896. *Phase Relationships in the Pyridine Series. Part I. The Miscibility of some Pyridine Homologues with Water.*

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The miscibility of pyridine, α-, β-, and γ-picoline and 2 : 4-, 2 : 5-, and 2 : 6-lutidine with water is examined. The first four compounds are miscible in all proportions at all temperatures, but α- and β-picoline show strong tendencies to separate from water in the regions of 110° and 80°, respectively, as shown by the appearance of opalescence, in 30% solutions, at these temperatures. The lutidines are only partially miscible with water, their behaviour being represented by closed loop solubility curves.

An unorthodox method is described whereby the phase relationships in the ternary system β-picoline–2 : 6-lutidine–water are studied with a maximum use of the synthetical method and a minimum recourse to analysis; the results are extended to the quaternary system β-picoline–γ-picoline–2 : 6-lutidine–water.

Several references to the solubilites of pyridine homologues in water are available (Seidell, " Solubilities of Organic Compounds," Van Nostrand, New York, 1941), but it is now apparent that in some cases the samples used were of unsatisfactory purity. As a number of these compounds have been prepared very pure in this laboratory we have made a more reliable determination of their solubilities than has been possible hitherto.

In agreement with earlier workers we found pyridine, α-picoline (2-methylpyridine), and γ-picoline (4-methylpyridine) completely miscible with water at all temperatures; we also found that β-picoline was completely miscible. This is contrary to Flaschner's results (*J.*, 1909, **95**, 668) in the temperature range 49—153° c, but in agreement with those of Heap, Jones, and Speakman (*J. Amer. Chem. Soc.*, 1921, **43**, 1936). There can be little doubt, judging by the method of purification used, that Flaschner's β-picoline was a mixture containing substances of low water solubility. The erroneous statement frequently found in text-books (*e.g.*, Glasstone "Textbook of Physical Chemistry," Van Nostrand, New York, 1947, and Findlay, "The Phase Rule and its Applications," Longmans Green, London, 1938) that the β-picoline–water system exhibits a closed loop solubility curve, appears to be derived from Flaschner's work.

Mixtures of β-picoline and water, containing 60—75% by weight of the latter, showed marked opalescence at 60—90°. An increase of temperature did not, however, cause phase separation; instead the opalescence faded, becoming undetectable by eye at 100°. A mixture of α-picoline with water (70% by weight) gave rise to rather fainter opalescence at 100—120°, but γ-picoline did not show the phenomenon. We believe that the opalescence is a property of the picolines themselves and is not due to residual and less soluble impurities, because any such impurities were present to the extent of not more than 0·25 mole %, and as will be seen later, some 4 moles % of 2 : 6-lutidine in β-picoline were required to bring about phase separation with water.

