Evidence for Interaction between Chloroform and Monoethylamine[1]

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Reagents are often removed from materials by washings with solvents, and often the solvent is reclaimed by some suitable process such as fractional distillation. In the decrystallization of cotton,[3] chloroform was used to remove anhydrous monoethylamine from the swollen fibers. The chloroform could be reclaimed easily by removing the ethylamine through neutralization with aqueous acid, but the recovery of the amine from the acidic solution was neither simple nor easy. Attempts to separate the amine and chloroform by distillation or by extraction with distilled water proved unexpectedly difficult, suggesting some type of interaction. The experiments to be reported were undertaken to explain these difficulties.

At first consideration no appreciable interaction between ethylamine and chloroform would be expected. A literature survey revealed little information on the system. Pauling[4] has pointed out that, from a consideration of the electronegativity scale, the C–H bond would not be attributed with sufficient ionic character to enter into hydrogen bonding to any degree. However, in hydrogen cyanide the electronegativity of the carbon atom is sufficiently enhanced by the attached electronegative nitrogen atom to permit the C–H ← N bond to form. In chloroform a similar effect might be expected due to the interaction of the three electro-negative halogen atoms attached to the carbon atom.[5]

There is evidence in the literature, based on azeotrope studies,[6] solubility studies,[7–9] infrared absorpton data,[10,11] and heats of mixing,[12–15] that chloroform is indeed capable of entering into hydrogen-bond formation with certain nitrogen- and oxygen-containing compounds. Since an effect of this nature seemed to be operating in the chloroform–ethylamine mixture, a brief investigation was made in which the behavior of chloroform–ethylamine and of hexane–ethylamine solutions was observed. In the latter system, no hydrogen bond formation would be expected.

Materials and Methods.—Gaseous monoethylamine (specified purity, 96% minimum) was drawn from a cylinder and condensed in all-glass apparatus cooled by circulating ice-water. It was collected and stored over potassium hydroxide pellets. Titration with standard acid indicated almost 100% purity.

Diethylamine (specified purity, 98% minimum) was stored over potassium hydroxide pellets before being distilled. The fraction distilling at 55° was collected and stored over potassium hydroxide. The boiling point of 55.5° indicated high purity.

Chloroform, U.S.P. grade, was washed, then dried over anhydrous calcium sulfate. The fraction distilling at 60–61° was collected and stored in brown glass bottles. The distilled solvent showed no test for acid.

The hexane used was a petroleum fraction distilling at 62–65°. It was collected and stored in brown glass bottles.

The amine concentrations in all the solutions were determined by rapid titration with 1.002 *N* hydrochloric acid. Samples, weighed or pipetted, were added to 100 ml. of chilled distilled water (4–10°), followed by 2 drops of methyl orange indicator. The flask was shaken and the acid was then led in rapidly until the end-point was approached. Only fair accuracy could be attained because of volatility of the amines.

One-liter solutions of ethylamine–chloroform and ethylamine–hexane were prepared by adding solvent to 200 ml. of anhydrous ethylamine. The concentrations of the solutions, determined by titration, were 128 g. per liter (approximately 2.8 molar). For distillation studies 700 ml. of solution was used, which if completely separated should give 140 ml. of ethylamine.

The distillations of the mixtures were carried out using an 11-section, bubble-cap, fractionating column, and condensers cooled by circulating ice-water. The amine concentrations of the solution and the distillate were determined after the distillation was stopped.

Boiling point diagrams were determined with the aid of an apparatus similar to that described by Daniels, *et al.*[16] Liquid temperatures were read from a tested Anschütz thermometer, totally enclosed in the system. Refluxing was permitted for at least 45 minutes in each determination. Fluctuations in barometric pressure never exceed 3 mm. In determining the compositions of the liquid and condensed vapor, the weighing bottles were emptied of the weighed samples under the surface of the chilled distilled water.

An Abbe-type refractometer was used to obtain the refractive indices, $n^{20}\text{D}$, of the solutions. Cooling water was maintained at 20 ± 0.2° at the instrument.

Extraction of the amine by water was performed in a separatory funnel by the successive addition and separation of 50-ml. portions of distilled water to 1 liter of the amine–solvent solution prepared as described above. After each addition the funnel was shaken and the layers allowed to separate. The amine concentration in the solvent layer, determined after each extraction, was plotted against the number of portions of water used.

The alkaline aqueous solution which was separated from the chloroform–ethylamine mixture gave off a strong odor of isocyanide which was probably formed by reaction between the dissolved amine and the small amount of dissolved chloroform (for aqueous ethylamine, $K_b = 5.6 \times 10^{-4}$).

