201. *Acid Salts of Monobasic Organic Acids. Part II.*

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It has been shown (J., 1933, 1016) that extensive compound formation between racemic mandelic acid and its normal potassium, sodium, lithium, barium, strontium, and calcium salts takes place, and that acid salts of these metals can be isolated. These series have now been completed by a study of the solubility curves for the rubidium, cæsium, ammonium, and magnesium salts at 25°. The system containing thallous mandelate has also been included.

Data relating to the number and stability of the acid salts formed are tabulated below. There is no obvious correlation between the extent of compound formation and electrochemical character of the metal, or between the solubility of the normal salt and the number of acid salts formed, for the systems containing rubidium, cæsium, and ammonium mandelates, all of which are more soluble than potassium mandelate, give fewer acid salts.

Metal.	Acid salts isolated.*	Stability in water.	Metal.	Acid salts isolated.	Stability in water.
Cs	1 : 1	Stable	Li	1 : 1	Stable
Rb	3 : 1	Stable	NH_4	3 : 1	Unstable
	1 : 1	Unstable		1 : 1	Stable
K	3 : 1	Stable	Tl	1 : 1	Stable
	2 : 1	Unstable	Ba	1 : 1	Stable
	1 : 1	Unstable	Sr	1 : 1	Stable
Na	3 : 1	Stable	Ca	1 : 1	Stable
	1 : 1	Stable	Mg	1 : 2	Unstable †

* The ratio is that of mols. of free acid to mols. of normal salt. † Crystallises as a dihydrate.

It has been frequently pointed out, however, that compounds may be present in solution which cannot be isolated in the solid state owing to their solubility conditions being unsuitable.

The effect of addition of metallic mandelates on the solubility of the acid has been studied as in Part I by plotting the concentration of acid against that of mandelate. For comparison with the previous results the curves for sodium and potassium have been included in the diagram (Fig. 1).

Increase in solubility of mandelic acid in presence of normal mandelates.

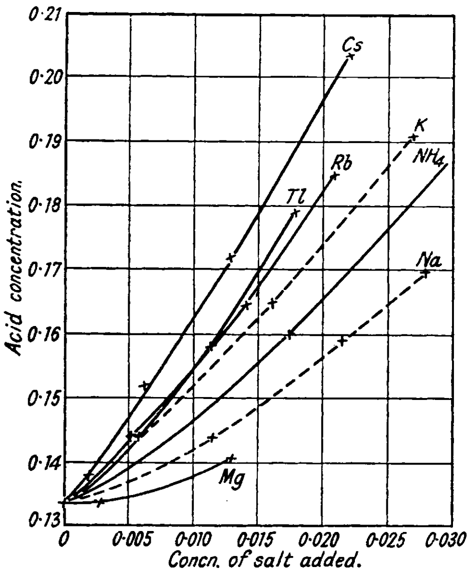
(All results are given in g.-equivs. per 100 g. of H_2O.)

Solubility of mandelic acid in water at 25° = 0·134.

Acid.	Salt.	Acid.	Salt.	Acid.	Salt.	Acid.	Salt.
	Cæsium.				*Rubidium.*		
0·138	0·002	0·172	0·013	0·144	0·005	0·185	0·021
0·151	0·006	0·204	0·022	0·165	0·014		
	Thallous.				*Ammonium.*		
0·135	0·0014	0·179	0·018	0·160	0·017	0·205	0·037
0·144	0·006	0·209	0·024				
0·158	0·011				*Magnesium.*		
				0·134	0·003	0·141	0·013
	Sodium.				*Potassium.*		
0·144	0·0114	0·170	0·028	0·144	0·005	0·191	0·027
0·159	0·021			0·165	0·016		

The order of the metallic mandelates with regard to their effect on the solubility of the acid is as follows : Cs, Tl, Rb, K, NH_4, Na, Mg. We might conclude from these results that the tendency towards complex formation is in the same order, greatest for cæsium and least for magnesium. We have, however, decided that other factors, principally that of the effect of variation in ionic size, which leads to a varying salting-out effect, should be considered in more detail. The two factors, *viz.*, compound formation and salting out, will affect the solubility of the acid in opposite directions. A study of the curves showing the salting-out action of a series of metallic salts with a common ion (chlorides, nitrates, etc.) upon other weak electrolytes, proves that the order and the extent of the effect produced by the metallic ion is similar to the effect found in the present investigation. We hope, by studying the variation in solubility of mandelic acid in presence of a series of chlorides of the alkalis and alkaline earths, to eliminate as far as possible the salting-out effect found in the case of the metal mandelates, and so to obtain a more exact criterion of the extent of compound formation in such solutions.

