CCCCVII.—*Selective Solvent Action. Part VII. Solubilities in Mixed Solvents.*

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Several cases are known of increased solubility in mixed solvents, even when the solute is only slightly soluble in one constituent (Holleman and Antusch, *Rec. trav. chim.*, 1894, **13**, 277; Anglescu and Dumitrescu, *Z. physikal. Chem.*, 1928, **132**, 127). Solutes which show this behaviour are generally of a complex character, and this suggests a possible explanation of the phenomenon. A given solvent dissolves certain types of solute more easily than others: water dissolves hydroxylic compounds, benzene dissolves hydrocarbons, and alcohol has intermediate properties; it therefore seems probable that the solubility of a complex solute in different solvents is due to the action of different groups in the solute. Hence, when such a solute is added to a binary mixed solvent, each constituent of the solvent acts on the appropriate radical of the solute, and the two-fold effect on the solute may result in increased solubility.

The organic acids (except oxalic acid) and their salts are simple examples of solutes with two different groups, and such substances might be expected to show an increased solubility in aqueous alcohol. The values in Table I are taken from Seidell's results (*U.S. Hyg. Labor. Bull. No.* 67) and from his tables, and the calculated values are based on the " mixture " rule. The results are in agreement with the view put forward, the double solvent attraction being that of the alcohol on the hydrocarbon radical and of water on the carboxyl group. It may also be noted that, if the solute is fairly soluble in both constituents, then abnormally high solubility occurs with all proportions of the mixed solvent, whereas if the solute is only slightly soluble in one constituent, then the maximum increase occurs with a mixture rich in the other constituent. Stearic acid shows no exaltation in solubility, but it is almost a hydrocarbon and has a very slight solubility in water, so an exaltation would only be expected in almost absolute alcohol.

TABLE I.

Solubilities of various organic salts and acids in aqueous ethyl alcohol at 25°.

(G. per 100 g. of solvent.)

EtOH, % by weight.

Solute.	0%.	10%.		50%.		90%.		100%.
		Found.	Calc.	Found.	Calc.	Found.	Calc.	
Benzoic acid ...	0·37	0·60	6·18	20·5	29·4	56·3	42·6	58·5
Salicylic acid ...	0·25	0·38	5·19	13·8	25·0	45·7	44·7	49·7
Camphoric acid	0·76	1·62	10·73	45·0	50·6	105·4	90·4	100·5
Stearic acid	0·03	0·04	0·93	0·18	4·54	3·41	8·13	9·05
Tartaric acid ...	137·5	127·3	126·5	88·6	82·5	40·8	38·6	27·6
Na benzoate ...	56·3	54·5	50·7	34·5	28·5	2·88	6·17	0·605
,, salicylate ...	115·5	109	104·3	73·1	59·7	17·6	15·12	3·97
NH_4 benzoate ...	22·9	21·9	20·7	20·4	12·3	4·37	3·77	1·65
,, salicylate ...	103	101·5	93·0	87·7	65·7	46·2	36·2	28·8

In the present paper the work has mainly been confined to an examination of the solubility of acetanilide in a number of binary solvent mixtures. The results (Table II) are in accordance with the views put forward. The solubility in water is probably due to the carbonyl and imino-groups; alcohol will probably act, in addition, on the hydrocarbon portion of the molecule, resulting in an increased solubility for certain compositions of the mixed solvent. The effect should be greater with the higher alcohols, as they have greater solvent power for hydrocarbons. Thus the effect is absent with water–methyl alcohol, and is greater with propyl alcohol than with ethyl alcohol. Again, in alcohol–benzene mixtures, the benzene probably acts only on the phenyl group,

TABLE II.

Solubilities of acetanilide in mixed solvents at 20°.

(G. per 100 g. of solvent.)

(a) *Aqueous alcohols.*

H_2O + MeOH.

% MeOH (by wt.).	Solubility. Found.	Solubility. Calc.
100	46·0 46·0	—
96·2	43·6 43·7	44·3
93·5	42·0 42·2	43·0
86·6	37·5 37·5	39·9
71·7	23·1 23·2	33·1
49·8	7·2 7·3	23·1
25·4	1·5 2·0	12·1
0·0	0·52 0·52	—

H_2O + EtOH.

% EtOH (by wt.).	Solubility. Found.	Solubility. Calc.
100	28·8 28·8	—
95·2	31·3 31·3	27·5
90·4	32·4 32·3	26·0
84·2	33·1 33·1	24·3
74·8	28·8 29·2	21·6
52·5	13·8 13·6	15·3
26·3	2·1 2·2	7·9
0·0	0·52 0·52	—

H_2O + PrOH.

% PrOH (by wt.).	Solubility. Found.	Solubility. Calc.
100	22·4 22·8	—
95·3	28·3 28·5	21·5
90·0	35·4 35·4	20·3
85·0	34·0 33·5	19·3
54·2	18·6 18·7	12·5
34·5	9·3 9·3	8·1
16·3	1·8 1·8	4·1
0·0	0·52 0·52	—

(b) *Benzene–alcohol mixtures.*

C_6H_6 + MeOH.

