

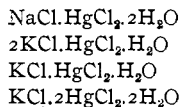
ON THE FORMATION OF DOUBLE SALTS.

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The object of this investigation was to determine the influence of various organic solvents on the formation of certain double salts which yield hydrates when crystallized from water. The facts regarding simple salts are much better known than those regarding double salts. Thus, Menshutkin,¹ among many others, has shown that an organic solvent may replace the water of crystallization in many cases, so that a salt crystallizing at a given temperature with a certain number of molecules of water will crystallize from an organic solvent with the same number—sometimes with a smaller number—of molecules of that solvent. Again, the water of crystallization of a simple salt can ordinarily be removed by suitable means, leaving the stable anhydrous salt, and the water of crystallization is in general not necessary in order that the salt itself should be formed. Whether the water, or more generally the solvent, of crystallization is necessary in order that a double salt shall form and whether the solvent affects the type of salt formed, has been but little investigated. Almost the only work on the formation of double salts from non-aqueous solutions has been done recently by Cambi,² but it is somewhat difficult to draw conclusions from his work which apply to the present problem, as it is not certain in the cases investigated by him that all the double salts capable of forming at a given temperature from any one solvent are known.

For the present investigation, the double salts of mercuric chloride with sodium and potassium chlorides were chosen. The double salts which these chlorides form from water at 25° have already been determined.³ These salts, all containing water of crystallization, have the following composition:



Mercuric chloride is much more soluble in some organic solvents than it is in water, and the alkali chlorides have an appreciable solubility in these solvents when mercuric chloride is present. Absolute alcohol was used as solvent for sodium and mercuric chlorides and both absolute alcohol and acetone were used when potassium chloride was present. The alcohol was purified by treating with sodium and distilling. The acetone was dried over anhydrous copper sulphate and distilled.

The same solubility method has been used for determining double salts that was previously used in determining the double mercuric chlo-

¹ *Z. anorg. Chem.*, **52**, 9, 152; **53**, 26; **54**, 89.

² *Atti. accad. Lincei*, [5] **16**, I, 403; *Gaz. chim. ital.*, **39**, I, 361.

³ Foote and Levy, *Am. Chem. J.*, **35**, 236 (1906).

rides formed from water. By this method, all salts forming from a solvent at a given temperature can be definitely determined. Varying proportions of the salts and solvent were mixed together in small bottles with ground glass stoppers. The salts were weighed and the volume of liquid measured to serve as guides in making other mixtures. The salts very often formed in lumps when first brought into contact with the liquid, due to the formation of double salts. When the lumps could not be broken by shaking they were crushed with a glass rod. The stopper and neck of the bottles were dipped in melted paraffin to make them perfectly water-tight and were then shaken in a thermostat, usually for 48 hours. A sample of the solution was then drawn through a filter of glass wool into a weighed specimen tube and analyzed. The residue was removed and dried on filter paper. Both solvents are very volatile and there was some evaporation as the salts were dried between filter papers. This tended to contaminate the residues with salts from the solution, so that the composition of the residues could not be determined with the same accuracy as the solutions.

Both solutions and residues were analyzed by precipitating mercury as sulphide from hydrochloric acid solution, filtering on a Gooch crucible, and drying at 110–120°. The filtrate was evaporated to dryness and the alkali determined as chloride. Alcohol or acetone crystallizing with the double salts was determined by difference except when otherwise stated. In the mixtures containing sodium and mercuric chlorides, the residues were not analyzed but their composition was calculated. This could be done with sufficient accuracy, since the composition of the solution and of the original mixture were known.

The following results were obtained:

TABLE I.—SOLUBILITY OF SODIUM AND MERCURIC CHLORIDES IN ABSOLUTE ALCOHOL AT 25°.

No.	Per cent. NaCl in solution.	Per cent. HgCl ₂ in solution.	Per cent. HgCl ₂ in residue.	Residue contains
1	3.05	47.25	98.17	NaCl and HgCl ₂ .
2	2.90	47.11	70.11	
3	3.09	46.19	12.16	

TABLE II.—SOLUBILITY OF POTASSIUM AND MERCURIC CHLORIDES IN ABSOLUTE ALCOHOL AT 25°.

