293. *The Solubilities of Metal and Ammonium Salts of Various Organic Acids in Methyl Alcohol and Acetone.*

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THE literature records the solubilities of a number of the salts of organic acids in ethyl alcohol and few or none of those in methyl alcohol or acetone.

The methyl alcohol was purified by first removing acetone by Menzies' method (J., 1922, **121**, 2790); aldehyde was abstracted by treatment with iodine (Castelli and Henri, *Bull. Soc. Chim. biol.*, 1924, **6**, 299), and distillation with concentrated sulphuric acid then removed basic substances as well as most of the water (Carlton, *J. Amer. Chem. Soc.*, 1922, **44**, 1471). Acid substances were removed by distillation from caustic potash, and the alcohol was finally distilled over metallic sodium; b. p. 66°/758 mm. The acetone was purified by way of its sodium iodide compound (Shipsey and Werner, J., 1913, **103**, 1255), dried over calcium chloride, and redistilled; b. p. 56·2°/759 mm.

Grams of salt in 100 *g. of solvent.*

	Methyl alcohol,			Acetone at 15°
	at 15°.	at b. p. of solution.		
Li acetate	30·37	32·47	at 67·2°	*i*
,, benzoate	20·52	19·71	67·0	,,
Na formate	3·52	3·68	66·6	,,
,, acetate	16·00	16·55	67·7	0·05
,, propionate	13·28	13·77	68·0	*i*
,, *n*-butyrate *	15·31	20·70	68·2	0·14
,, succinate	0·72	1·80	66·6	*i*
,, benzoate	8·22	7·55	66·2	,,
,, salicylate *	26·28	34·73	67·2	,,
,, benzenesulphonate	6·51	8·00	66·6	,,
,, naphthalenesulphonate	1·37	2·10	65·8	,,
,, potassium tartrate	*i*	*i*	66·0	6·70
,, cyanide	6·44	4·10	67·4	*i*
K acetate *	24·24	53·54	73·4	,,
,, propionate *	39·00	55·33	71·3	,,
,, *n*-butyrate *	51·04	120·84	70·9	,,
,, succinate	3·16	3·75	66·6	,,
,, benzoate	7·07	8·33	66·0	,,
,, benzenesulphonate *	2·67	9·67	66·1	0·12
,, ferrocyanide	*i*	0·90	66·0	*i*
,, ferricyanide	,,	0·31	66·0	,,
,, tetroxalate	2·07	1·55	66·4	2·44
,, hydrogen tartrate	*i*	0·60	66·0	*i*
,, ethyl sulphate *	1·72	13·87	65·8	,,
NH_4 acetate *	7·89	131·24	94·2	,,
,, benzoate *	6·39	13·07	66·0	,,
,, salicylate *	71·55	163·78	72·8	69·65
,, succinate	1·62	5·84	65·6	0·47
,, ferrous oxalate	0·47	0·78	66·0	*i*
,, ferric oxalate	0·42	0·72	66·0	,,
Ca formate	0·27	0·23	66·0	,,
,, acetate *	0·75	1·01	66·0	,,
,, propionate *	1·25	3·31	66·1	,,
,, lactate	13·33	73·81	69·8	,,
,, oleate	0·30	0·57	66·0	2·26
,, benzoate *	0·24	0·39	66·0	*i*
Sr acetate	0·26	0·18	66·0	,,
Ba acetate	0·55	0·23	66·0	,,
,, oxalate	*i*	0·31	66·0	,,
,, lactate	1·14	1·30	66·2	,,
,, benzoate	0·47	0·60	66·0	,,
,, benzenesulphonate	0·40	0·40	66·0	,,
Mg acetate	5·25	7·50	68·2	,,
,, lactate	2·27	1·14	66·1	,,
,, benzoate *	1·24	70·98	71·9	2·38
Hg^{I} acetate	1·24	1·40	66·3	*i*
Hg^{II} acetate *	7·54	49·84	66·7	0·60
,, cyanide *	34·55	59·84	67·0	10·30
,, benzoate	3·67	3·67	66·5	7·23
Pb acetate, $3H_2O$ *	74·75	214·95	—	*i*
,, acetate (anhyd.) *	—	102·75	66·1	—
,, benzoate	1·32	2·65	66·0	0·20
Cu acetate	0·48	0·48	66·0	0·28
,, benzoate	0·49	1·97	66·6	2·03
Zn acetate	1·90	1·90	66·6	*i*
,, benzoate	9·90	6·62	65·9	1·00
Cr acetate	4·76	8·66	66·9	0·20
Cd acetate	21·08	39·47	68·9	*i*
La acetate	0·64	0·77	66·0	,,
Ce acetate	3·33	3·71	66·6	,,
Mn acetate	4·76	12·30	66·2	,,
Co acetate	1·49	5·50	66·4	,,
U acetate	0·74	0·83	66·0	2·37
Ni benzoate	0·29	0·30	66·0	*i*
Al stearate	*i*	0·20	66·0	0·88
,, oleate	2·49	4·47	66·0	0·39