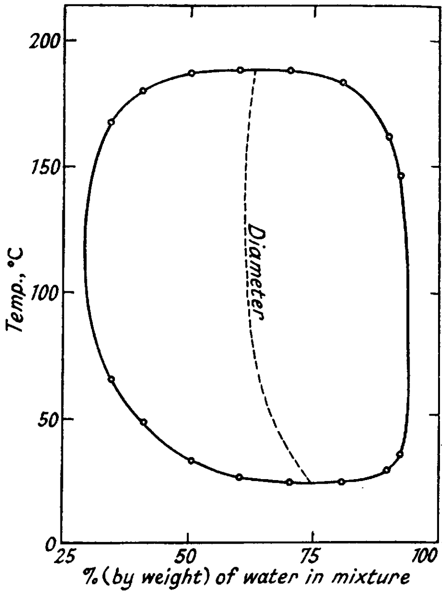


FIG. 1. *Solubility curve for the system 2 : 4-lutidine–water.*

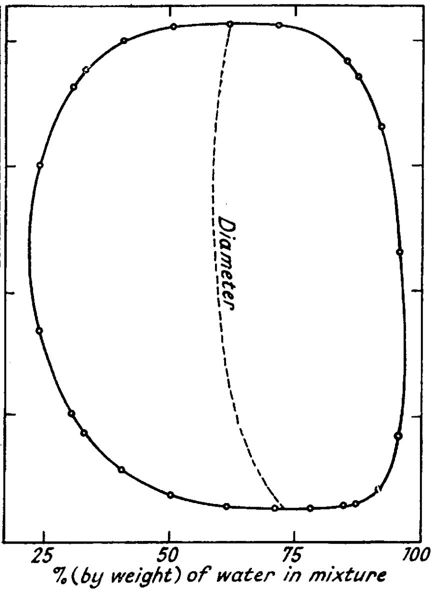


FIG. 2. *Solubility curve for the system 2 : 5-lutidine–water.*

Closed loop solubility curves were obtained, by Alexejeff's method, for each of the systems 2 : 4-, 2 : 5-, and 2 : 6-lutidine (2 : 4-, 2 : 5-, and 2 : 6-dimethylpyridine, respectively) with water (see Figs. 1, 2, 3*a*). Near the critical compositions, all three systems exhibited strong opalescence both below the lower and above the upper consolute temperatures. The more important data are summarised in Table 1.

TABLE 1. *Critical solution data for the lutidine–water systems.*

	Lower consolute point,		Upper consolute point,	
System	temp., ° c	water, % by wt.	temp., ° c	water, % by wt.
2 : 4-Lutidine–water	23·4 ± 0·2	74·5	188·7 ± 0·3	63
2 : 5- ,, ...	13·1 ± 0·2	73	206·9 ± 0·5	62
2 : 6- ,, ...	34·0 ± 0·2	70	230·7 ± 1	59

Flaschner (*loc. cit.*) gave 45° and 165° as the two consolute temperatures for the 2 : 6-lutidine–water system, and Coulson and Jones (*J. Soc. Chem. Ind.*, 1946, **65**, 169) found 33·9° for the lower consolute temperature, in excellent agreement with our result; again it is likely that Flaschner's material was grossly impure. Jones and Speakman (*J. Amer.*

Chem. Soc., 1921, **43**, 1869) gave 22·5° as the lower consolute temperature for the 2 : 4-lutidine–water system but did not investigate the upper consolute point. Solubility data for 2 : 5-lutidine have not previously been reported.

Commercial "β-picoline" is a mixture of β- and γ-picoline with 2 : 6-lutidine, and fractional distillation of the azeotropes with water has sometimes been used to separate the three bases (Cislak and Karnatz, U.S.P. 2,335,823; B.P. 580,048). The phase relationships in this quaternary system were therefore of interest, but we preferred in the first place to make a limited examination of the ternary system β-picoline–2 : 6-lutidine–water. Rather than attempt to construct a series of binodal curves for the whole temperature range of interest (30—230°), we have determined the shapes of sections in two directions at right angles across the phase model (planes *NOPQ* and *KLM* in Fig. 4) and a further series of sections along planes such as *AGHD* and *AIJD* (Fig. 4). It was thus possible to determine the shape of the binodal surface accurately, without an undue expenditure of effort.

FIG. 3. *Solubility curves of* (a) *the system* 2 : 6-*lutidine–water, and* (b) *and* (c) *the system β-picoline*–2 : 6-*lutidine–water* (see *Table* 2).

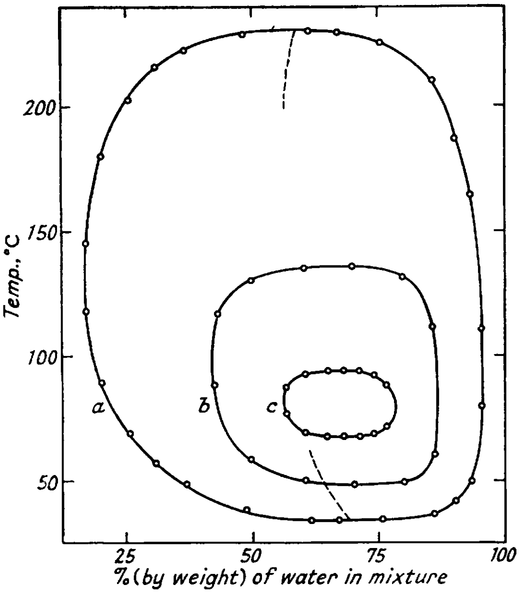
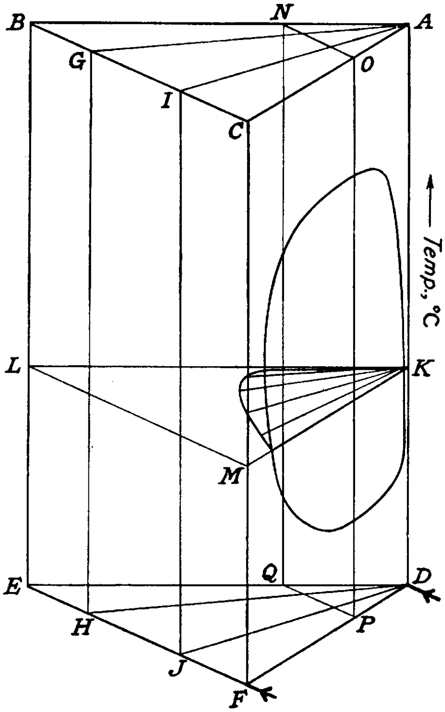


