene is added 1 c.c. at a time until the solution turns turbid; if sodium chloride is now added to the turbid mixture, the liberated alcohol (due to the removal of water for the formation of salt hydrates) will dissolve the excess of benzene and cause the solution to become clear.

Quantitative determinations of this increase of solubility in 50% (by weight) aqueous alcohol have been made with benzene, carbon tetrachloride, and methyl salicylate as alcohol-soluble solutes, and with sodium chloride, sodium nitrate, potassium chloride, potassium bromide, and potassium nitrate as water-soluble salts. It will be noted that none of the salts crystallises with water of crystallisation.

In the method employed, about 12 g. of the aqueous alcohol were weighed in a stoppered tube and excess of salt was added. The benzene, or other organic compound, was weighed in a weight burette and added to the solution in the tube, in small quantities, until turbidity was produced, the quantity of benzene thus added being found by a second weighing. The turbid mixture was shaken in a thermostat at 20° ± 0·1° for 6 hours until the solution was saturated with both solutes. About 2 c.c. of the solution were then weighed in a stoppered bottle and the salt was estimated by evaporation to dryness and weighing. Since the proportion of benzene to aqueous alcohol in the solution is known, the percentage of both salt and benzene dissolved in the aqueous alcohol can be calculated and compared with the percentage when only one solute—benzene or salt—is present. The results obtained are in Tables I and II, and it will be seen that the solubility of each semi-solute is increased by the presence of the other, the increase being considerable in the case of the organic compound.

TABLE I.

Solubilities of organic compounds in 100 g. of 50% aqueous alcohol saturated with different salts at 20°.

Salt present.	None.	NaCl.	$NaNO_3$.	KCl.	KNO_3.	KBr.
Benzene	5·8	9·6	9·5	6·7	6·4	7·8
Carbon tetrachloride...	6·4	13·4	8·2	9·9	7·1	9·9
Methyl salicylate	6·2	8·2	8·1	7·2	6·9	7·9

TABLE II.

Solubilities of salts in 100 g. of 50% aqueous alcohol saturated with organic compounds at 20°.

Organic compound.	None.	Benzene.	Carbon tetrachloride.	Methyl salicylate.
Sodium chloride	9·8	10·6	10·7	10·2
,, nitrate	19·4	21·2	20·8	20·4
Potassium chloride	6·0	6·5	6·8	6·2
,, nitrate	3·7	3·9	3·8	3·8
,, bromide	16·4	17·4	17·4	17·3

Four determinations of the solubility of the salt were made in each case, and the results seldom differed by more than one unit in the first decimal place. The solubility of the organic substance was less accurate and, since it was determined by the appearance of turbidity, was always too great, the error being about three units in the decimal place. This error is of less importance in that the increase in solubility of the organic substance is always much greater than that of the salt.

A somewhat more accurate investigation was carried out in the case of benzene and sodium chloride. The solubility of benzene in 50% alcohol was determined at a series of temperatures by adding a weighed quantity of benzene to a definite weight of the solvent and raising the temperature until the turbidity disappeared. A second series was also carried out after 5% of sodium chloride had been added to the aqueous alcohol. The results—which are in Table III—when plotted give two curves practically parallel to each other. The solubility of sodium chloride in 50% alcohol containing small quantities of benzene was also determined, the quantity of benzene being less than that which would produce turbidity. The results are in Table IV.

TABLE III.

Solubility of benzene in 50% aqueous alcohol.		Solubility of benzene in 50% alcohol with 5% NaCl.	
% Benzene.	Temp.	% Benzene.	Temp.
4·57	11·2°	5·80	9·1°
4·78	13·2	6·10	11·8
5·05	15·5	6·39	14·2
5·30	18·0	6·76	16·7
5·61	20·2	7·23	19·2
5·97	22·6	7·57	21·3

TABLE IV.

Solubility at 20° of sodium chloride in 100 g. of 50% aqueous alcohol containing a varying percentage of benzene.

% Benzene	0·00	1·91	4·10	5·34	7·95
% Sodium chloride	9·80	9·86	9·95	10·10	10·35

As is well known, the addition of potassium carbonate to aqueous alcohol causes the formation of two liquid phases, the greater concentration of the salt being found in the lower (aqueous) layer. The amount of carbonate required to produce turbidity increases with the amount of water present, hence a system which contains just sufficient carbonate to produce turbidity can be cleared by a slight addition of water. This small amount of water can be produced by the desolvation of aqueous alcohol caused by the addition of benzene. For example, if about 0·05 g. of potassium carbonate be dissolved in 2 c.c. of water and 10 c.c. of alcohol be added, a turbid mixture will result, which can be cleared by the addition of either a little water or a larger amount of benzene. A large excess of benzene will again produce turbidity, the benzene forming a layer on top of the aqueous alcohol. Also, if the system contains a larger proportion of carbonate, it is possible, by the addition of benzene, to produce a system of three liquid phases, the benzene and the aqueous salt solution being separated by a layer of aqueous alcohol. That potassium carbonate—like other salts—increases the solubility of benzene in aqueous alcohol is shown by the results given in Table V.

TABLE V.

Solubility at 20° of benzene in 100 g. of aqueous alcohol containing a varying percentage of potassium carbonate.

% Potassium carbonate	0·00	1·12	1·67	2·18	2·48	2·68*	2·86
% Benzene	5·8	6·4	6·5	7·1	7·3	7·6	8·0

* Two phases separate.

It is evident from the results shown that with 50% aqueous alcohol there is a mutual increase in solubility of the two types of semi-solute when they are present together. It has not been considered advisable to attempt to assign any definite degree of solvation to the semi-solutes, as the number of equilibria involved would render any such calculation of very doubtful value.

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