CCCLXVII.—*The Systems Sodium Iodide–Acetone and Sodium Iodide–Methyl Ethyl Ketone.*

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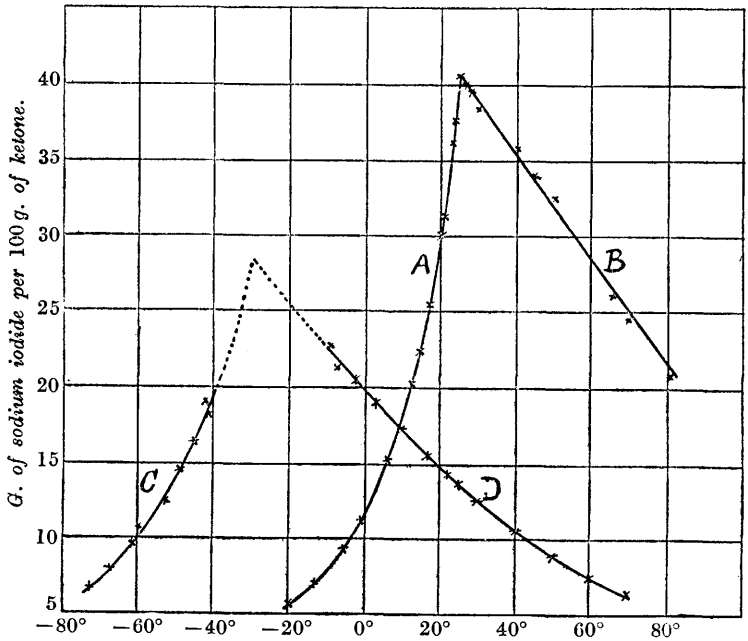
In connexion with the purification of acetone for use in experiments on the reaction between acetone and iodine, the authors were led to inquire into the relations underlying the sodium iodide method described by Shipsey and Werner (J., 1913, **103**, 1255). The inquiry was subsequently extended to ascertain whether the same method could be used for the purification of methyl ethyl ketone. Although the experiments with the latter are not as complete as it was hoped to make them, it seems desirable to place our results on record, more particularly since observations on the system sodium iodide–acetone have just been published by Macy and Thomas (*J. Amer. Chem. Soc.*, 1926, **48**, 1547).

In general, our results for acetone are in agreement with those of Macy and Thomas. At low temperatures the stable solid phase is the compound $NaI,3CMe_2O$, which is converted into the simple iodide at 25·7°. The solubility of the acetone salt complex increases rapidly with rise of temperature, whereas the simple salt shows a rapid fall.

Corresponding measurements with sodium iodide and methyl ethyl ketone show that this system is very similar to the acetone system. Between — 75° and — 45°, the concentration of the sodium iodide in the liquid phase increases rapidly with rise of

temperature, whilst between — 10° and + 70° the proportion of sodium iodide in the saturated solution shows a rapid fall. Over the higher range of temperature, the solid phase is the simple iodide, and the close similarity between the curve systems for the two different ketones suggests that the complex NaI,3COMeEt is the solid phase at lower temperatures. The point at which this complex is transformed into the simple salt is apparently not far removed from — 30°.

FIG. 1.



Solubility of sodium iodide in acetone (*curves* A *and* B) *and in methyl ethyl ketone* (*curves* C *and* D).

The observations made with methyl ethyl ketone indicate that this also may be purified by the use of sodium iodide. The conditions necessary for such purification are, however, radically different from those prescribed by Lochte (*Ind. Eng. Chem.*, 1924, **16**, 956), whose method consists in boiling the moist ketone with excess of sodium iodide, filtering the saturated solution, and allowing it to crystallise at the ordinary temperature. The fact that no result was obtained by Lochte when dry sodium iodide and dry ketone were used is quite in harmony with our observations. The fact that a maximum yield of crystals was obtained by him when the water present was just sufficient to form sodium iodide dihydrate

suggests, however, that the crystalline substance which separates out in the procedure recommended by Lochte is hydrated sodium iodide, and it is clear that his method cannot possibly lead to the desired result.

The conditions actually required for the successful and economic purification of methyl ethyl ketone and of acetone can be deduced from the respective solubility curves shown in the diagram, and need not be further discussed. Solubility data taken from the smooth curves are given below for even temperatures.

Solubility Data (g. of sodium iodide per 100 *g. of solvent).*

(The numbers in italics refer to solutions saturated with the sodium iodide–ketone complex.)

Acetone.

Temp.	−20°	−10°	0°	10°	20°	25·7°	30°	40°	50°	60°	70°	80°
Sol.	*5·5*	*7·8*	*11·8*	*18·2*	*30·0*	40·7	39·2	35·6	32·0	28·6	25·1	21·8

Methyl ethyl ketone.

Temp.	−70°	−60°	−50°	−10°	0°	10°	20°	30°	40°	50°	60°	70°
Sol.	*7·3*	*10·0*	*14·0*	22·8	20·1	17·4	15·0	12·7	10·7	8·9	7·4	6·2

EXPERIMENTAL.

Acetone "A.R." was dried and fractionated; b. p. 56·1—56·2°.

Methyl ethyl ketone was dried and purified by repeated fractionation; b. p. 78—79°.

Sodium iodide was purified by dissolving it in acetone, crystallising the complex, and removing the acetone by heating to constant weight.

At the lower temperatures, saturated solutions were prepared by mechanical stirring of the solution in contact with the solid phase, a sample being removed for analysis. Precautions were taken to exclude moisture. The data for higher temperatures were obtained by enclosing weighed quantities of sodium iodide and ketone in sealed tubes, the contents of which were effectively shaken while the temperature was very slowly raised or lowered. The temperatures at which the solid phase just disappeared on cooling, or made its appearance on warming, agreed closely, usually within 0·1°. In other words, there was little tendency towards formation of supersaturated solutions. In the experiments at the highest temperatures, the vapour space was kept as small as possible, and the requisite small correction applied to obtain the amount of solvent actually in the liquid state.

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