FIG. 4. *Construction of the phase model for the system β-picoline*–2 : 6-*lutidine–water.*



K corresponds to water (100%)
L ,, *β-picoline* (100%).
M ,, 2 : 6-*lutidine* (100%).

As all points on plane *AGHD* correspond to compositions containing the two bases in a fixed ratio, the construction of the cross section on this plane involved making up a mixture of the bases in known proportions and plotting the solubility curve of this mixture as for a binary system (*i.e.* the mixed base was treated as a single component). Two such curves were obtained (curves *b* and *c* in Fig. 3) and further curves could readily be drawn by interpolation; the required cross section on *AGHD* could then be obtained by projecting curve *b*, drawn on *ACFD*, on to *AGHD* in the direction shown by the arrows (Fig. 4). To determine the section on plane *NOPQ*, mixtures were made up containing varying known amounts of the two pyridine bases but a constant proportion (70% by weight) of water. It was then only necessary to determine the temperatures of phase transition for each mixture, the resulting curve being reproduced in Fig. 5 (curve *a*). The proportion of water was fixed at 70% because this figure was approximately the average of the upper and lower consolute compositions; curve *a* thus represented a near-maximal section across the phase model. The section in the plane *KLM* of Fig. 4 was obtained by heating various ternary mixtures to 79°, followed by sampling and analysing the two phases; 79° appeared from Fig. 5*a* to be the temperature of the maximal cross section in the direction parallel to plane *DEF*. Although our method of analysis was not sufficiently precise to give points lying exactly on a smooth curve (Fig. 6), we were able to show that the tie-lines converged on a point very close to the "water" apex of the triangular diagram. Thus water shows very little, if any, selective solvent power for the two bases, a fact which can be related to the strong tendency of β-picoline to separate from water at this temperature. The position of the plait point (at 68% of water, 1·3% of 2 : 6-lutidine, and 30·7% of β-picoline) agreed well with the position deduced from Figs. 3 and 5. The approximate shapes of the binodal curves for this and other temperatures could also be determined from the solubility curves of Fig. 3. The method of construction is described by Jones (*J.*, 1929, 799).

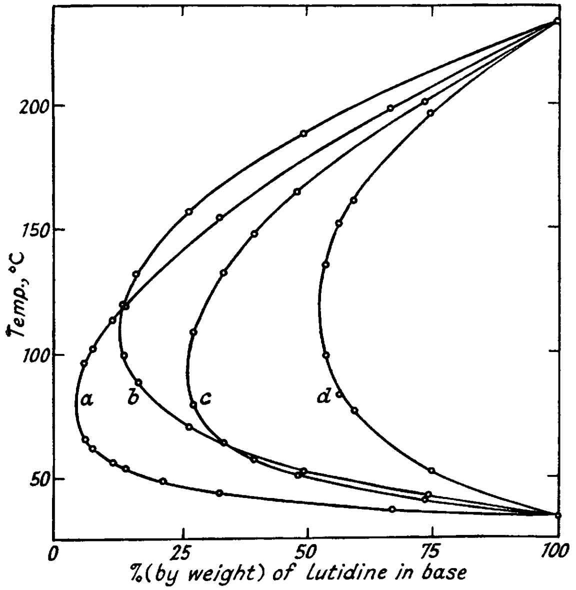


FIG. 5. *Solubility curves for the systems* 2 : 6-*lutidine–water–*X *where* X *is* (a) *β-picoline,* (b) *α-picoline,* (c) *γ-picoline, and* (d) *pyridine.* (*See Table* 3.)