The salts were either purchased as the purest obtainable or were prepared from pure materials. If possible, they were recrystallised twice from either water or methanol and heated at 100° for

4 hours; the less soluble ones were washed alternately with each of the above boiling liquids and then dried. Those which decompose at 100°, *e.g.*, ammonium salts and cyanides, were dried, after purification, at 50° for 4 hours; those forming hydrates were heated at 110°. Each salt was analysed by a suitable method.

The apparatus used for the measurements at 15° was similar to that described by Brönsted and Petersen (*J. Amer. Chem. Soc.*, 1921, **43**, 2265); it was immersed in a thermostat registering to within ± 0·1°. At boiling temperature, the solutions were made in a wide flask under reflux. Difficulty was experienced with some salts owing to unavoidable bumping of the liquid. To determine the quantities of solutes, portions of the saturated solutions were weighed at 15° in a graduated pipette of the type used by Chattaway and Lambert (J., 1915, **107**, 1766); to separate undissolved salt, a filter thimble was introduced into the solution (Ward, *Analyst*, 1919, **44**, 137). Where crystallisation occurred on cooling, the pipette was reheated till solution was attained, the contents being discharged into a weighing bottle, the pipette washed with the boiling solvent, and the residue weighed after evaporation of solvent; thus the weights of solute and solvent were both obtained.

To ensure that all residues were alcohol-free, each was heated at 100° for an hour, except those salts mentioned above, which were heated at 50° for 2 hours. (Certain salts, see below, contained alcohol of crystallisation.) The mean of three determinations with each salt is recorded in the table; results which diverged more than 1% from the mean of the actual weights obtained were discarded. An asterisk indicates that the salt may be recrystallised from boiling methanol; *i* = insoluble.

With the exception of the following (for which solubilities are given in g./100 g. of solvent at 15°), all were insoluble in benzene: Mercury benzoate 2·49, zinc benzoate 4·20, calcium oleate 3·44, aluminium oleate 0·58, aluminium stearate 0·18. The following were insoluble in all three solvents: Silver acetate and benzoate, aluminium acetate and benzoate, bismuth salicylate, lithium urate, and, with the exception of those already mentioned, all oxalates, tartrates, and citrates.

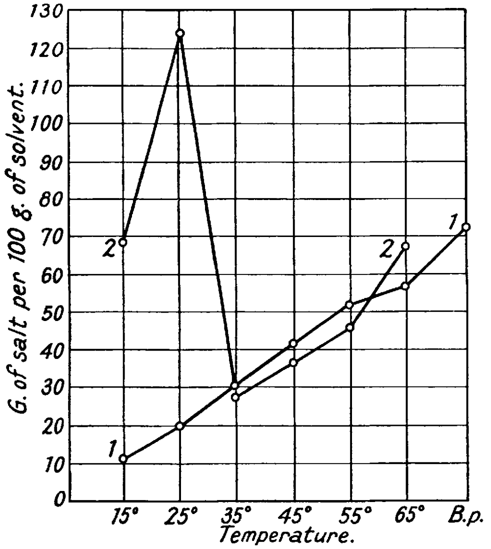
The accuracy of the method was tested by means of those salts crystallisable from hot methanol, in which saturated solutions were made and kept for 24 hours at 15°, to complete crystallisation. Samples of the mother-liquor were taken in the pipette and treated as above; figures almost identical with those given for 15° in the table resulted. Five salts were further examined: Potassium acetate gives extremely hygroscopic crystals of an *alcoholate* (Found: loss on heating at 100° for 30 mins., 26·27. $CH_3{\cdot}CO_2K,CH_3{\cdot}OH$ requires CH_4O, 24·61%); the *alcoholate* of calcium benzoate forms non-hygroscopic crystals [Found: loss, 10·00. $(C_6H_5{\cdot}CO_2)_2Ca,CH_3{\cdot}OH$ requires CH_4O, 10·19%]; magnesium benzoate *trialcoholate* also forms non-hygroscopic needles [Found: loss, 26·06. $(C_6H_5{\cdot}CO_2)_2Mg,3CH_3{\cdot}OH$ requires $3CH_4O$, 26·51%]; calcium propionate *alcoholate*, non-hygroscopic prisms [Found: loss, 14·68. $(C_2H_5{\cdot}CO_2)_2Ca,CH_3{\cdot}OH$ requires CH_4O, 14·68%]; ammonium benzoate, non-hygroscopic ditetragonal prisms [Found: loss at 70° during 30 mins., 25·28. $C_6H_5{\cdot}CO_2NH_4,1\frac{1}{2}CH_3{\cdot}OH$ requires loss, 25·66%).