% C_6H_6 (by wt.).	Solubility. Found.	Solubility. Calc.
100	1·05 1·08	—
81·5	35·4 34·8	9·4
62·8	49·3 50·5	17·9
42·5	54·6 54·5	27·0
21·8	52·9 52·7	36·3
0·0	46·2	—

C_6H_6 + EtOH.

% C_6H_6 (by wt.).	Solubility. Found.	Solubility. Calc.
100	1·08 1·08	—
83·8	21·1 21·1	5·6
63·8	31·5 32·0	11·1
41·7	35·7 35·8	17·2
20·0	33·3 33·4	23·3
0·0	28·8	—

C_6H_6 + PrOH.

% C_6H_6 (by wt.).	Solubility. Found.	Solubility. Calc.
100	1·05 1·08	—
83·0	17·5 17·5	4·7
58·0	28·3 28·1	10·0
42·0	29·7 29·5	13·6
18·8	27·7 27·5	18·3
0·0	22·6	—

(c) *Mixed alcohols.*

MeOH + EtOH.

% MeOH (by wt.).	Solubility. Found.	Solubility. Calc.
100	46·2 46·2	—
83	42·5 42·5	43·3
71·4	40·6 40·6	41·2
50·3	37·2 37·3	37·7
33·7	34·2 34·3	34·7
17·7	31·4 31·5	31·9
0·0	28·8 28·8	—

EtOH + PrOH.

% EtOH (by wt.).	Solubility. Found.	Solubility. Calc.
100	28·8 28·8	—
90·0	27·9 27·9	28·1
79·4	27·7 27·5	27·3
59·1	26·5 26·3	25·9
40·7	25·5 25·4	24·6
19·9	23·9 23·9	23·2
0·0	21·8 21·8	—

$Pr^{\alpha}OH + Pr^{\beta}OH$.

% $Pr^{\alpha}OH$ (by wt.).	Solubility. Found.	Solubility. Calc.
100	21·8 21·8	—
83·3	22·9 23·0	22·5
71·2	23·3 23·6	22·9
46·2	24·9 25·0	24·0
24·7	25·6 25·4	24·9
0·0	25·9 25·9	—

and the alcohol acts in addition on the carbonyl and imino-groups. The increased solubility is less marked in mixtures of the higher alcohols with benzene, for such alcohols are more similar to benzene in their solvent properties and hence the two constituents of the solvent do not have different effects. When the constituents of the mixed solvent resemble one another very closely, the solubility almost follows the mixture rule. Methyl–ethyl alcohol and ethyl–propyl alcohol mixtures behave in this manner.

The above view is, however, incomplete, since it neglects the action of the solvent constituents on one another. Solvate formation, since it decreases the latent valencies, should diminish solvent power; and dissociation, of one or both constituents due to the presence of the other, should increase it. Again, since hydrocarbons possess only one type of radical, they should not show abnormal solubility in mixed solvents. Few measurements have been made with these substances, but Tyrer (private communication to Seidell) has shown that anthracene in benzene–pentane or benzene–heptane mixtures always shows a sub-normal solubility. The results found by the authors for phenanthrene in mixtures of water and the alcohols are in Table III, and, like those for anthracene, show only a decreased solubility. On the other hand, Disselkamp (*Z. physikal. Chem.*, 1926, **123**, 99) has found an increased solubility for anthracene in several liquid mixtures, and attributes the result to interaction between the solvent constituents. He further draws a parallelism between the solvent power and the vapour pressure of a mixed solvent; but such a view must also be incomplete, since it would necessitate a constant form of solubility curve, independent of the solute, for any given binary solvent.

TABLE III.

Solubility of phenanthrene in aqueous alcohol at 20°.

(G. per 100 g. of solvent.)

H_2O + MeOH.			H_2O + EtOH.			H_2O + PrOH.		
% MeOH (by wt.).	Solubility. Found.	Calc.	% EtOH (by wt.).	Solubility. Found.	Calc.	% PrOH (by wt.).	Solubility. Found.	Calc.
100	3·17 3·18	—	100	4·16 4·13	—	100	3·53 3·49	—
96	2·24 2·30	3·05	95·6	2·75 3·07	3·96	95·4	2·93 2·93	3·34
88·7	1·22 1·32	2·82	90·4	2·14 2·21	3·75	93·5	2·68 2·65	3·28
79·0	0·63 0·60	2·51	80·0	1·25 1·29	3·32	79·0	1·50 1·50	2·77
59·8	0·10 0·13	1·89	61·4	0·33 0·23	2·55	69·8	1·04 1·05	2·45
0·0	0·0	—	37·9	0·0	1·57	0·0	0·0	—

Experimental.—The methyl alcohol, ethyl alcohol, and benzene were the purest obtainable from the British Drug Houses, and boiled over a range of less than 0·1°. The propyl alcohol was prepared from the commercial product, and its b. p. varied over 1°. The determinations were carried out by shaking solvent and solute in a thermostat in a small stoppered tube, withdrawing a sample by means of a pipette, and evaporating it to dryness at 40° under diminished pressure. Preliminary tests showed that the solutes were not volatile under such treatment.

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