Results and Discussion

When ethylamine and chloroform were first mixed in preparing the solution for separation by distillation, a noticeable increase in the temperature of the solution was evident. When the operation was repeated using equal volumes of the liquids, both at 5°, the maximum temperature observed after mixing was 28°, a rise of 23°. No temperature rise was found when ethylamine and hexane, also at 5°, were mixed.

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(1) Report of a study made under the Research and Marketing Act of 1946. Article not copyrighted.

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(3) L. Segal, M. L. Nelson and C. M. Conrad, *J. Phys. Chem.*, **55**, 325 (1951).

(4) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 2nd Ed., 1940, pp. 294–295.

(5) M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1936).

(6) R. N. Ewell and L. M. Welch, THIS JOURNAL, **63**, 2475 (1941).

(7) M. J. Copley, E. Ginsberg, G. F. Zellhoefer and C. S. Marvel, *ibid.*, **63**, 254 (1941).

(8) M. J. Copley, G. F. Zellhoefer and C. S. Marvel, *ibid.*, **60**, 2666 (1938).

(9) G. F. Zellhoefer, M. J. Copley and C. S. Marvel, *ibid.*, **60**, 1337 (1938).

(10) W. Gordy, *Nature*, **142**, 831 (1938); *J. Chem. Phys.*, **7**, 93 (1939); THIS JOURNAL, **60**, 605 (1938).

(11) A. M. Buswell, W. H. Rodebush and M. F. Roy, *ibid.*, **60**, 2528 (1938).

(12) C. S. Marvel, M. J. Copley and E. Ginsberg, *ibid.*, **62**, 3109 (1940).

(13) D. B. McLeod and F. S. Wilson, *Trans. Faraday Soc.*, **31**, 596 (1935).

(14) R. W. Spence, *J. Phys. Chem.*, **45**, 304 (1941).

(15) G. F. Zellhoefer and M. J. Copley, THIS JOURNAL, **60**, 1343 (1938).

(16) F. Daniels, J. H. Mathews and J. W. Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 2nd Ed., 1934, p. 66.

This observed rise should be related to the heat data on higher alkylamines reported by Spence[14] and by Marvel and co-workers.[12] According to these, heats of mixing of 700–800 cal. per mole of solution are found for solutions of chloroform with *n*-butyl, *n*-hexyl- and cyclohexylamines. All of these workers, on the basis of their data, assume that chloroform and the amines form equimolar complexes through the formation of C–H←N bonds. Following the Lewis concept, this heat given off on mixing could be conceived as being heat of neutralization of the basic amine and the weak acid $Cl_3C–H^+$.

Separation of ethylamine by distillation, at first consideration, should have been easily accomplished since the amine boils at 17°, whereas chloroform and hexane boil at around 60°. This was not true for the ethylamine–chloroform mixture. As the distillation proceeded, the vapor temperature at the top of the column rose steadily. After rising to 60° and after 400 ml. of distillate had been collected, the solution in the boiling flask was found to still have an amine content amounting to 14 g. per liter.

The ethylamine–hexane mixture on the other hand behaved more normally. A distillate of 160 ml. was collected with no increase over room temperature of the vapor temperature at the top of the column. A sample from the boiling flask showed upon titration an amine concentration of only 8 g. per liter. With the application of more heat, distillate was collected until the vapor temperature had risen to 39°. The amine concentration in the boiling flask was found to be only 2 g. per liter.

The tenacious hold of chloroform for ethylamine, as evidenced in the distillation, might be explained by a change in association of the amine. Distribution measurements at different concentrations indicated that the abnormal behavior did not arise from such an effect, the distribution coefficient remained essentially constant at these concentrations.

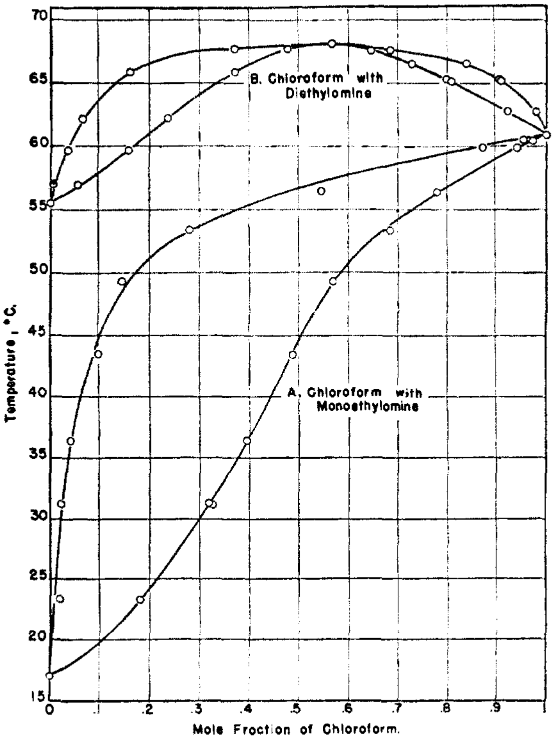


Fig. 1.

