A Phase Study of the Complexes formed by 2,6-Lutidine, Urea, and Water

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THE formation of a crystalline complex by 2,6-lutidine and urea formed the basis of a process[1,2] for the extraction of 2,6-lutidine from aqueous mixtures of picolines, lutidines, and collidines. A molar ratio of 1 : 2 was suggested for the complex which yielded 2,6-lutidine readily by treatment with NaOH. The crystal structure of a 1 : 1 complex has been published,[3] with the suggestion that more than one complex existed, possibly depending on the degree of hydration.

Analysis of the complex proved unsuccessful because it decomposed readily unless it was in contact with its mother liquor and because it was uncertain how many solid phases were present. A ternary phase diagram (Figure 1) was constructed to determine the number and composition of the phases. Known amounts of 2,6-lutidine, urea, and water were allowed to equilibrate, and the composition of the saturated solution was determined. The percentage of 2,6-lutidine was found by titration with HCl using Screened Methyl Orange, and by subtracting this from the total nitrogen (micro-Dumas) the urea content was calculated. The water content was obtained by difference. The lines were drawn through the composition of the starting mixture and the corresponding saturated solution point.

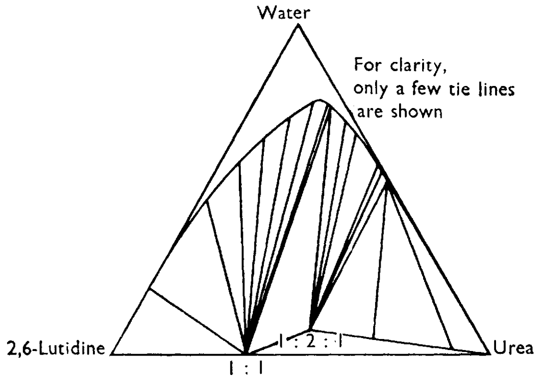

FIGURE 1

The isotherm at 24·5° C (Figure 1) shows that a 1 : 1 lutidine–urea complex is formed over a wide range of mixtures and that a lutidine–urea hydrate of molar ratio 1 : 2 : 1 is formed over a narrow range of mixtures. If the region near the triple point is drawn on a larger scale (Figure 2), it is apparent that urea exists as a single phase over a very limited range of composition.

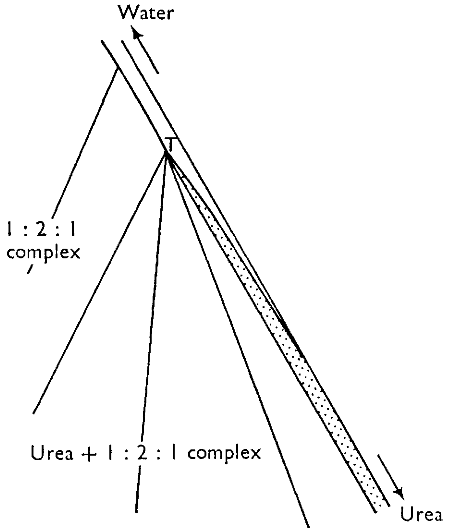

FIGURE 2. *An enlarged portion of Figure 1. Urea exists as a single phase in the stippled area.*

T = *triple point.*

The hydrate was vacuum-dried for one hour and analysed rapidly for 2,6-lutidine, total nitrogen, and water (Karl Fischer) and gave a molar ratio 0·93 : 2·04 : 1. A preliminary *X*-ray examination shows that the hydrate is orthorhombic, with unit-cell dimensions $a = 8{\cdot}15 \pm 0{\cdot}03$, $b = 7{\cdot}34 \pm 0{\cdot}03$, $c = 20{\cdot}49 \pm 0{\cdot}06$ Å, $U = 1225{\cdot}7$ Å^3, $D_{\text{obs}} = 1{\cdot}32_6$ g. cm.$^{-3}$, $Z = 4$, $D_{\text{calc}} = 1{\cdot}327$ g. cm.$^{-3}$

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[1] G. Riethof, U.S. Patent, 1944, 2,295,606.

[2] G. Riethof, U.S. Patent, 1945, 2,376,008.

[3] J. D. Lee and S. C. Wallwork, *Acta Cryst.*, 1965, **19**, 311.