XCVI.—*The Mutual Solubility of 2-Methylpiperidine and Water.*

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It is impossible to draw many general conclusions as regards the influence of constitution on the mutual solubility of liquids, because only a very few members of any one homologous series are suitable for

* The molecular weights have been doubled throughout because of facility of comparison with mercurous nitrite, which, there is reason to believe, has the formula $\text{Hg}_2(\text{NO}_2)_2$, and also with the nitrites of the alkaline earths.

† Cæsium and rubidium are, of course, left out of consideration for the present.

the determination of the complete solubility curve or even of one of the two critical solution-temperatures. An upper critical temperature with water has been observed in the following homologous series :

In the series of alcohols (Alexéeff, *Wied. Annalen*, 1886, 28, 305) :

<i>iso</i> Butyl alcohol	130°
<i>sec.</i> -Butyl alcohol.....	113·7

In the series of aliphatic acids (Rothmund, *Zeitsch. physikal. Chem.*, 1898, 26, 460) :

<i>n</i> -Butyric acid	- 2·3°
<i>iso</i> Butyric acid	24·5°

The corresponding lower critical solution-temperatures, on account of the appearance of a solid phase, cannot be obtained.

On the other hand, in the following series, the lower critical solution-temperature can be determined, whilst the upper one lies too high for observation :

In the series of aliphatic amines :

Diethylamine (Guthrie, <i>Phil. Mag.</i> , 1884, [v], 18, 499)	about 121°
Triethylamine (Rothmund, <i>loc. cit.</i>).....	18·7°

In the pyridine series :

2 : 6-Lutidine (Timmermans, <i>Zeitsch. physikal. Chem.</i> , 1907, 58, 144) ...	40°
2 : 4 : 6-Trimethylpyridine (Rothmund, <i>loc. cit.</i>)	6·42°

In the piperidine series (Flaschner, *Zeitsch. physikal. Chem.*, 1908, 62, 493) :

1-Methylpiperidine	48·3°
1-Ethylpiperidine	7·5°

If, as suggested by Rothmund, the solubility of two not completely miscible liquids is represented by a closed curve, all these solubility rings of one liquid, for example, water when used in conjunction with the members of homologous series, seem to have the same "centre." The higher the member in the homologous series the less is the mutual solubility, and therefore the wider the theoretical ring, that is, the lower critical solution-temperature occurs at a lower point in the thermometric scale, and the upper critical temperature at a higher point (Timmermans, *Zeitsch. physikal. Chem.*, 1907, 58, 145). From the examples given, it is evident that the increase of mutual solubility is due to the oxygen and nitrogen atoms, whilst, on the other hand, carbon and hydrogen atoms cause a decrease. The larger the carbon-hydrogen group attached to the oxygen or nitrogen, or the nearer such a group to these atoms, the smaller is the mutual solubility. A decrease in the

number of carbon or hydrogen atoms produces an increase in the mutual solubility. α -Picoline is miscible with water in all proportions, whilst 2-methylpiperidine, which has six atoms of hydrogen more, is not miscible with water within certain limits of temperature. Considering that 1-ethylpiperidine is completely analogous to triethylamine and contains only one carbon atom more, one would expect a depression of the lower critical solution-temperature, and this is found to be the case, for the lower critical solution-temperature of the cyclic compound is lower by 11° than that of triethylamine. Therefore the ring formation itself can have little or no influence on the solubility.

Further, it appeared to be of interest to determine the influence of the position which an organic group in a cyclic compound occupies. As one of us has found that the piperidines form a class of substances which give with water an easily obtainable lower critical solution-temperature, and from the values of the dielectric constants (Ladenburg, *Zeitsch. Elektrochem.*, 1901, 7, 816) other examples are to be expected, we have made determinations with 2-methylpiperidine. This substance was prepared according to Ladenburg's method (*Annalen*, 1888, 247, 5). The fraction of commercial picolines boiling from 128° to 134° was purified by recrystallising the mercury salt, and the α -picoline was reduced with sodium and absolute alcohol. The 2-methylpiperidine obtained in this way was fractionated several times, and the single fractions were tested for purity by Crismer's method, by determining the lower critical solution-temperature. Finally, the fraction boiling at 117.5 – 118.5° was regarded as the purest, and was used for the following experiments.

The determination of the solubility curve was made by Alexéeff's well-known synthetic method. To determine the lower half of the curve, definite quantities of the base and water were introduced by means of a capillary pipette into a narrow tube, which was blown out at one end into a small bulb and at the other end drawn out into a capillary; the mixture was weighed. The capillary was sealed and the temperature was determined, at which separation into two layers took place; the capillary was then broken off, and, after a further quantity of the liquids had been added, it was used for another experiment. The determination of the upper half of the curve was carried out in small tubes of Jena glass (5 mm. external, 3 mm. internal diameter), drawn out into thick capillaries at one end. These liquid mixtures were only used for one determination, although even at 230° the glass was only slightly attacked by the base. In the following table, the amount of 2-methylpiperidine is given in percentage by weight of the solution. In the neighbourhood of the lower critical solution-point, a distinct critical opalescence was observed. The results are reproduced in the diagram.

2-Methylpiperidine.	Solution point.	2-Methylpiperidine.	Solution point.
72.3	165°	9.5	82.4°
64.7	112	8.6	86.5
52.4	94	7.8	92.4
47.0	88.8	6.8	homogeneous up to 170°
39.7	87	60.4	221°
33.7	87.2 opalescence	52.4	225
29.2	83	28.3	227
24.0	81	20.1	227
19.4	79.3	15.0	220
13.8	79.8	9.7	188
10.6	80.4	8.2	171

It is thus evident that the complete solubility ring of water-2-methylpiperidine can be followed; the only other case in which similar observations have been made is that of nicotine and water (Hudson, *Zeitsch. physikal. Chem.*, 1904, 47, 113). The lower half of the curve has a

shape similar to that of mixtures of 2:4:6-trimethylpyridine and of 1-methyl- and 1-ethyl-piperidine with water, namely, somewhat abruptly curved, whilst the upper nearly symmetrical half is similar to that of the known liquid pairs with upper critical solution-temperatures. Also, the law of rectilinear diameters, as Rothmund first showed, holds fairly well for the upper point, whilst the diameter for the lower part is sharply curved. The regularity indicated above is observed here also. In consequence of the greater distance of the methyl group from the nitrogen atom in 2-methylpiperidine compared with 1-methylpiperidine, the lower critical solution-temperature of the former is increased by 31° and the upper one is depressed by about 60°.

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