The boiling point diagram for monoethylamine and chloroform, Fig. 1A was found to deviate considerably from Raoult's law, indicating an interaction. However, it did not show the azeotropic behavior which might be expected of an associated binary mixture. Ewell and Welch[6] found that triethylamine and chloroform also did not form an azeotrope. They concluded from their studies that maximum boiling mixtures result with donor liquids whose boiling points lie within a range centered about the boiling point of the given chloroparaffin. For chloroform this range was found to be 38°, the lower limit being 42.5°; the upper 80.5°. Monoethylamine (b.p. 17°), as well as triethylamine (b.p. 89°), lies outside this range and hence should not produce an azeotrope.

A prediction, based on Ewell and Welch's conclusion, that diethylamine (b.p. 55.5°) should form maximum boiling azeotrope was verified by experiment (B in Fig. 1). The maximum of 68.2° which occurs at a mole fraction of 0.57 chloroform suggests a possible association ratio of 1:1.

Since evidence for a 1:1 complex between chloroform and monoethylamine could not be obtained from the boiling point diagram, consideration that the refractive index might be effected by association resulted in the data presented in Fig. 2. The break in curve A occurring near mole fraction 0.5 chloroform seems to be indicative of 1:1 ratio.

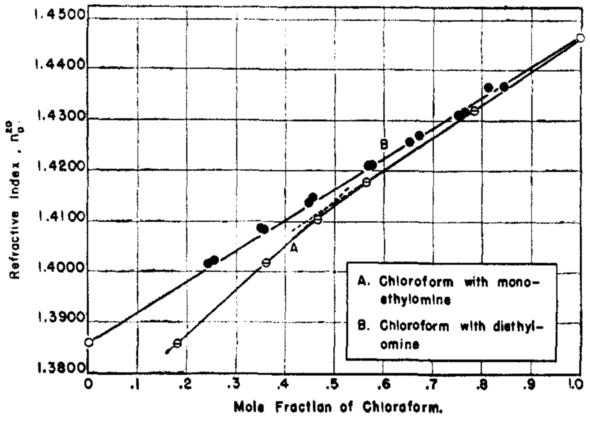
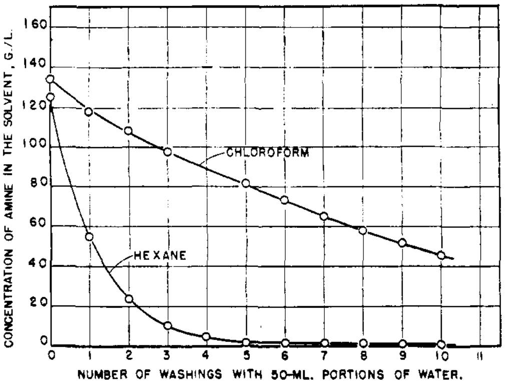


Fig. 2.

When refractive index data for diethylamine and chloroform were plotted, the resulting curve B did not show any break. Whether this can be correlated with the findings of Ewell and Welch concerning the boiling point range and the appearance of the azeotrope in the boiling point diagram has not yet been established.

Further evidence for an associated binary mixture is shown by the effects observed when extraction of the amine with water was attempted (see Fig. 3). Here the curve for the chloroform solution indicates that the C–H←N bond which is believed to have been formed must be of consider-



Fig, 3.

able strength, since the contacts with water were only partially effective in reducing the amine concentration in the solvent. This concept is supported, too, by the work of Smith[17] who determined the distribution coefficient for the system chloroform–water–ethylamine. Unfortunately, however, Smith's work dealt only with amine concentrations of the order of millimoles, whereas the present investigation is concerned with molar quantities.

On the other hand, the hexane–ethylamine solution, in which hydrogen bond formation can be ruled out, behaved differently toward water extraction. The curve shows that water was highly effective in reducing the amine concentration of the hexane. In fact, cold water was required for at least the first two extractions of the hexane solution, in order to reduce the vigor of the interaction between the water and the amine.

[17] H. O. Smith, *J. Phys. Chem.*, **25**, 204 (1921).

