

THE CHEMISTRY OF HEPTANE AND ITS SOLUTION.*¹

NO. 7. THE SOLUBILITY OF METHYLAMINE IN HEPTANE.

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While studying the action of methylamine on arsenic trichloride in heptane solution, it seemed desirable to learn something about the solubility of the base in the hydrocarbon. For this purpose a commercial 33 per cent alcoholic solution of methylamine (Eastman Kodak Co.) was transferred to an Erlenmeyer flask connected with a reflux condenser, which, in turn, was connected with a calcium chloride tower and this with four flasks containing heptane surrounded by a freezing mixture.

In order to liberate the methylamine in the Erlenmeyer, it was not necessary to heat the alcoholic solution. A current of nitrogen, the rate of which was regulated by bubbling it through glycerin, released the base. Any alcohol carried over with it was held back in the CaCl_2 tower. The first receiving flask was regarded as saturated when methylamine escaped from the fourth.

The methylamine content of the heptane solution, after it had stood at room temperature (22°), was determined in 5-cc. portions as the platinum double salt and by titration. The amount of platinum obtained after ignition of the double salt revealed the amount of methylamine when computed after the formula $\text{B}_2\text{H}_2\text{-PtCl}_6$ in which B, the base, stands for methylamine. In the titration, 5-cc. portions were shaken with 25 cc. of $N/100$ HCl (1) and the excess of acid titrated back with $N/100$ NaOH (2) using phenolphthalein as indicator. Duplicates by both methods gave the following results recorded as grams per cc. of heptane.

| Platinum Double Salt. | Titration. |
|-----------------------|--------------|
| 1. 0.00109 Gm. | 0.000595 Gm. |
| 2. 0.00113 Gm. | 0.000595 Gm. |
| Average 0.00111 Gm. | 0.000595 Gm. |

Hence the titration method yielded results 45.9 per cent lower than the platinum double salt method. Both methods were repeated, but in the titration method the methylamine was shaken out four successive times with four separate portions of $N/100$ HCl, namely, 25 cc., 15 cc., 5 cc. and 5 cc., respectively. This time the following results were obtained:

| | |
|---------------------|-------------|
| 1. 0.00115 Gm. | 0.00127 Gm. |
| 2. 0.00112 Gm. | 0.00125 Gm. |
| Average 0.00114 Gm. | 0.00126 Gm. |

Whereas the results obtained by the platinum chloride double salt method were essentially the same as those obtained before, the modified titration method gave much higher results than those obtained in the first series, indeed 9.6 per cent higher than the precipitation method.

* Scientific Section, A. P. H. A., Madison meeting, 1933.

¹ From the laboratory of Edward Kremers.

In order to determine the solubility of methylamine in heptane at different temperatures, 5-cc. quantities were saturated with the base. Before shaking out the base with acid, nitrogen was passed over the heptane solution for 10 minutes to remove gaseous methylamine from the flask. The results of a duplicate series of determinations are herewith tabulated as grams per 1 cc. of solvent.

| t. | I. | II. |
|------|-------------|-------------|
| 40° | 0.00024 Gm. | 0.00024 Gm. |
| 20° | 0.00031 Gm. | 0.00028 Gm. |
| 10° | 0.00048 Gm. | |
| 3° | 0.00072 Gm. | 0.00081 Gm. |
| 0° | 0.00120 Gm. | 0.00123 Gm. |
| -5° | 0.00137 Gm. | 0.00168 Gm. |
| -10° | 0.00128 Gm. | 0.00127 Gm. |
| -13° | 0.00075 Gm. | 0.00081 Gm. |

Methylamine is reported to liquefy at -7° at which temperature it shows its maximum solubility in heptane, the solubility diminishing not only above this point, but below as well.

In order to check the solubility at the higher temperatures used, heptane was saturated at 0° and the temperature raised to 20° and kept there for 15 min. before 5-cc. portions were withdrawn for titration. The same performance was repeated at 40° . Again the results are tabulated:

| | | |
|-----|--------------|--------------|
| 40° | 0.000139 Gm. | 0.000149 Gm. |
| 20° | 0.00027 Gm. | 0.00028 Gm. |

The accompanying curve reveals graphically the solubilities at different temperatures as already stated.

REFERENCES.

- (1) The standard HCl was prepared by the method of a constant boiling mixture as described by C. W. Foulk and M. Hollingsworth, *J. A. C. S.*, 45 (1923), 1220.
- (2) The standard NaOH was prepared by precipitating the carbonates from a concentrated solution of NaOH with barium chloride and diluting with carbon dioxide-free water in an atmosphere of nitrogen.

A. Ph. A. Resolution No. 11. Historical Material for Museum and Library of Headquarters Building.

Resolved, that the Local Branches of the AMERICAN PHARMACEUTICAL ASSOCIATION, State Pharmaceutical Associations, Boards and Colleges of Pharmacy as well as other organizations and individuals interested in the progress and development of pharmacy be urged to supply documents of historical interest, relics and museum material to the museum and library of the Headquarters Building of the AMERICAN PHARMACEUTICAL ASSOCIATION at Washington.

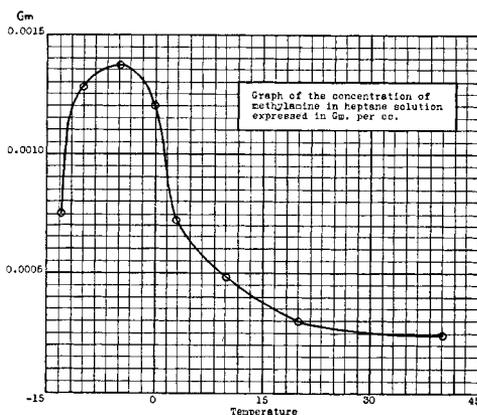


Fig. 1.