CLXXXVII.—*Selective Solvent Action.   Part VI.   The Effect of Temperature on the Solubilities of Semi-solutes in Aqueous Alcohol.*

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THE formation of complexes between its constituents has frequently been assumed to account for the deviation of certain physical properties (*e.g.*, viscosity, refractive index, and density) of aqueous alcohol from those calculated from the mixture rule.   If such solvates exist, then it may be expected that rise of temperature will decrease the extent of solvation, since, as a rule, complexes dissociate at higher temperatures.   Such a decrease in solvation should affect the solvent power of the mixed solvent for a semi-solute.   For example, if 50% aqueous alcohol at 100° contains a higher proportion of free (desolvated) alcohol and water than the same mixture at 20°, this increase in the amount of free water and alcohol should cause an increase in the solubility of a water-soluble salt, or of an alcohol-soluble organic substance.   Such an increase in solubility is distinct from the ordinary increase in solubility which takes place in a simple solvent with rise of temperature.   In Table I are given the solubilities of five salts (none of which crystallises with water of crystallisation) at 20° and at 100°, both in water and in 50% (by weight) aqueous alcohol.   The ratio of the solubilities at the two temperatures is also given for each salt both in water and in the mixed solvent. It will be seen that the ratio is always greater for the mixed solvent than for pure water.   If the extent of water–alcohol solvation remained the same at 100° as at 20° there would be the same pro-

portion of free water at the two temperatures, and consequently the ratio of the solubilities of a salt at the two temperatures should be the same for the mixed solvent as it is for pure water. Since this ratio is always greater in the case of the aqueous alcohol, it is concluded that rise of temperature tends to decompose the water–alcohol complexes, this increase in free water producing the abnormal increase in salt solubility.

TABLE I.

Solubilities of salts in water and in 50% (by weight) aqueous alcohol at 20° and 100°.

(G. of solute per 100 g. solvent.)

	Water, 20°.	Water, 100°.	Ratio, 100°/20°.	50% EtOH, 20°.	50% EtOH, 100°.	Ratio, 100°/20°.
NaCl.	36·0	39·1	1·09	9·8	12·1	1·24
	36·0	39·1		9·8	12·1	
KCl.	34·3	56·5	1·64	6·0	15·3	2·55
	34·3	56·0		6·0	15·3	
KClO$_3$.	7·2	56·8	7·84	1·1	14·0	12·8
	7·2	56·0		1·1	14·2	
K$_2$SO$_4$.	11·1	23·9	2·15	0·15	0·51	3·64
	11·2	24·1		0·13	0·51	
Ba(NO$_3$)$_2$.	9·1	33·5	3·69	1·0	4·7	4·65
	9·1	33·6		1·0	4·6	

The solubilities of potassium nitrate in aqueous alcohol of varying composition at 20° and 60° are given in Table II, the values being taken from Seidell's solubility tables. The ratio of the solubilities at the two temperatures is given in each case and it will be seen that it is always greater for aqueous alcohol, of whatever composition, than for pure water. Judging from the values of the ratios, the desolvation with rise of temperature would seem to be greatest with alcohol of about 20% strength. It is obvious that aqueous alcohol which contains only a small proportion of one component, whether alcohol or water, will on desolvation only slightly alter the amounts of its free constituents. Hence the values of the ratios for 90% alcohol and for 5% alcohol are nearer the ratio given by pure water than are those for alcohol–water mixtures of intermediate strength.

TABLE II.

Solubility of potassium nitrate in aqueous alcohol of various concentrations.

(G. per 100 g. solvent.)

Alcohol, %	0	5·5	9·4	13·6	19·1	30	40	60	90
20°	31·6	24	20	16	11	7	5	2	0·3
60°	110	93	79	69	52	31	21	8	1·1
Ratio	3·48	3·87	3·95	4·31	4·72	4·43	4·20	4·00	3·67

For alcohol-soluble solutes, the same result was obtained, but here it was necessary to take into consideration the solubility of the substance in water, which was never negligible, and, in the case of succinic acid, was comparable with that in alcohol.   In Table III are given the solubilities at 20° and 30° of four substances in water, alcohol, and the 50% mixture.   The ratio of the solubilities at the two temperatures is also given in each case both for the mixed and for the unmixed solvents ; with the unmixed solvents the sum of the solubilities is used in calculating the ratio.   Again it will be seen that the increase of solubility is always greater with the mixed solvent.

It is thus obvious that a considerable amount of desolvation of the aqueous alcohol takes place with rise of temperature, although it is not possible to calculate the exact extent of such a change.   It is, however, not complete at 100°, for in such an event the alcohol would have no effect on the solvent power of water, and the solubility of a salt in 50% alcohol would be simply half of its solubility in pure water.

TABLE III.

Solubilities of some organic substances in water, alcohol, and 50% (by weight) aqueous alcohol, at 20° and 30°.

(G. of solute per 100 g. solvent.)

At 20°.

Solvent.	Succinic acid.	Benzoic acid.	Salicylic acid.	Acetanilide.
Water.	6·8	0·34	0·21	0·53
	6·7	0·35	0·23	0·52
Alcohol.	10·0	53·0	51·0	28·8
	10·1	52·0	52·0	28·8
50% EtOH.	13·6	17·0	11·8	11·9
	13·8	16·9	11·8	11·9

At 30°.

Water.	10·5	0·41	0·30	0·70
	10·4	0·43	0·32	0·72
Alcohol.	12·0	66·0	57·0	40·7
	11·8	65·6	57·5	40·3
50% EtOH.	20·8	25·4	17·9	18·9
	21·0	25·0	18·0	18·7

Ratios of solubilities, 30°/20°.

Unmixed solvents.	1·33	1·25	1·11	1·42
Mixed solvents.	1·52	1·48	1·52	1·58

EXPERIMENTAL.

The solubilities at 20° and 30° were determined in the usual manner.   The saturated solutions were prepared in stoppered tubes in a thermostat, weighed portions were taken, and the amount of

solute was estimated either by titration or by evaporation to dryness. In the case of acetanilide, the evaporation was carried out under reduced pressure at 40°.   At 100°, in addition to the usual necessity of obtaining a saturated solution free from excess of suspended solute, care had to be taken to guard against alteration in the composition of the mixed solvent by evaporation.   The method of carrying out a determination was as follows.   To a test-tube of 10 mm. diameter and 5 c.c. capacity was sealed a 20 cm. length of tubing about 4 mm. in diameter.   After cleaning and drying, a sufficient quantity of dry salt was placed in the tube and about 3 c.c. of solvent were added by means of a pipette, care being taken to avoid wetting the walls of the narrower tube.   This tube was then bent round until it lay parallel with the test-tube (see Fig. 1), and was finally sealed off as shown, the whole forming a U with one limb wider than the other.   The sealed tube was rocked in a bath at 100° for 4 hours until saturation was complete.   It was then held in a special pair of tongs, and, while still under the boiling water, was manipulated so that the excess solid was brought into the narrow limb, the wide limb being left about three-quarters full of the clear saturated solution.   The tube was now removed from the bath and allowed to cool to room temperature; part of the salt crystallised during the cooling, but as the tube was sealed no alteration in the composition of the solvent could take place.   The wide limb was cut off above the level of the solution and weighed with its contents, and the solubility of the salt was found by evaporation to dryness and a second weighing.

FIG. 1.