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Absorption Spectra of 8-Amino-6-quinolinol Types

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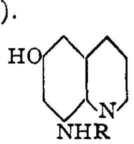
Interest in 8-(3-dimethylamino-1-methylpropylamino)-6-quinolinol (SN-191,[1] Certuna, I) led us to compare its ultraviolet absorption spectra in neutral, acid, and alkaline media with those of 8-(4-diethylamino-1-methylbutylamino)-6-quinolinol (II), 8-amino-6-quinolinol (III) and 3-hydroxy-1-naphthylamine (IV).



I, R = $CH(CH_3)CH_2CH_2N(CH_3)_2$
II, R = $CH(CH_3)CH_2CH_2CH_2N(C_2H_5)_2$
III, R = H

In Fig. 1 there are presented the absorption spectra of 8-amino-6-quinolinol (III) in acidic, basic and ethanolic solution. The comparison of these with corresponding ones of 6-quinolinol[2] shows that the 8-amino group has very little influence on the spectra. It may be noted that the spectra (Fig. 2) of 3-hydroxy-1-naphthylamine (IV), the naphthalene analog of (III), bear no simple relation to those of the contributing parents 2-naphthol[2] and 1-naphthylamine.[3] In acidic solution, the ionic contributions of (IV) cause it to be closely

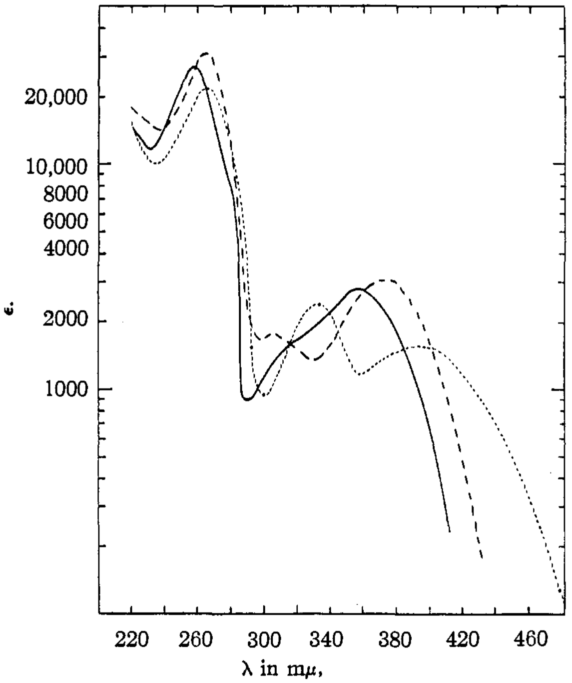


Fig. 1.—Spectra of 8-amino-6-quinolinol in: —, 95% EtOH; ------, 0.01 N HCl; - - -, 0.01 N NaOH.

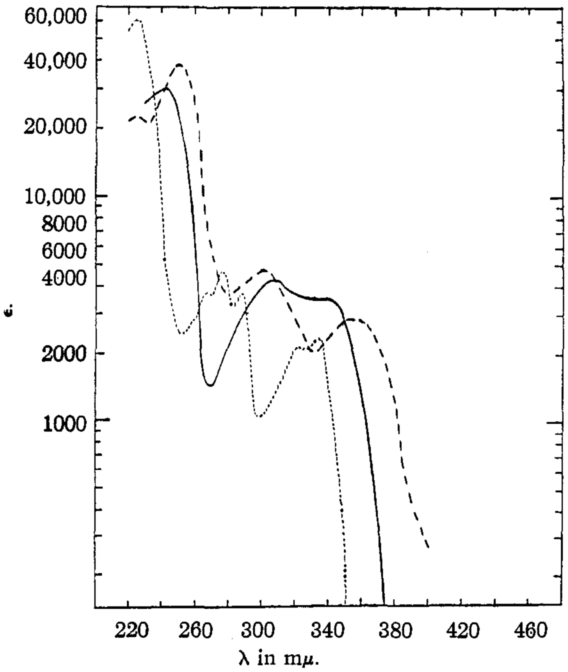


Fig. 2.—Spectra of 3-hydroxy-1-naphthylamine in: —, 95% EtOH; - - - - -, 0.01 N HCl; – –, 0.01 N NaOH.

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[1] All drugs identified by Survey Numbers (SN) in the files of the Antimalarial Survey have been tabulated, with antimalarial activities, in "Antimalarial Drugs. 1941–1945" (F. Y. Wiselogle, editor), Edwards Bros., Ann Arbor, Mich., 1946.

[2] G. W. Ewing and E. A. Steck, THIS JOURNAL, **68**, 2181 (1946).

[3] E. A. Steck and G. W. Ewing, *ibid.*, **70**, 3397 (1948).