CCXX.—*A Class of Salts which Contain two Solvents of Crystallisation.*

By James Ernest Marsh.

Many halogen salts, which individually are very sparingly soluble in organic solvents, readily dissolve when two are mixed together, thereby forming a double salt. One of the two is an alkali or alkaline earth salt, and the other the salt of a heavy metal. This applies especially to the iodides, less to the bromides, and still less to the chlorides. The organic solvents in question belong to the following types: alcohols, ethers, esters, ketones, and aldehydes. Thus potassium mercuri-iodide, KI,HgI_2, is readily soluble in alcohol, ether, ethyl acetate, acetone, aldehyde, methylal and others, although the solubility of potassium iodide and mercuric iodide separately is very slight. Frequently such double salts crystallise with the solvent. Thus we have a series of alkali-metal silver iodides with acetone of crystallisation, ammonium mercuribromide with ethyl ether, potassium mercuri-iodide with camphor, and rubidium mercuri-iodide with methylal of crystallisation. In some cases, if the solvent contains water or if water is added to the solvent, a hydrated salt crystallises from the organic solvent. Examples of salts of this type are described below.

Potassium iodide and mercuric iodide in equal molecular proportions dissolve in hot methyl carbonate, and, on cooling, a salt crystallises out. The addition of one molecular proportion of water to one of the salt greatly increases the solubility of the latter, and the compound $KHgI_3,H_2O,3Me_2CO_3$ crystallises out on cooling. If more than one molecular proportion of water is added, the salt which separates is not altered in composition. As much as ten molecular proportions of water to one of the salt have been used. The whole dissolves in hot methyl carbonate, although water alone is not appreciably soluble in this solvent. On cooling both the salt crystallises, and the excess of water separates as an aqueous solution. When a large excess of water is taken, the salt which separates is liable to be mixed with a little mercuric iodide. This is prevented by taking sufficient potassium iodide in excess to saturate the water which separates in the cold. The salt $KHgI_3,H_2O,3Me_2CO_3$ is also produced by crystallising the hydrated salt $KHgI_3,H_2O$ from methyl carbonate. When the hydrated salt is brought into contact with methyl carbonate, the clear, yellow crystals immediately begin to disintegrate, and form a nearly colourless, bulky precipitate, which dissolves very readily on warming, and the new salt then crystallises out. The salt prepared in both ways was analysed by determining the loss of weight when heated in a current of dry air. The water given off was also found by absorption with calcium chloride, and the potassium iodide, left after ignition at a low temperature, was weighed.

Found, $H_2O + Me_2CO_3 = 31{\cdot}43$, $31{\cdot}37$, $31{\cdot}06$; $H_2O = 2{\cdot}14$.

$KHgI_3,H_2O,3Me_2CO_3$ requires $H_2O + Me_2CO_3 = 31{\cdot}72$; $H_2O = 1{\cdot}98$ per cent.

The dried salt gave $KI = 26{\cdot}75$; $KHgI_3$ requires $KI = 26{\cdot}77$ per cent.

The salt begins to lose methyl carbonate on exposure to the air at the ordinary temperature. It is difficult, therefore, to guard against a slight loss of methyl carbonate during the manipulation of the crystals before weighing. It does not lose the whole of the methyl carbonate even when heated for some time at 100°, but still retains one molecule. In order to remove the whole of the methyl carbonate and the water, the salt was heated to about 160°.

The *ammonium* salt was prepared in a similar way. Ammonium iodide and mercuric iodide in molecular proportions dissolve sparingly in methyl carbonate, but on the addition of one molecular proportion of water, solution takes place readily, and the salt, $NH_4HgI_3,H_2O,2Me_2CO_3$, crystallises on cooling. This salt also effloresces on exposure to air.

Found, $H_2O + Me_2CO_3 = 24{\cdot}77$; $H_2O = 2{\cdot}27$.

$NH_4HgI_3,H_2O,2Me_2CO_3$ requires $H_2O + Me_2CO_3 = 24{\cdot}86$; $H_2O = 2{\cdot}26$ per cent.

The *rubidium* salt, $RbHgI_3,H_2O,2Me_2CO_3$, was found to be too insoluble to dissolve in any moderate amount of the solvent. It was obtained as a crystalline powder by adding the well-crystallised salt $RbHgI_3,H_2O$ to methyl carbonate. It loses the whole of its water and methyl carbonate at about 100°.

Found, $H_2O + Me_2CO_3 = 21{\cdot}86$; $H_2O = 2{\cdot}00$.
$RbHgI_3,H_2O,2Me_2CO_3$ requires $H_2O + Me_2CO_3 = 22{\cdot}91$; $H_2O = 2{\cdot}08$ per cent.

The *sodium* salt was found to be so soluble that it did not crystallise until the whole solution set to a solid crystalline, yellow mass. By taking the theoretical amounts of sodium iodide, mercuric iodide, and water, the quantity of methyl carbonate required to form the dry, crystalline mass was determined. The quantities used were: sodium iodide, 2·505 grams; mercuric iodide, 7·560 grams; water, 0·296 gram; and methyl carbonate, 1·5816 grams. Although no great accuracy is claimed, the result agrees with the formula $NaHgI_3,H_2O,Me_2CO_3$.

Sodium iodide and silver iodide dissolve in warm methyl carbonate in the proportion NaI to 2AgI. If less silver iodide is taken, some of the sodium iodide remains undissolved. With sufficient methyl carbonate, the solution separates into two layers. The lower layer contains nearly the whole of the salts, the upper layer only a trace. On cooling, the lower layer solidifies to a mass of crystals. The addition of water causes liquefaction and also diminution in volume of the lower layer. Further addition of water brings about a fresh separation of crystals. When sodium iodide and silver iodide are mixed with methyl carbonate and water is added, the salts dissolve in equimolecular proportions, and in these proportions the best crystallisation is obtained. When prepared in this way, the crystals have the composition $NaI,AgI,2H_2O,2Me_2CO_3$.

Found, $Me_2CO_3 = 30{\cdot}3$; $H_2O = 6{\cdot}4$.
$NaI,AgI,2H_2O,2Me_2CO_3$ requires $Me_2CO_3 = 29{\cdot}9$; $H_2O = 6{\cdot}0$ per cent.

The dried salt gave $AgI = 62{\cdot}2$; NaI,AgI requires $AgI = 61{\cdot}5$ per cent.

The *potassium* salt was prepared in a similar way, and obtained in nearly colourless crystals of the formula KI,AgI,H_2O,Me_2CO_3.

Found, $Me_2CO_3 = 17{\cdot}77$; $H_2O = 3{\cdot}43$.
KI,AgI,H_2O,Me_2CO_3 requires $Me_2CO_3 = 17{\cdot}68$; $H_2O = 3{\cdot}54$ per cent.

The dried salt gave $AgI = 58{\cdot}4$; KI,AgI requires $AgI = 58{\cdot}5$ per cent.

I wish to acknowledge the help of a grant from the Royal Society towards the expenses of this work.

UNIVERSITY CHEMICAL LABORATORY,
OXFORD.