FIG. 1.



EXPERIMENTAL.

Rubidium Mandelate.—60 G. of rubidium sulphate dissolved in water were treated with a slight excess of concentrated barium hydroxide solution. Barium sulphate was filtered off, and excess barium precipitated by passage of carbon dioxide through the solution. The filtrate was evaporated on the water-bath to small bulk, and neutralised with mandelic acid. The gum obtained on evaporation was thoroughly dried at 90° in a vacuum. The resulting glass was dissolved in as small an amount of methyl alcohol as possible, and the mandelate precipitated as a fine powder by addition of 500 c.c. of acetone. This procedure was repeated to give a pure product (Found : Rb, 36·3. Calc. : Rb, 36·1%).

Cæsium Mandelate.—The normal salt, obtained in the usual way from mandelic acid (50 g.) and cæsium carbonate (50 g.), was crystallised from methyl alcohol, forming fine needles (Found : Cs, 46·9. Calc. : Cs, 46·8%).

Acid Cæsium Mandelate.—Only one acid salt could be isolated in preliminary experiments. 30 G. of mandelic acid and 9·6 g. of cæsium carbonate were dissolved in water and the solution evaporated to small bulk. On further concentration in a desiccator, the salt separated in short pointed prisms; after being washed and dried, it contained 34·7% of acid ($C_8H_8O_3,C_8H_7O_3Cs$ requires 34·9%). An attempt to prepare the 3 : 1 acid salt was unsuccessful, the solid obtained being almost pure acid.

Ammonium Mandelate.—20 G. of mandelic acid dissolved in 150 c.c. of water were neutralised with ammonia, the solution was evaporated to a gum, and 100 c.c. of acetone added. The salt which separated was crystallised from aqueous acetone (10% water) and dried at room temperature. Prolonged evacuation was necessary to remove the last traces of acetone, but on heating, the salt decomposed with evolution of ammonia. The mandelate was also prepared by passing dry ammonia into an ethereal solution of mandelic acid (McMaster, *J. Amer. Chem. Soc.*, 1915, **36**, 1916), the precipitated salt being collected and dried as before.

Thallous Mandelate.—This salt was prepared from thallous sulphate as for the rubidium salt; it crystallised well from aqueous methyl alcohol (1 : 1) (Found : Tl, 57·5. Calc. : Tl, 57·5%).

Magnesium Mandelate.—20 G. of mandelic acid were neutralised with 2·7 g. of magnesium oxide, the solution boiled for some time, and filtered. After standing for several days at room temperature, the salt slowly crystallised out. In view of the discordant values published for the solubility of magnesium mandelate (see p. 871), the salt was also prepared by a different method. Concentrated solutions containing equivalent amounts of magnesium chloride and potassium mandelate were mixed and kept for some time; the precipitated salt was washed thoroughly and dried at 25° [Found: Mg, 7·3; H_2O, 3·1. Calc. for $(C_8H_7O_3)_2Mg,\frac{1}{2}H_2O$: Mg, 7·4; H_2O, 2·7%].

The solubility determinations were carried out as described previously.

1. *The System Mandelic Acid–Rubidium Mandelate–Water.*—In the earlier experiments with dilute solutions of rubidium mandelate, filtration was carried out in the thermostat as described previously. The more viscous solutions encountered at higher concentrations had to be filtered outside the thermostat, with use of suction; a Jena sintered-glass funnel was used, and before filtration, both funnel and receiving vessel were warmed to about 25°. Filtration by this means was complete in such a short time that there could be little change in the equilibrium of the systems.

The residue method of Schreinemakers was used in the analysis of the solid phase, since with the very viscous solutions obtained the mother-liquor could not be satisfactorily removed from the solid by simply pressing on a porous plate.

Rubidium was determined by evaporation to dryness and conversion into sulphate.

FIG. 2.

