897. *Phase Relationships in the Pyridine Series. Part II.** *The Miscibility of Some Pyridine Homologues with Deuterium Oxide.*

By J. D. Cox.

The miscibility of the picolines and of three lutidines with deuterium oxide is studied. α-Picoline is only partially miscible (see also Timmermans and Poppe, *Compt. rend.*, 1935, **201**, 608) as also is β-picoline; γ-picoline is completely miscible. The partial miscibility of β-picoline with deuterium oxide affords a simple method of analysing deuterium oxide–water mixtures, and a suitable procedure is suggested.

It has been known for some years that the consolute temperatures of aqueous binary systems are appreciably altered by changing the isotopic composition of the water, and it appears to be a general rule (Timmermans, *J. Chim. phys.*, 1949, **46**, 546) that an upper consolute temperature is raised while a lower consolute temperature is lowered, if water enriched in deuterium oxide is used, in the appropriate binary system. Timmermans and

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* Part I, preceding paper.

Poppe (*Compt. rend.*, 1935, **201**, 608) found that although α-picoline is completely miscible with water at all temperatures, it is only partially miscible with deuterium oxide at 92—112·5°. This has been confirmed in the present work. As β-picoline shows a stronger tendency to separate from water than does α-picoline (cf. Part I), it was expected that the β-isomer would separate from deuterium oxide to give a solubility ring much wider than 20°. It has now been found that the β-picoline–deuterium oxide system gives a closed loop solubility curve 78·5° wide (Fig. 1), the consolute temperatures being 38·5° [a mixture containing 28% (by weight) of β-picoline] and 117·0° [34% (by weight) of β-picoline]. The centre of the solubility ring, at 78°, corresponds closely with the temperature of the terminal plait point, 79°, for the system β-picoline–2 : 6-lutidine–water (Part I). It is clear that at this temperature the tendency for β-picoline to separate from water reaches a maximum.

Because of the difference between the two consolute temperatures of the β-picoline–deuterium oxide system, a potential method of analysing D_2O–H_2O mixtures becomes apparent. The use of solution temperatures for such an analysis was first advocated by Patterson (*J.*, 1937, 1745) who suggested phenol as the third component. Clearly β-picoline would be superior for this purpose, as the rate of change of solution temperature with respect to the content of deuterium oxide is some three times as great. In addition, the fact that β-picoline–deuterium oxide–water systems have two solution temperatures allows two independent determinations to be made on each sample of water. In actual analyses it is obviously preferable to use a two-dimensional calibration curve rather than a phase model, so that the proportion of one constituent of the ternary mixtures should be kept constant. This condition was satisfied in the present work by keeping the proportion of β-picoline constant at 30% (by weight), a compromise between the two consolute compositions of the β-picoline–deuterium oxide system. The solubility curve thus obtained (Fig. 2) shows that the method is applicable to the analysis of water containing 20—100% of deuterium oxide, an accuracy of ±0·4% being attainable if solution temperatures are determined with an accuracy of ±0·1°. It cannot be claimed that this method of deuterium analysis can compete with some of the well-established methods (Kirshenbaum, "Physical Properties and Analysis of Heavy Water," McGraw-Hill, New York, 1951) in respect of the accuracy obtainable, although it would not be difficult to refine the method so that solution temperatures could be determined with an uncertainty no greater than 0·01° (cf. Rowden and Rice, *J. Chem. Phys.*, 1951, **19**, 1423). The merit of the method obviously lies in the extreme simplicity of the apparatus and technique required.

FIG. 1. *Solubility curve for the system β-picoline–deuterium oxide.*

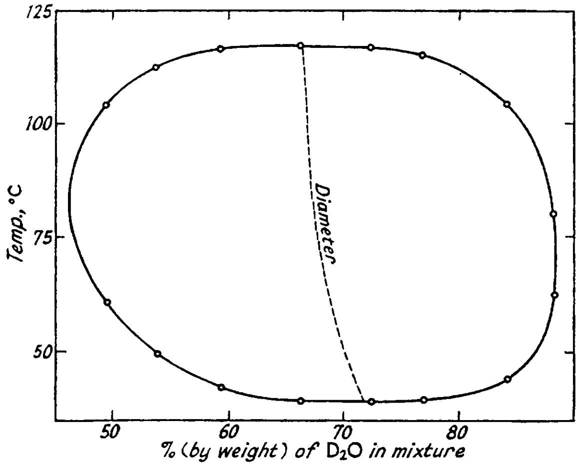
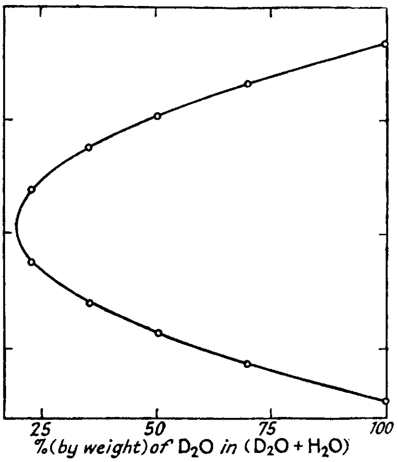


