Partial Vapor Pressures of Aqueous Ethylamine Solutions

BY B. P. DAILEY WITH W. A. FELSING

Object of the Investigation.—In a previous paper[1] there were reported the partial vapor pressures of methylamine solutions, the investigation being one of a series dealing with the possible uses of these amines as refrigerating fluids in the absorption type of refrigerating units. The ethylamines have been suggested by Taylor[2] for use in such systems and Mehl[3] has investigated some of the pertinent properties of monoethylamine for the same purpose.

In this investigation it was decided to determine experimentally the partial vapor pressures of aqueous solutions of the ethylamines in order to aid in evaluating these substances as refrigerants. The data obtained were used to calculate the free energy decrease attending the solution of these amines in water.

Previous Investigations.—The literature records but few determinations of the partial vapor pressures of ethylamine solutions. Lattey[4] cites values for two concentrations at 2° intervals from 6 to 50°, which values were calculated from total pressure determinations. Doyer[5] gives one value at 60° for both mono- and diethylamine.

Method of the Investigation.—The method used was the dynamic, air-saturation method previously described.[1] The complete apparatus, as described there, was used in this investigation.

The amine solutions were prepared by dissolving in cold distilled water of conductivity grade either the gaseous or liquid amines. They were generated from repurified c. p. Eastman Kodak Co. hydrochlorides by the action of concentrated potassium hydroxide solution. Standard **acid** and **base** solutions were prepared with the usual precautions for highest accuracy. Weight burets were used throughout: the indicator was methyl red.

The Results Attained.—The partial vapor pressures were calculated by the procedure described[1]; five to six acceptable determinations were made at each concentration, the mean of

which is reported in the table. The results are believed to be accurate to better than ±0.02 mm.

(1) Felsing and Phillips, THIS JOURNAL, **58**, 1973 (1936).
(2) Taylor, J. Am. Soc. Refrig. Eng., **17**, 136 (1929).
(3) Mehl, Brihefte Z. ges. Kälte-Ind., Reihe 1, Heft 3, 7 (1933).
(4) Lattey, J. Chem. Soc., **91**, 1059 (1909).
(5) Doyer, Z. physik. Chem., **6**, 481 (1890).

TABLE I

PARTIAL PRESSURES OF ETHYLAMINE SOLUTIONS AT 25°

Concn. C (moles/1000 g. H₂O)	Pressure, p, mm.	p/C (obsd.)	Best "K"
		Monoethylamine	
0.2529	1.97	7.789	
.5410	4.27	7.893	
1.0867	8.84	8.134	
2.2602	17.78	7.866	7.86
		Diethylamine	
0.2228	3.79	17.010	
.3926	6.28	15.995	
.8585	13.73	15.993	
1.8142	29.58	16.304	16.25
		Triethylamine	
0.0550	4.72	85.818	
.0919	8.84	96.191	
.2654	25.55	96.269	
.3330	31.43	94.384	95.00

The best "K" was obtained by plotting the pressure as a function of the molarity; a straight line reproduces well the observed data over the range of concentrations investigated.

The partial vapor pressures of the amine solutions at exactly 1 molar are calculated to be 7.86 mm. for the mono-, 16.25 mm. for the di-, and 95.0 mm. for the triethylamine. With the aid of these data, the following free energy values were calculated for the reaction: Amine (760 mm.) = Amine (1 M) + (−ΔF). The values of −ΔF were found to be 2709 cal./mole for the mono-, 2278 cal./mole for the di-, and 1232 cal./mole for the triethylamine.

Mehl[3] has given vapor pressure relations for the three liquid amines; from these the vapor pressures at 25° were found to be 1059 mm. for the mono-, 235 mm. for the di- and 78.5 mm. for the triethylamine. From these values the free energy decrease attending the change: Amine (p, mm.) = Amine (760 mm.) was calculated and combined with the preceding free energy values to yield the free energy decrease attending the change: Amine (liquid) = Amine (1 M) + (−ΔF). The results obtained for (−ΔF) were

2905 cal./mole for the mono-, 1583 cal./mole for the di-, and −103 cal./mole for the triethylamine.

