

ment with the views correlating addition compound formation with diversity in character of the components developed in previous articles of this series. It is apparently in disagreement, however, with the fact that Dawson and Mountford succeeded in isolating definite compounds from phenol-cresol mixtures in five out of six systems.

A brief consideration of the equilibria existent in binary mixtures of associated liquids has shown that the compounds obtained by Dawson and Mountford are to be regarded as substitution rather than as addition compounds. Under this view, no conflict exists between the results of Dawson and Mountford and those of the present work; both fall directly into line with the general theory.

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SOME PHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS OF CERTAIN PYRIDINE BASES.

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The physical properties of mixtures of pyridine and water have been the subject of a number of investigations.¹ The optical and thermal constants of pyridine and the mono methylpyridines have been determined by Constam and White.² More aqueous solutions of the higher homologs of pyridine have not been examined up to the present with the exception of 3 and 4 methylpyridines and 2,6-dimethylpyridine, studied by Flaschner.³ In the present article are given measurements of densities and other physical characteristics of aqueous solutions of some of these higher homologs.

Preparation of Materials.

The bases used had been purified by the methods described elsewhere.⁴ On account of their hygroscopicity they were redistilled before use from solid sodium hydroxide, in an apparatus previously dried by the passage of air dried with sulfuric acid, and the receiver was protected from the external air by a calcium chloride tube. They were then preserved in desiccators kept in the dark. The aqueous solutions were made up by weight with conductivity water in the type of weighing bottle recommended by Hartley, Thomas and Applebey, having its stopper fitting over the outside of the neck.

¹ "Absorption by Electric Waves," Bredig, *Z. Elektrochem.* **7**, 767 (1901); "Densities and Viscosities," Dunstan, Thole and Hunt, *J. Chem. Soc.*, **91**, 1718 (1907); "Densities, Viscosities and Surface Tensions," Hartley, Thomas and Applebey, *ibid.*, **93**, 538 (1908); "Refractive Indices and Partial Vapor Pressures," Zawidzki, *Z. physik. chem.*, **35**, 129 (1900), "Composition of Constant Boiling Mixtures," Goldschmidt and Constam, *Ber.* **16**, 2977 (1883).

² Constam and White, *Am. Chem. J.*, **29**, 1 (1903).

³ Flaschner, *J. Chem. Soc.*, **95**, 668 (1909).

⁴ Heap and Jones, *THIS JOURNAL*, **43**, 1936 (1921).

Densities.

It was originally intended to employ the determinations of the densities of aqueous solutions of pyridine made by Hartley, Thomas and Applebey,¹ for the purpose of finding the composition of the constant-boiling mixture. Since a different value for the density of anhydrous pyridine was found, it was necessary for our needs to redetermine the densities. Freshly distilled samples were used. Our values are corrected for air displacement and are here tabulated. The table also embodies the results obtained by us for 2- and 3-methylpyridines.

TABLE I.
DENSITIES.

| Water. % | Pyridine. d_4^{25} | 2-Methylpyridine. d_4^{25} | 3-Methylpyridine. d_4^{25} |
|-------------|-------------------------|---------------------------------|---------------------------------|
| 0 | 0.9776 | 0.9404 | 0.9515 |
| 10 | 0.9888 | 0.9637 | 0.9675 |
| 20 | 0.9979 | 0.9787 | 0.9778 |
| 30 | 1.0018 | 0.9867 | 0.9845 |
| 40 | 1.0028 | 0.9911 | 0.9881 |
| 50 | 1.0032 | 0.9936 | 0.9905 |
| 60 | 1.0029 | 0.9952 | 0.9924 |
| 70 | 1.0020 | 0.9960 | 0.9938 |
| 80 | 1.0008 | 0.9965 | 0.9950 |
| 90 | 0.9991 | 0.9968 | 0.9962 |
| 100 | 0.9971 | 0.9971 | 0.9971 |

Compositions of the Constant-boiling Mixtures.

Goldschmidt and Constam¹ who were the first to prepare the constant-boiling mixture in the case of aqueous pyridine, concluded that it was an undissociated compound, $C_5H_5N \cdot 3H_2O$, basing their conclusions on its nitrogen content and its vapor density, which they gave as 1.19 to 1.16, referred to air. This value of the vapor density, however, corresponds with complete dissociation, and the accuracy of the value given by them is borne out by our experiments, in which the Victor Meyer method was used. The vapor density of the constant-boiling mixture of 2-methylpyridine and water also corresponds with complete dissociation.

We have also undertaken determinations by the cryoscopic method of the molecular weights of the bases in aqueous solution. For this purpose we prepared standard aqueous solutions of pyridine and of 2-methylpyridine by adding known weights of the constant-boiling mixtures to known weights of water. In solutions containing less than 4% of the bases the molecular weights obtained are those of the bases, namely, 79 and 93 respectively. With 6% solutions our results indicate that, if it may be assumed that we are still dealing with dilute solutions, either there is polymerization of the base, which is improbable, or there is partial conversion into hydrate.