No.	Per cent. KCl in solution.	Per cent. HgCl ₂ in solution.	Per cent. KCl in residue.	Per cent. HgCl ₂ in residue.	Per cent. alcohol in residue.	Residue contains
1	0.21	33.69	95.60	HgCl ₂ and 5KCl.6HgCl ₂ .2C ₂ H ₆ O
2	0.28	33.80	82.03	
3	0.22	24.84	17.63	78.00	4.37	5KCl.6HgCl ₂ .2C ₂ H ₆ O
4	0.28	6.21	18.27	77.29	4.44	
5	0.25	1.65	73.24	5KCl.6HgCl ₂ .2C ₂ H ₆ O and KCl
6	0.17	1.57	66.21	
7	0.38	1.03	4.20	

TABLE III.—SOLUBILITY OF POTASSIUM AND MERCURIC CHLORIDES IN ACETONE AT 25°.

No.	Per cent. KCl in solution.	Per cent. HgCl ₂ in solution.	Per cent. KCl in residue.	Per cent. HgCl ₂ in residue.	Per cent. acetone in residue.	Residue contains
1	1.29	61.87	96.37	HgCl ₂ and KCl.5HgCl ₂ .C ₃ H ₈ O
2	1.25	61.88	94.29	
3	1.39	60.68	4.74	89.85	5.41	KCl.5HgCl ₂ .C ₃ H ₈ O
4	2.33	56.59	5.01	90.28	4.71	
5	2.58	55.85	5.51	89.75	4.74	
Calculated for KCl.5HgCl ₂ .C ₃ H ₈ O			5.02	91.08	3.90	
6	2.77	54.48	87.44	KCl.5HgCl ₂ .C ₃ H ₈ O and 5KCl.6HgCl ₂ .2C ₃ H ₈ O
7	2.79	54.35	83.87	
8	2.93	48.13	15.91	80.16	3.93	5KCl.6HgCl ₂ .2C ₃ H ₈ O
9	2.82	38.94	15.90	79.50	4.60	
10	2.51	18.04	17.25	78.00	4.75	
11	3.34	13.26	19.40	76.34	4.26	
Calculated for 5KCl.6HgCl ₂ . 2C ₃ H ₈ O			19.64	76.87	5.47	
12	2.91	10.93	67.04	5KCl.6HgCl ₂ .2C ₃ H ₈ O and KCl
13	2.99	11.37	28.68	
14	2.87	10.66	9.14	

In the tables just given, a series of two or more results showing constant solubility and varying residue indicates a mixture of two salts, while variable solubility and constant composition of the residue show the presence of a pure double salt. Referring to Table I, it will be seen that the solubility of the mixtures remains practically constant, showing that the same solid phases are present in every case. The residues vary in composition from nearly pure mercuric chloride to sodium chloride containing only twelve per cent. of mercuric chloride, so that no double salt can be present and the residues consist of varying proportions of the single salts. This conclusion will perhaps be clearer if the results are considered in another way. If a double salt were present, the residue in No. 1 would consist of a mixture of the double salt and mercuric chloride, and No. 3 would consist of the double salt and sodium chloride. As different solids are present in the two cases, the solubilities would be different. The fact that this is not the case shows that the same solids are present. These can only be the single salts, as the composition of the residue varies between such extreme limits.

Sodium and mercuric chlorides therefore do not form any double salt at 25° from absolute alcohol. From water, the salt NaCl.HgCl₂.2H₂O forms. The conclusion appears justified that the water of crystallization is essential to the formation of the double salt, and if the water were

removed from the double salt it is to be expected that the residue at 25° would consist of an uncombined mixture of the single salts.