Summary

1. The partial vapor pressures of aqueous solutions of mono-, di- and triethylamine have been determined at 25° over a range of concentration of approximately 0.05 to 2.2 M.

2. The free energy decreases attending the change: Amine (liquid) = Amine (1 M) have been evaluated from the observed data.


[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Infrared Absorption Studies. VIII. Hydrazoic Acid

BY A. M. BUSWELL, G. W. MCMILLAN, W. H. RODEBUSH AND F. T. WALL

In the study of the tendency of hydrogen compounds of nitrogen to form hydrogen bonds, our attention was attracted to hydrogen azide. This compound has interested inorganic chemists for many years but because of its dangerously explosive character it has remained a substance little known. Dr. L. F. Audrieth[1] of this Laboratory kindly furnished us with the material for, and advice concerning, the preparation of the pure substance and we wish to acknowledge our indebtedness to him.

Hydrazoic acid has about the same strength as acetic acid and readily forms salts. The molecule is supposed to involve a resonance between the two structures

$$N=N=N—H \text{ and } N≡N—N—H$$
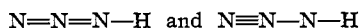
while the ion has the possibility of at least one more resonance structure thus accounting to some extent for the acid strength. The azide group is known to be linear but the hydrogen must be attached at an angle with the azide group. Hydrogen azide is much more soluble in ether than in water, the distribution ratio being 7:1. This peculiar behavior would seem to require some explanation since acetic acid shows no such surprising behavior.

Experimental.—The prism spectrometer used in this work has been described previously.[2]

The hydrogen azide was generated by dropping concentrated sulfuric acid on the dry potassium salt. Since the vapor as well as the pure liquid is very explosive, the substance was prepared in carbon tetrachloride solution.

The salt was immersed in carbon tetrachloride which had been prepared from the technical material by chlorination and subsequent fractional distillation. A calculated amount of concentrated sulfuric acid was added slowly

from a dropping funnel. A trap of methanol was set up beyond the generator to prevent diffusion of hydrogen azide into the laboratory. It was regarded as advisable to use a generator flask whose volume was some three to four times that of the solution it contained. After generation the solution was carefully decanted from the sulfuric acid layer into tubes and sealed until used. In this way solutions of the order of 0.1 molar could be obtained anhydrous with a minimum of handling. The entire operation was performed behind screens.

Careful tests showed that sulfuric acid did not dissolve in the carbon tetrachloride in sufficient amounts to produce any noticeable absorption in the infrared. The solution prepared in this way from the pure salt was evidently free from any appreciable contamination by impurities.

Deuterium azide was prepared by shaking the carbon tetrachloride solution of hydrogen azide with 99% D_2O. This resulted in a 75–80% conversion. Excess water and D_2O was removed with calcium chloride.

Results.—In the drawings the molal absorption coefficient (so-called) is plotted against wave number. This coefficient is defined by the expression

$$\frac{1}{cd} \log \frac{I_0}{I}$$

where c is the concentration (moles per liter of solution), d is the cell thickness in centimeters and I and I_0 the galvanometer deflections obtained through equal paths in solution and pure solvent, respectively. Since the control of concentrations was difficult the accuracy of the calculated coefficients is not good and it was not always possible to maintain constant values for cd.

Three frequencies are always observed in hydrogen azide which remain unchanged in intensity as long as cd is maintained constant. One of these occurs at 4.75 μ and is also found in deuterium azide and phenyl azide (Fig. 1). This is evidently the linear N–N–N vibration which already has been assigned to the 4.8 μ absorption

(1) For an excellent review of the literature concerning hydrogen azide see L. F. Audrieth, *Chem. Rev.*, **15**, 169 (1934).

(2) A. M. Buswell, Victor Dietz and W. H. Rodebush, *J. Chem. Phys.*, **5**, 501 (1937).