A consideration of these results reveals certain regularities and irregularities. For instance, the salts of di- and tri-basic acids are practically insoluble in methanol, *i.e.*, the more oxygen contained in the molecule the less is the solubility, being the opposite condition to that with respect to water as a solvent. An exception to this is the greater solubility of the salicylates over the benzoates, a fact which is partly attributable to the hydroxyl group of the former; on the other hand, the hydroxyl groups of tartrates and citrates do not operate in this way. Also, in general, the higher the atomic weight of the metal the less is the solubility of its salts in methanol, although striking exceptions are lead acetate and mercuric acetate and cyanide. The solubilities of most sodium salts are below those of potassium, yet the latter crystallise more readily; in fact, it was possible by this means to effect an almost complete separation of the benzenesulphonates of the two metals.

A few salts seemed to be anomalous, and two were taken for more particular investigation; their solubilities between 15° and 65° are depicted in Fig. 1, where the temperatures are plotted against g. of salt per 100 g. of solvent. The curve for calcium lactate in methanol solution rises fairly regularly up to 55°, where it breaks a little and rises less steeply to 65°. At 55° a definite solvate was found; the lowering of solubility is due to this solvate and not to any formed below 55°. On driving off the excess methanol at 50° from the solution of this *solvate*, it was left as a colourless, crystalline solid, and after further heating at 110° an amorphous mass of anhydrous calcium lactate remained [Found: loss, 44·51. $(C_3H_6O_3)_2Ca,5\frac{1}{2}CH_3{\cdot}OH$ requires loss, 44·44%].

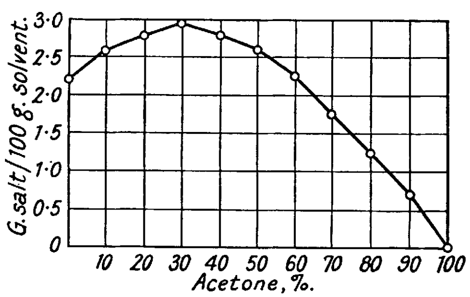
The solubility of ammonium salicylate in acetone, after rising sharply to 124 g. at 25°, drops as suddenly to 28·8 g. at 35°. No definite solvate was found, but the solution became dark orange-red in colour and, after excess acetone was evaporated at 60°, the substance, on cooling, solidified to a dark red crystalline solid. There is no doubt that this is a different substance from the original salt, for it is almost insoluble in water, whereas sodium salicylate is very soluble; also, if it is heated at 100° for 20 minutes, it melts, gives off ammonia, and does not reform crystals but becomes resinous; such properties are not those of the original salt. From 35° to 65° the solubility again rises; this part of the curve is due chiefly to the solubility of the red substance. This substance is probably a compound of the salt with acetone and not a solvate; the colour suggests a quinonoid structure. On heating, ammonium salicylate easily loses ammonia, and forms a compound, $CH_3\cdot CO\cdot CH_2\cdot CMe_2\cdot NH\cdot CMe_2\cdot NH_2$, with acetone (Patterson and McMillan, J., 1921, **119**, 269). At the same time, it is possible that the hydroxyl group of the salicylate may also react, since Berl and Schwebel (*Z. angew. Chem.*, 1922, **35**, 189; 1921, **34**, 278 *et seq.*), from vapour-tension measurements, conclude that molecular compounds of cresols and acetone are formed.

FIG. 1.



1. *Calcium lactate in methyl alcohol.*
2. *Ammonium salicylate in acetone.*

FIG. 2.



Solubility of potassium ethyl sulphate in methyl alcohol and acetone.

In attempts to precipitate some of the salts from methanol solution by the addition of acetone, it was found that potassium ethyl sulphate acted abnormally; its solubility at 20° in the mixed solvents is plotted in Fig. 2. Although the salt is insoluble in acetone, the curve rises with increasing acetone content up to 30%, and then falls regularly to 100% acetone. No distinct solvate or compound was isolated by the evaporation of solvent or other simple means, though it is probable that a solvate is responsible for the rise. Marden and Dover (*J. Amer. Chem. Soc.*, 1916, **38**, 1235; 1917, **39**, 1) describe the solubilities of acetanilide in benzene–acetone mixtures, and find a similar rise from 0 to 10% acetone, but they are unable to account for it except by the postulation of unstable solvates. Since one such undoubted solvate of calcium lactate has now been isolated, it seems probable that their conception is the correct one.

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