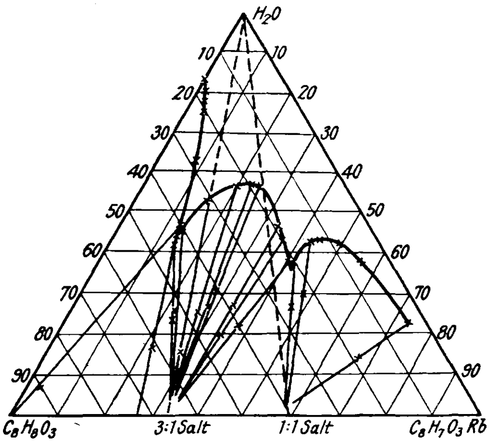
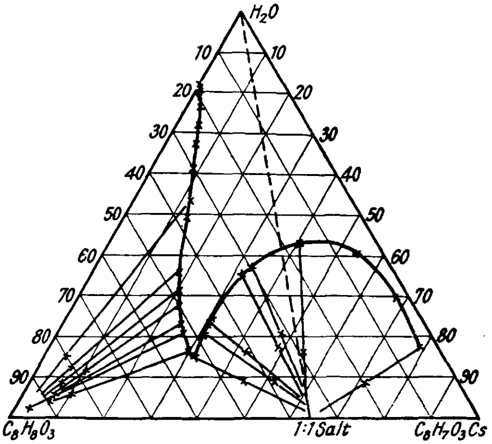


FIG. 3.



The results for this system are collected below, and the corresponding curve given in Fig. 2. Two acid salts are formed, the 3 : 1 salt being stable in contact with its saturated solution, whereas the 1 : 1 salt is not.

Rubidium mandelate.

Composition, %.				
Solution.		Residue.		
Acid.	Salt.	Acid.	Salt.	Solid phase.
16·95	0·0	—	—	Acid
17·8	1·0	—	—	,,
19·5	2·6	—	—	,,
21·1	3·7	—	—	,,
28·9	7·8	—	—	,,
40·1	12·9	90·3	2·6	Acid + 3 : 1 salt
42·2	13·7	61·5	21·8	,,
43·5	13·9	53·8	22·4	3 : 1 Salt
40·5	13·8	52·3	21·8	Acid + 3 : 1 salt
30·8	15·8	55·9	28·5	,,
23·2	20·1	47·0	27·2	3 : 1 Salt
20·1	22·8	44·6	28·5	,,
18·8	24·8	40·3	28·8	3 : 1 Salt
18·3	27·5	—	—	,,
19·7	33·7	38·9	34·1	,,
20·0	36·1	—	—	,,
20·3	38·1	45·0	34·9	,,
21·0	40·1	40·8	37·4	,,
20·7	41·0	26·8	46·2	1 : 1 Salt
14·3	42·1	22·1	46·9	,,
12·5	43·7	—	—	,,
8·4	48·9	—	—	,,
6·5	55·1	—	—	,,
3·9	73·2	19·0	66·4	,,

2. *The System Mandelic Acid–Cæsium Mandelate–Water.*—The estimation of cæsium as sulphate required several precautions owing to the stability of the hydrogen sulphate and the volatility of cæsium sulphate. After evaporation of the solution, the volatile matter was driven

off at as low a temperature as possible, and a slight excess of sulphuric acid added. The carbon was found to burn off readily at a low red heat under these conditions. A small amount of ammonium carbonate was added to the white residue and the crucible again heated to dull redness.

The results are shown below, and in Fig. 3. The 1 : 1 salt alone is formed at 25°, and is stable in presence of its saturated solution. This is in agreement with the preliminary experiments described above.

Cæsium mandelate.