The results in Table II show that one double salt of potassium and mercuric chlorides forms from absolute alcohol at 25°. This salt forms under wide conditions. It was present in pure condition in Nos. 3 and 4 of the table, where the solubility varies. Nos. 1 and 2 consist of a mixture of the double salt and mercuric chloride and Nos. 5-7 of a mixture of the double salts and potassium chloride. The double salt appears to be of an unusual type. A sample was prepared by dissolving mercuric and potassium chlorides in hot alcohol in such proportions that only three or four grams crystallized from about 300 grams of alcohol containing but a small percentage of mercuric chloride. The hot solution was placed in the thermostat at 25° and deposited a mass of silky needles of the double salt. They appeared pure under the microscope. The solution, after standing in contact with the double salt, contained 6.8 per cent. of mercuric chloride, also showing that the pure double salt was present. The salt was removed from the mother liquor, dried very rapidly between filter paper, and analyzed. Alcohol was determined directly by Penfield's method for water. The results, with those previously obtained (Nos. 3 and 4, Table II), are given in Table IV, also the calculated composition of two assumed double salts.

TABLE IV.—RESULTS OF THE ANALYSES OF THE DOUBLE SALT FORMING FROM ALCOHOL.

No.	KCl.	HgCl ₂ .	Alcohol.
3	17.63	78.00	4.37 (Diff.)
4	18.27	77.29	4.44 (Diff.)
(Crystallization)	17.07	77.82	4.76 = 99.65
Calculated for 5KCl.6HgCl ₂ .2C ₂ H ₆ O	17.84	77.76	4.40
Calculated for 3KCl.3HgCl ₂ .1C ₂ H ₆ O	20.67	75.08	4.25

The three analyses agree among themselves as closely as could be expected, considering that they were all formed under different conditions. The results agree with the formula 5KCl.6HgCl₂.2C₂H₆O, which is a new type of salt so far as known. The results are so different from the calculated composition of the simpler 3 : 3 : 1 salt that it appears necessary to accept the more complicated formula.

The results, using acetone as solvent, are in Table III. A pure double salt was present in Nos. 3-5 and another in Nos. 8-11. The first corresponds fairly well with the 1 : 5 : 1, the calculated composition of which is given in the table. The results showing the composition of the second salt (Nos. 8-11) vary considerably, as would be expected from the wide variation in the composition of the solutions from which the salt formed. Acetone is much more volatile than alcohol and evaporates so fast that the residues were considerably contaminated with salts from the solution. No. 11 should be the purest sample, as it formed from a solution contain-

ing the smallest amount of dissolved salts. It agrees fairly well with the calculated composition of the 5 : 6 : 2 salt, which forms also from alcohol. The salt can be recrystallized. Mercuric chloride and potassium chloride were therefore dissolved in hot acetone in the proportion in which they are present in the 5 : 6 : 2 salt and the solution was allowed to crystallize at 25°. The analytical results were:

	Found.	Calculated for 5KCl.6HgCl ₂ .2C ₃ H ₆ O.
HgCl ₂	77.52	76.87
KCl.....	17.46	17.64
C ₃ H ₆ O.....	5.02 (Diff.)	5.47

Acetone is lost rapidly by both salts in the air, so this constituent varies considerably from the calculated values in most of the analyses.

The salts with potassium chloride obtained from the three solvents are summarized in the following table:

From water.	From alcohol.	From acetone.
.....	KCl.5HgCl ₂ .C ₃ H ₆ O
KCl.2HgCl ₂ .2H ₂ O
.....	5KCl.6HgCl ₂ .2C ₃ H ₆ O	5KCl.6HgCl ₂ .2C ₃ H ₆ O
KCl.HgCl ₂ .H ₂ O
2KCl.HgCl ₂ .H ₂ O

It will be noticed that none of the types of salts formed from water are formed from the other solvents, and further, that the 1 : 5 : 1 salt from acetone is not formed either from water or from alcohol. The 1 : 5 salt without water has, however, been prepared with rubidium and with caesium.

From the results obtained in this investigation the conclusion may be drawn that when a double salt is formed containing the solvent, the latter is an essential constituent of the salt and is as important in determining the type of double salt formed, as are the individual salts. The substitution of one solvent for another may even prevent a double salt from forming.

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ADDITIONAL NOTES ON THE ALKALI AND ALKALI EARTH AMALGAMS.

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The problem as to the nature of the solid amalgams was first systematically investigated by Kerp,¹ who carried out exact solubility determinations with certain members of the class. In every case the solid as well as the saturated solution in equilibrium with it was analyzed.

¹ *Z. anorg. Chem.*, 17, 284 (1898).