Variation of the Composition of the Constant-boiling Mixtures with Pressure.

The method of investigation here employed was that of Roscoe.⁵ Our results were as follows:

TABLE II.
VARIATION OF COMPOSITION OF CONSTANT-BOILING MIXTURES WITH THE PRESSURE.

| Pressure. Mm. Hg. | Boiling point. °C. | Density of distillation. d_4^{20} |
|----------------------|-----------------------|--|
| | Pyridine. | |
| 767.0 | 93.0 | 1.00315 |
| 633.5 | 87.7 | 1.00313 |
| 483.0 | 80.8 | 1.00311 |
| 358.5 | 73.7 | 1.00316 |
| 235.5 | 64.2 | 1.00316 |
| | 2 = Methylpyridine. | |
| 753.0 | 93.5 | 0.99318 |
| 653.0 | 89.5 | 0.99318 |
| 572.5 | 86.4 | 0.99318 |
| 401.5 | 77.5 | 0.99318 |
| 194.0 | 61.5 | 0.99320 |
| | 3 = Methylpyridine. | |
| 768.0 | 96.2 | 0.99247 |
| 596.0 | 89.6 | 0.99255 |
| 450.0 | 82.2 | |
| 425.5 | 80.8 | 0.99259 |
| 270.0 | 70.0 | 0.99276 |

From these results we deduce that the variation in density is slight but real. Therefore, in view of our vapor-density results and of this fact, we can state definitely that these constant-boiling distillates are mixtures and not compounds.

Making use of our density data we find that the constant-boiling mixture of water with pyridine contains 42% of water; with 2-methylpyridine, 48% of water; and with 3-methylpyridine, 61% of water. In the case of 2-methylpyridine this corresponds with the formula $4 C_6H_7N.19H_2O$, and in the case of 3-methylpyridine, with $3C_6H_7N.25H_2O$, which is further confirmation of the non-existence of compounds.

TABLE III.

MISCIBILITY OF 2,4-DIMETHYLPYRIDINE⁶ WITH WATER.

| | | | | | | | | | | |
|------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Water, % by Wt. | 15.99 | 23.14 | 30.92 | 37.50 | 45.14 | 55.11 | 67.96 | 79.54 | 93.00 | 95.06 |
| Lower solution point, °C.... | >150 | >150 | 68.5 | 53.0 | 39.0 | 27.2 | 23.0 | 23.0 | 35.0 | 54.3 |

The minimum critical solution temperature is 22.5°. The composition of the constant-boiling mixture of 2,4-dimethylpyridine and water

⁵ Roscoe, *J. Chem. Soc.*, 13, 146 (1861); 15, 270 (1862).

⁶ The solubility of this base in water was determined by Alexéeff's method.

was determined by means of the solubility curve. A mixture of 2,4-dimethylpyridine and water was distilled, and the distillate which boiled constantly at 96.5° consisted of two layers. When the distillate was cooled below 23.2° , it became homogeneous. Reference to the miscibility data showed that it contained 66% of water.

Summary.

The densities of aqueous solutions of pyridine, 2-methylpyridine and 3-methylpyridine have been determined. The compositions of the constant-boiling mixtures have also been ascertained, and found to be 42%, 48% and 61% of water respectively. Solubility data for 2,4-dimethylpyridine have also been given.

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A THEORY OF ALLOTROPY.

BY MAURICE COPISAROW.

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The term *allotropy* was first introduced by Berzelius,¹ as denoting the appearance of an element in several states distinguished from one another by different properties, a definition lacking in precision, owing to the numerous possible interpretations of the "different properties."

Allotropy is taken as a term covering the different physical states of matter, and also isomerism, polymerism and polymorphism,² and in this sense might appear, perhaps, to be an unnecessary term without exact meaning in chemical nomenclature.

This inclusion of different phenomena, along with Ostwald's and Nernst's definition of allotropy on the basis of energy changes, and Benedick's, Honda's and Le Chatelier's conception based upon the discontinuity of forms, phases and properties, is due to the consideration of *effects* of, instead of *causes* underlying phenomena.

While a close study of the various properties of matter consequent to a certain phenomenon may help us in comprehending the phenomenon itself and its relationship to other natural manifestations, it is wrong to define a phenomenon by its effects, especially when these effects are anything but specific or characteristic. A far truer and more productive definition would be based upon the study of the *causes* of a phenomenon, the unmasking of which should naturally throw much light upon the phenomenon itself and its probable effects.

The possible causes of allotropy may be either (a) a variation in the intramolecular structure of elements, or (b) a change in the intermolecular association or aggregation of elements.

¹ Berzelius, *Jahresber.* 20, [II] 13 (1841).

² Lehmann, *Z. Kryst. Min.*, 1, 97 (1877); Lowry, *Trans. Faraday.*, 11, 150 (1916).