Composition, %.				
Solution.		Residue.		
Acid.	Salt.	Acid.	Salt.	Solid phase.
16·95	0·0	—	—	Acid
17·3	0·4	—	—	,,
18·4	1·4	—	—	,,
20·1	2·8	—	—	,,
22·6	4·5	—	—	,,
25·6	6·3	—	—	,,
29·1	9·0	—	—	,,
33·7	12·3	—	—	,,
36·0	13·5	—	—	,,
39·4	15·3	79·8	4·9	,,
45·2	18·3	80·0	7·0	,,
47·4	20·7	84·5	6·8	,,
49·2	22·2	77·7	10·4	,,
50·0	23·8	94·3	2·8	,,
50·8	25·6	89·1	6·3	Acid
51·3	27·2	87·9	6·6	,,
52·5	30·7	83·2	10·7	,,
52·5	32·2	45·0	45·3	1 : 1 Salt
47·3	31·9	38·5	52·0	,,
45·6	31·3	—	—	,,
44·3	31·1	40·9	42·3	,,
32·1	32·6	33·4	48·9	,,
29·1	33·4	31·1	47·7	,,
16·1	40·6	29·0	55·0	,,
5·3	53·8	—	—	,,
2·9	67·3	—	—	,,
3·7	79·2	19·6	72·1	,,

3. *The System Mandelic Acid–Ammonium Mandelate–Water.*—The following method of analysis was found to give sufficiently accurate results. The solutions were diluted to a known volume, if necessary, and portions taken. The acid content was determined by titration with sodium hydroxide solution and methyl-red as indicator. The end-point was detected by comparison of the colour of two solutions, one just acid and the other just alkaline. A measured excess of alkali was then added, and the ammonia boiled off. The excess alkali was titrated with standard hydrochloric acid. This method was applied both to solutions and to moist residues.

The results are collected below, and the curve is shown in Fig. 4. Two acid salts are formed, 3 : 1 and 1 : 1, of which only the latter is stable in presence of its saturated solution; the former is stable over a very short range of concentrations.

Ammonium mandelate.

Composition, %.				
Solution.		Residue.		
Acid.	Salt.	Acid.	Salt.	Solid phase.
16·95	0·0	—	—	Acid
19·1	2·3	—	—	,,
22·7	4·5	—	—	,,
24·7	5·6	—	—	,,
28·0	7·3	—	—	,,
31·1	8·9	—	—	,,
39·7	14·0	—	—	,,
44·2	15·9	66·4	9·4	,,
47·1	18·0	—	—	,,
47·9	19·8	72·0	11·5	,,
50·8	24·5	—	—	,,
50·4	25·4	—	—	,,
51·2	25·4	64·0	18·2	Acid
50·9	26·3	76·4	15·1	Acid + 3 : 1 salt
50·5	27·4	62·4	27·5	3 : 1 Salt
49·7	28·7	60·7	28·0	,,
47·0	32·3	60·7	29·6	,,
47·2	32·2	47·5	40·5	1 : 1 Salt
41·1	33·9	42·2	39·4	,,
35·2	36·1	39·9	42·3	,,
28·3	42·1	35·1	45·2	,,
25·4	45·7	34·9	47·6	,,
20·7	50·9	—	—	,,
17·2	56·2	30·5	54·1	,,

4. *The System Mandelic Acid–Thallous Mandelate–Water.*—Analyses of the solutions were carried out by precipitation of thallium as thallous iodide in the cold, and weighing the iodide in a Gooch crucible. At a few points the composition of the solid phase was determined by the residue method, and at others by direct analysis.

The results are given below, with the corresponding curve in Fig. 5. One stable acid salt is formed of the 1 : 1 type.

FIG. 4.

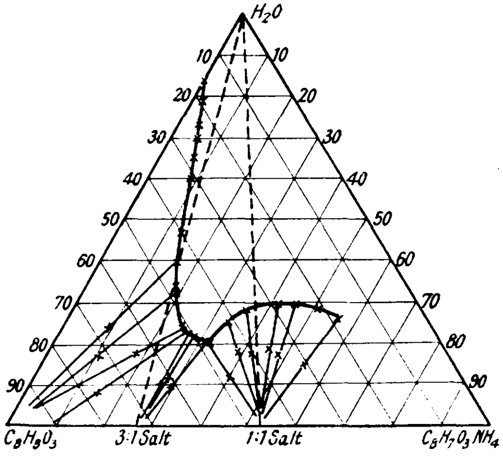
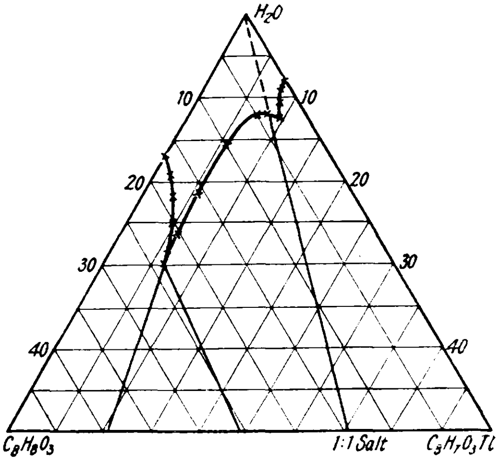


FIG. 5.



