394. *Polyiodides in Benzonitrile.*

By John H. Martin.

When attempting to titrate by sodium thiosulphate the iodine present in a benzonitrile solution (about $N/50$), to which water and potassium iodide had been added, it was found that the addition of starch solution produced no blue coloration. Since more concentrated solutions of iodine showed the same abnormal equilibrium, even with large excess of potassium iodide, a series of approximate distribution experiments was studied, and these showed that iodine and potassium iodide each enhanced to an enormous extent the tendency of the other to pass from the aqueous into the benzonitrile layer, the increments of the two solubilities being always approximately in equimolecular ratio (KI : I_2).

The formation of polyiodides in aqueous solution is well established, and the power of benzonitrile to withdraw them from such a solution implies that some very stable compound is formed, for which search was made. Potassium iodide and iodine in the molar ratio 1 : 1 were dissolved in benzonitrile, and the solution allowed to evaporate in the air. Long feathery crystals of the composition $KI_3,2C_7H_5N$ separated. A similar sodium *compound* was obtained, and lithium iodide yielded $LiI_3,4C_7H_5N$. Ammonium, cæsium, and rubidium yielded only the normal (unsolvated) polyiodides. From hydrogen iodide a yellow *substance* of formula $HI_3,4C_7H_5N$ was obtained.

It thus seems that, although the hydrated series is incompletely known, the tri-iodides form a regular series in association with benzonitrile, the compounds with heavier kations requiring less benzonitrile to stabilise them.

Each of these compounds shows a sharp m. p. (those of the lighter alkali metals having the higher m. p.), and possesses a definite vapour pressure of benzonitrile, the concentration of iodine in the vapour being negligible. In accordance with the views of Cremer and Duncan (J., 1931, 2252), the higher m. p. is associated with a lower dissociation pressure.

EXPERIMENTAL.

Benzonitrile Derivatives.—The *compound* $KI_3,2C_7H_5N$ crystallised from PhCN solution in brownish-green feathery crystals, which were dried between filter papers and then over P_2O_5, which absorbed PhCN. The dried material, m. p. 53°, was analysed by the method of Grace (J., 1931, 398) as adapted for the benzene compounds; care had to be taken in the regulation of the temp. of the silver-foil absorption tube, as the PhCN tended to decompose, depositing tarry matter (Found : KI, 25·63, 25·91, 25·56, mean 25·70; I_2, 39·79, 40·39, 39·89, mean 39·99. $KI_3,2C_7H_5N$ requires KI, 26·56; I_2, 40·58%).

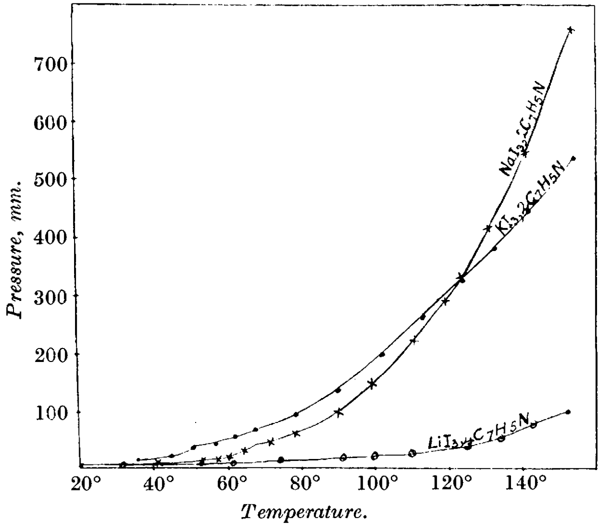
The dissociation press., measured in a glass-spring manometer, showed a break at the m. p. The dissociation pressures of three of the polyiodides are given in the figure; absolute accuracy is not claimed for them, but they clearly show the order of stability of the compounds. The vapour recombines rapidly with the solid on cooling (cf. this vol., p. 588).

The *sodium* compound, $NaI_3,2C_7H_5N$, dark green-brown feathery crystals, was prepared and examined similarly; m. p. 67° (Found : NaI, 23·72, 23·36, 23·53, mean 23·54; I_2, 41·63, 41·73, 41·60, mean 41·65. $NaI_3,2C_7H_5N$ requires NaI, 24·59; I_2, 41·64%).

In the prepn. of the *lithium* compound, $LiI_3,4C_7H_5N$, the evaporation of the PhCN solution had to be carried out in vac. over P_2O_5, because atm. moisture decomposed the material. This formed dark green needles, m. p. 92·5°, showing a very low dissociation pressure (Found: LiI, 16·47, 16·40, 16·36, mean 16·41; I_2, 32·57, 32·69, 32·64, mean 32·63. $LiI_3,4C_7H_5N$ requires LiI, 16·74; I_2, 31·67%).

$HI_3,4C_7H_5N$ separated in pale brown crystals from an ice-cooled mixture of 70% HI aq. and a solution of I in PhCN [Found: total I (mean value, by Grace's method), 46·23. $HI_3,4C_7H_5N$ requires I, 47·97%]; m. p. 97°. Strong alkali slowly decomposed it with liberation of PhCN, and Na decomposed its solution in dry Et_2O, liberating H.

Dissociation pressures of polyiodides combined with benzonitrile.



The only recorded compound resembling this is $C_7H_5N,2HI$, m.p. 135—140° (Biltz, *Ber.*, 1892, **25**, 2536).

Derivatives of Other Nitriles.—*o*-Toluonitrile gave a corresponding green Li compound, $LiI_3,4C_8H_7N$, closely resembling that from PhCN; MeCN and $CH_2Ph{\cdot}CN$ gave no compounds, though iodides and iodine enhanced each other's solubilities in these solvents.

Summary.

1. In the presence of potassium iodide, benzonitrile removes iodine almost completely from aqueous solutions.

2. Solid tri-iodides of Li, Na, and K containing benzonitrile and *o*-toluonitrile have been crystallised. Rb, Cs, and NH_4 tri-iodides do not combine with benzonitrile.

3. A solid compound, $HI_3,4C_7H_5N$, has been obtained.

4. The m. p.'s of the polyiodides rise, and the dissociation pressures fall, with descending atomic weight in this series.

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