FIG. 2. *Solubility curve for the system β-picoline (30%)-deuterium oxide–water.*



No changes in the solution temperatures either of binary mixtures of β-picoline and deuterium oxide or of ternary mixtures containing water could be detected during the course of a week, but over a period of two months small but significant shifts were found. Lower solution temperatures were depressed by an average of 0·2° while upper solution temperatures were elevated by the same amount. It can therefore be said that isotopic exchange does not invalidate the analytical method, provided solution temperatures are determined within a few days of preparation of the mixtures.

Although several studies have been made of the effect of substituting deuterium oxide for water in systems with either an upper or a lower consolute temperature, the effect in systems having both temperatures has not been described hitherto. Results for three lutidines, summarised in Table 1, bear out Timmermans' generalisation (*J. Chim. phys.*, 1949, **46**, 546), based on observations of systems with one consolute point, that the substitution causes the region of partial miscibility to increase. In the cases of 2 : 4- and 2 : 5-lutidine the depression of the lower temperature is approximately equal to the elevation of the upper temperature. This does not appear to apply to 2 : 6-lutidine but the uncertainty attaching to the Δ value for the upper point is unfortunately too great to warrant further comment.

TABLE 1. *Solution temperatures of lutidine–water and lutidine–deuterium oxide systems.*

System.	Lower soln. temp.*	Δ †	Upper soln. temp.*	Δ †
2 : 4-Lutidine–H_2O	23·5 ± 0·2°	7·3°	188·5 ± 0·3°	−7·5°
,, –D_2O	16·2 ,,		196·0 ± 0·5	
2 : 5-Lutidine–H_2O	13·1 ± 0·2	4·6	206·0 ± 0·5	−5·6
,, –D_2O	8·5 ,,		211·6 ± 1	
2 : 6-Lutidine–H_2O	34·0 ± 0·2	5·3	228·7 ± 1	+0·7
,, –D_2O	28·7 ,,		228 ± 1	

* These temperatures apply to solutions containing 30% (by weight) of base; they are certain to be very close to the consolute temperatures (cf. Part I).

† Δ represents the solution temperature of a water system minus that of the corresponding deuterium oxide system.

EXPERIMENTAL

The purities of the pyridine homologues used and the method of determining solution temperatures were as described in Part I. The deuterium oxide was stated to contain 99·75% of D_2O, d_4^{20} 1·10514; approximately 0·1 g. was taken for each determination.

A mixture of α-picoline and deuterium oxide containing 30·1% (by weight) of the former had solution temperatures 93·8° and 111·8°. A solution of γ-picoline of the same concentration remained as a single phase between 20° and 150°. Results for the β-picoline–deuterium oxide system are shown graphically in Fig. 1 while those for three lutidine systems (each containing 30% by weight of base) are given in Table 1. Data for ternary mixtures of β-picoline, deuterium oxide, and water are summarised in Table 2.

TABLE 2.

Wt. %, β-picoline in total mixture	Wt. %, D_2O in $H_2O + D_2O$	Lower soln. temp.	Upper soln. temp.
29·6	69·8	46·8°	108·0°
31·1	50·3	53·6	100·9
30·3	35·3	60·1	94·0
30·5	22·8	69·0	84·7

It was found that the relation between the percentage, x, of deuterium oxide in a deuterium oxide–water mixture and the solution temperature, t (° c), of a ternary mixture containing 30% of β-picoline could be represented by an equation of the type :

$$x = A + Bt + Ct^2 + Dt^3$$

For lower solution points A, B, C, and D were 236·0, −2·122, $-6{\cdot}56 \times 10^{-2}$, and $7{\cdot}50 \times 10^{-4}$, respectively; for upper solution points values of 47·7, −1·111, $-1{\cdot}345 \times 10^{-3}$, and $1{\cdot}250 \times 10^{-4}$, respectively, fitted the experimental results between $x = 100$ and $x = 25$.

This work formed part of the programme of the Chemistry Research Board and is published by permission of the Director of the Chemical Research Laboratory.

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[*Received, July 2nd*, 1952.]