[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF INDIANA UNIVERSITY]

A Solubility Study of Di-*n*-propylamine

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A less common type of binary liquid system is that which has a lower consolute temperature. It has been noted[2] that almost invariably this type consists of either a hydroxy compound and an amine, or a hydroxy compound and a compound containing a keto or ether group. For example, the systems diethylamine–water,[3] triethylamine–water,[4] and monoethers of ethylene glycol and water[5] exhibit this behavior. The last type also have upper consolute temperatures.

It was the purpose of this investigation to construct the solubility curves for the binary system di-*n*-propylamine–water and the ternary system di-*n*-propylamine–water–ethanol.

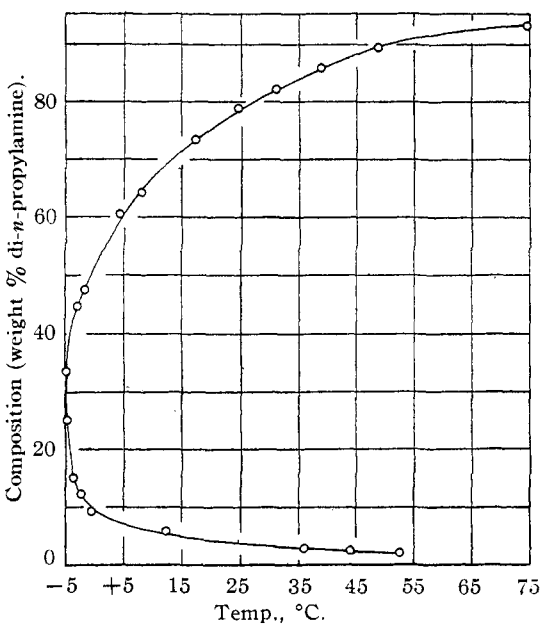

Fig. 1.—Mutual solubility curve for the system di-*n*-propylamine–water.

Experimental

Materials.—The di-*n*-propylamine was obtained from the Eastman Kodak Co.; upon analysis it was found to be 99.9% pure. Pure water was prepared using the same procedure as is followed in making conductivity water. Absolute alcohol was prepared by refluxing with calcium oxide, followed by triple distillation.

Procedure.—Alexejeff's synthetic method[6] was followed in studying the di-*n*-propylamine–water system. All temperatures were read from a calibrated Beckmann thermometer. For temperatures below 15°, the determinations were carried out in an unsilvered dewar flask. The bath was air-stirred and cooled by adding very small portions of chipped ice and salt.

The modified titration method of Walton and Jenkins[7] was followed in determining the data for the amine–alcohol–water system. All temperatures were read from a calibrated Beckmann thermometer.

The data obtained for the system di-*n*-propylamine–water are shown in Table I and the solubility curve for this system in Fig. 1. The characteristic blue opalescence associated with compositions lying near that of the critical solution temperature was observed slightly below the critical solution temperature (sample 8 in Table I). The critical solution temperature was found to be −4.8° (below that of diethylamine (143.5°) and triethylamine (18.5°)). The composition at this temperature is approximately 34% amine and 66% water. In those samples containing only a few per cent. of amine that are homogeneous at room temperature, some colorless particles (possibly hydrate crystals) were observed.

The sample containing 33.69% amine and 66.31% water was heated in an air-bath. Two layers could still be noted at the critical tem-

TABLE I

MUTUAL SOLUBILITY OF DI-*n*-PROPYLAMINE AND WATER AT VARIOUS TEMPERATURES

Weight % amine	Temp., °C.	Weight % amine	Temp., °C.
1.96	52.6	47.54	− 1.5
2.42	44.1	60.40	4.2
2.91	36.1	64.06	8.0
5.86	12.2	73.33	17.5
9.33	− 0.6	78.69	24.7
12.27	− 2.2	82.15	31.2
15.28	− 3.5	85.83	39.0
25.21	− 4.5[a]	89.26	49.0
33.69	− 4.8	93.25	74.8
44.68	− 2.9		

[a] Upon cooling to −5.0° the first blue opalescence was noted at −4.9°.

(1) This paper is constructed from the thesis submitted by R. W. Hobson in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Indiana University, June, 1941.

(2) See S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, N. Y., 1940, p. 718.

(3) Lattey, *Phil. Mag.*, [6] **10**, 397 (1905); see also Guthrie, *ibid.*, [5] **16**, 22, 105, 495 (1885).