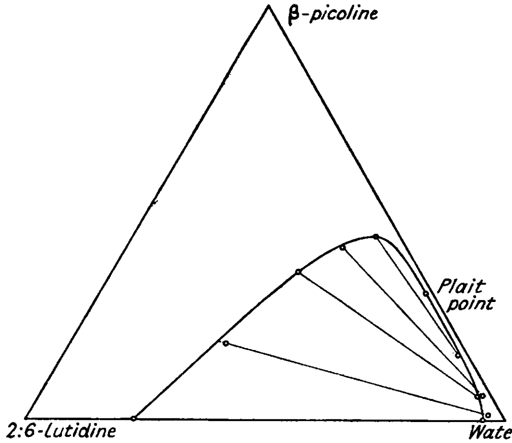


FIG. 6. *Binodal curve for the system β-picoline–*2 : 6-*lutidine–water at* 79°. (*See Table* 4.)

The system γ-picoline–2 : 6-lutidine–water was next studied by using mixtures containing a constant proportion (70% by weight) of water. From the shape of the resulting solubility curve (curve *c*, Fig. 5) it is obvious that the shape of the binodal surface for this ternary system will resemble that of the system previously discussed. It follows therefore, that the phase model for the quaternary system β-picoline–γ-picoline–2 : 6-lutidine–water at 79° will be similar in form to that described by Brancker, Hunter, and Nash (*J. Phys. Chem.*, 1940, **44**, 683) for the chloroform–acetic acid–acetone–water system at 25°.

For completeness, the solubility curves at constant water content (70%) for the two ternary systems 2 : 6-lutidine and water with, respectively, pyridine and α-picoline, were determined (curves *d* and *b* of Fig. 5). It may be deduced from the four curves of Fig. 5 that the widths of the " negative " solubility rings (Timmermans, *Z. physikal. Chem.*, 1907, **58**, 129) of the four bases follow the sequence: pyridine > γ-picoline > α-picoline > β-picoline. It is noteworthy that the same sequence was obtained by Flaschner (*loc. cit.*) by using potassium chloride to render the first three bases partially miscible with water. Finally it may be noted that the nearest approaches of curves *a* and *b* (Fig. 5) to the ordinate corresponding to 0% of lutidine, lie at temperatures 79° and 109°, respectively, the temperatures at which the corresponding systems without 2 : 6-lutidine exhibit their maximum opalescence (see above).

EXPERIMENTAL

The purities, expressed in moles %, of the materials used were : pyridine, 99·85; α-picoline, 99·8; β-picoline, 99·75; γ-picoline, 99·75; 2 : 4-lutidine, 99·65; 2 : 5-lutidine, 99·85; and 2 : 6-lutidine, 99·8. The preparation of these bases will be described elsewhere. The residual impurities were related alkylpyridines and water; hydrocarbons were absent.

Procedure for Binary Systems.—Water and the appropriate base were weighed into thick-wall " Pyrex " tubes which were then sealed. Phase-transition temperatures were determined with the specimens in a high capacity oil-bath the temperature of which, measured by means of a set of laboratory standard thermometers graduated in fifths of a degree, could be raised or lowered at any rate down to 0·1° per minute. The thermometers were of N.P.L. " Class A " standard. For work above 200°, an electrically-heated metal block was used. At lower solution points, the temperature of formation of a single phase, when the temperature was lowered, generally agreed with the temperature of the cloud point to within ±0·1°; duplicate determinations also agreed with one another to within ±0·1°. The same reproducibility (y) applied to upper solution points below 200°. Between 200° and 220° the reproducibility fell to about ±0·3° while in the region of 230° it amounted to about ±0·6°. The estimated errors, shown in Table 1, are equal to $\pm\sqrt{x^2 + y^2}$, where x is the maximum permissible error in the graduation of the thermometer used.