Composition, %.				
Solution.		Residue.		
Acid.	Salt.	Acid.	Salt.	Solid phase.
16·95	0·0	—	—	Acid
17·0	0·4	—	—	,,
17·2	0·6	—	—	,,
17·7	1·6	—	—	,,
18·8	3·1	99·5	—	,,
20·4	4·7	—	—	,,
22·6	6·0	50·1	12·4	Acid + 1 : 1 salt
24·0	6·0	28·4	41·4	1 : 1 Salt
20·9	5·8	—	—	,,

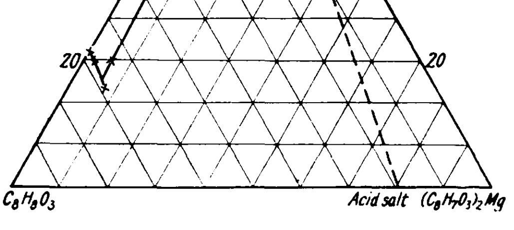
Thallous mandelate.

Composition, %.				
Solution.		Residue.		
Acid.	Salt.	Acid.	Salt.	Solid phase.
16·0	5·4	—	—	1 : 1 Salt
12·2	5·3	30·4	—	,,
9·1	5·7	30·1	—	,,
4·8	7·1	—	—	,,
3·7	8·2	16·5	37·9	,,
2·8	9·5	9·6	—	1 : 1 Salt + normal salt
1·9	8·5	—	—	Normal salt
1·0	8·1	—	—	,,
0·0	7·8	0·0	—	,,

5. *The System Mandelic Acid–Magnesium Mandelate–Water.*—In determinations of this system, 15—20 c.c. of water were used. The amount of magnesium mandelate was determined by ignition to oxide. Owing to the slowness at which the systems attained equilibrium, it was necessary to stir the solutions for much longer than usual (40—60 hours). The solubility of the normal salt was found to be 2·61 g. per 100 g. of solution : McKenzie (J., 1899, **75**, 969) found 1·8 g. at 18°, whereas Findlay and Campbell (J., 1930, 2721) reported 0·95 g. at 25°.

The results for this system are shown below, and the curve is given in Fig. 6. The acid salt was analysed [Found : $Mg(C_8H_7O_3)_2$, 77·6; $C_8H_8O_3$, 17·9; H_2O, 4·2. Calc. for $C_8H_8O_3,2Mg(C_8H_7O_3)_2,2H_2O$: $Mg(C_8H_7O_3)_2$, 77·6; $C_8H_8O_3$, 18·1; H_2O, 4·3%].

FIG. 6.



Magnesium mandelate.

Acid, %.	Salt, %.	Solid phase.
16·95	0·0	Acid
16·9	0·4	,,
17·3	1·8	,,
16·0	1·4	1 : 2 Salt
9·6	1·4	,,
6·2	1·5	,,
3·7	2·1	,,
3·3	2·3	,,
5·9	2·6	Normal salt
1·7	2·1	,,
0·0	2·6	,,

SUMMARY.

The series of solubility curves for the optically inactive systems mandelic acid–metal mandelates–water at 25° has been completed by an examination of the systems for rubidium, cæsium, ammonium, thallous, and magnesium mandelates. The following acid salts have been isolated: $C_8H_8O_3,C_8H_7O_3Rb$; $3C_8H_8O_3,C_8H_7O_3Rb$; $C_8H_8O_3,C_8H_7O_3Cs$; $C_8H_8O_3,C_8H_7O_3NH_4$; $3C_8H_8O_3,C_8H_7O_3NH_4$; $C_8H_8O_3,C_8H_7O_3Tl$; $C_8H_8O_3,2(C_8H_7O_3)_2Mg,2H_2O$.

The effect of variation of the metallic radical upon the extent of compound formation is discussed, and attention directed to one of the factors, namely, ionic size, which tends to obscure the interpretation of the results.

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