(4) Rothmund, *Z. physik. Chem.*, **26**, 459 (1898).

(5) Cox and Cretcher, THIS JOURNAL, **48**, 451 (1926); Cox, *ibid.*, **49**, 1080 (1927).

(6) See Glasstone, ref. 2, p. 713.

(7) Walton and Jenkins, THIS JOURNAL, **45**, 2555 (1923).

perature of the amine (277°) but, since the critical temperature of the mixture is evidently higher than 277°, it may be possible that an upper critical solution temperature exists.

Results of the study of the three-component system are given in Table II and the solubility curve for this system at 25° is shown in Fig. 2. The broken part of the curve represents those compositions where the transition temperature was found to be indistinct. The composition corresponding to a maximum in the curve is approximately 31.5% amine, 26.5% ethanol, and 42.0% water.

TABLE II

MUTUAL SOLUBILITIES OF AMINE AND ETHANOL IN WATER

Weight, % amine	Weight, % ethanol	Weight, % amine	Weight, % ethanol
77.6	1.8	34.4	26.1
68.9	8.8	31.7	26.3
67.2	10.0	29.9	26.2
63.8	12.1	26.7	26.1
62.9	13.0	24.4	25.8
60.9	14.0	22.2	25.6
58.6	16.1	20.6	25.1
56.3	17.9	19.1	24.7
54.5	19.0	16.8	24.1
54.2	18.7	14.9	23.7
49.1	22.0	12.3	22.8
45.6	23.6	9.4	21.6
41.6	25.4	8.1	20.8
38.8	25.9	7.1	19.9
37.9	26.4	5.1	18.6
36.5	26.0	4.4	17.5

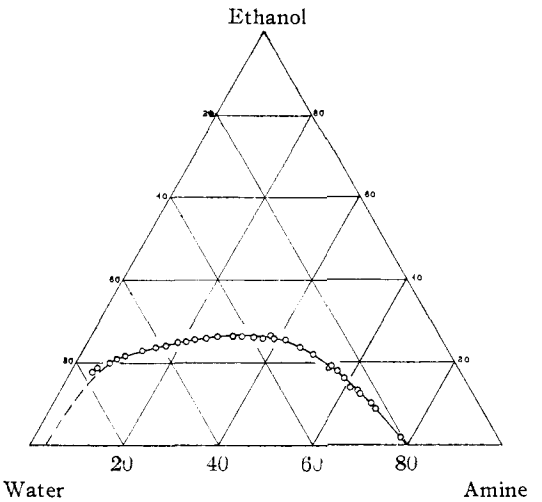

Fig. 2.—Solubility curve at 25° for the system di-*n*-propylamine–water–ethanol.

Summary

The mutual solubility of di-*n*-propylamine and water has been determined and the critical solution temperature found to be near −4.8°. The critical solution composition is approximately 34% amine and 66% water. No upper consolute temperature was found.

The solubility curve of the ternary system di-*n*-propylamine–ethanol–water has also been investigated at 25°.

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The Crystal Structure of *dl*-Alanine

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Introduction

The determination of the crystal structure of *dl*-alanine was undertaken as a continuation of X-ray diffraction studies which are a part of a program of research upon the constitution and configuration of proteins. In earlier investigations the structures of crystals of diketopiperazine[1] and of glycine[2] were determined and the interatomic distances and bond angles of their molecules thereby established. Definite data were thus made available for the construction of a tentative model of the polypeptide chain. In discussions of these data[1,2] and in a more recent consideration of their application to the problem of the configuration of the polypeptide chain[3] in protein molecules the presence of certain anomalies among the interatomic distances found in glycine and in its cyclic anhydride have been mentioned. Thus in both of these compounds a C–N distance near 1.40 Å. is found which is shorter than that predicted from the covalent radii (1.47 Å.). In diketopiperazine the C–C distance, 1.47 Å., is surprisingly short compared to that which might be anticipated (1.54 Å.); however, in glycine the distance 1.52 Å. is in agreement with the normal

(1) R. B. Corey, THIS JOURNAL, **60**, 1598 (1938).
(2) G. Albrecht and R. B. Corey, *ibid.*, **61**, 1087 (1939).
(3) R. B. Corey, *Chem. Rev.*, **26**, 227 (1940).