TABLE 2.

System	Curve	Wt. % water	Lower soln. temp.	Upper soln. temp.	Wt. % water	Lower soln. temp.	Upper soln. temp.
Mixture (i) and water	Curve *c*, Fig. 3	76·5	71·2°	87·9 °	65·0	67·5°	93·7°
		74·1	68·4	91·7	60·5	69·4	92·4
		71·2	67·6	93·2	58·2	70·6	92·1
		68·0	67·5	93·8	56·7	76·7	87·0
Mixture (ii) and water	Curve *b*, Fig. 3	86·0	60·1	110·9	60·6	49·9	134·5
		79·9	49·5	131·4	50·0	58·5	129·9
		69·9	48·6	135·8	43·5	77·2	116·3

Results for the three lutidine–water systems are presented graphically in Figs. 1, 2, and 3*a*.

Ternary Systems.—The solution temperatures of mixtures of β-picoline and (i) 5·27% (by weight) and (ii) 21·9% (by weight) of 2 : 6-lutidine with water, found by the method described for binary systems, are summarised in Table 2.

The solution temperatures of mixtures containing water (70 ± 2% by wt.), 2 : 6-lutidine, and respectively pyridine, α-, β-, and γ-picoline were found in the usual way. Results are summarised in Table 3.

Four mixtures of water, β-picoline, and 2 : 6-lutidine were heated to 79° in a closed system, kept at this temperature, with shaking, for 15 minutes, and samples then drawn from the upper and lower phases, for analysis by an ultra-violet spectroscopic method (Table 4). This

TABLE 3.

System	Curve	Wt. % 2 : 6-lutidine in base	Wt. % water in total mixture	Lower soln. temp.	Upper soln. temp.
Water, 2 : 6-lutidine, and pyridine	Curve *d*, Fig. 5	74·7	69·4	52·6°	195·3°
		59·6	69·7	76·4	160·7
		56·5	71·9	83·0	151·3
		53·8	69·4	98·5	135·0
Water, 2 : 6-lutidine, and α-picoline	Curve *b*, Fig. 5	74·1	68·0	42·2	—
		49·4	70·6	52·4	187·6
		26·7	68·8	70·6	156·7
		16·4	70·6	88·2	131·8
		13·6	69·2	99·4	119·4
Water, 2 : 6-lutidine, and β-picoline	Curve *a*, Fig. 5	66·9	71·0	36·9	197·6
		32·7	70·9	43·9	154·2
		21·4	70·2	49·1	134·5
		11·6	70·5	56·5	113·4
		6·0	69·4	65·7	96·2
Water, 2 : 6-lutidine, and γ-picoline	Curve *c*, Fig. 5	73·5	70·1	40·7	200·0
		48·3	69·7	50·4	164·2
		39·7	69·0	57·7	147·4
		33·6	69·8	64·6	132·5
		27·4	69·9	79·5	108·6

TABLE 4. *Analysis of phases in equilibrium at* 79° (% *by weight*).

Composition of original mixture			Composition of upper layer			Composition of lower layer		
2 : 6-lutidine	β-picoline	water	2 : 6-lutidine	β-picoline	water	2 : 6-lutidine	β-picoline	water
6·8%	23·2%	70·0%	13·2%	41·8%	45·0%	1·7%	6·1%	92·2%
3·0	29·9	67·1	4·8	44·6	50·6	1·9	15·9	82·2
28·0	12·2	59·8	48·9	18·6	32·5	2·7	1·2	96·1
15·9	24·5	59·6	25·6	36·0	38·4	2·9	6·0	91·1

method entailed measuring the optical densities of solutions of the samples in dilute sulphuric acid at 262·5 mμ, the wave-length at which standard spectral curves for the two bases intersected, and at 280 mμ where the optical density of a standard solution of 2 : 6-lutidine was 40 times greater than that of a standard β-picoline solution. The first measurement gave an estimate of the total base in the sample, and the second of 2 : 6-lutidine (cf. Herington, *Discuss. Faraday Soc.*, 1950, **9**, 26).

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