[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND OF LAWRENCE COLLEGE]

The Densities of Some Aliphatic Amines

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In the course of an investigation of the properties of solutions in some of the simpler aliphatic amines, it was found that existing data on the physical properties of the pure amines were not in very close agreement. This investigation was carried out to obtain precise values of the densities of five aliphatic amines in the temperature range 0–35°.

Experimental

Purification of the Amines

Dimethylamine.—Eastman dimethylamine hydrochloride was converted into the *p*-toluenesulfonamide in the usual manner, and then recrystallized three times from 70% ethanol until a sharp melting point was obtained (80–80.5° uncor.). It was then hydrolyzed with hydrochloric acid, excess sodium hydroxide added and the amine distilled through a tower of activated alumina[1] and collected in a tube cooled in dry-ice and ether. The product was distilled slowly through a five-foot adiabatic column, arranged for a partial take-off reflux ratio of 1 to 20, which was used for all the amines purified. A fraction boiling over a range of about 0.01° was collected under an atmosphere of nitrogen and sealed in vacuum. Before use, this sample was allowed to stand over solid potassium hydroxide to remove water and carbon dioxide and desiccated by dissolving sodium fluorenone[2] in it. It was then twice distilled in vacuum to remove any solid impurities.

Diethylamine.—This was purified in the same manner, except that the amide was recrystallized from pure, dry ligroin (b. p. 90–120°) until a sharp melting point was obtained. Only activated alumina was used as a desiccant.

Ethylamine.—Eastman Kodak Co. anhydrous ethylamine was distilled slowly, a fraction of 0.01° range being collected under nitrogen. The amine was dried over potassium hydroxide, desiccated with sodium fluorenone, and twice distilled in vacuum.

Trimethylamine and Triethylamine.—The Eastman Kodak Co. anhydrous amines were distilled from acetic anhydride to remove traces of primary and secondary amines, a fraction of about 0.02° range being collected. These were dried over activated alumina and the trimethylamine further desiccated with sodium fluorenone. Two distillations in vacuum followed.

Thermostat.—Temperatures constant to 0.01° were maintained in a gallon "Thermos" jug.[3] The 0° measurements were made in crushed ice in a wide-mouthed Dewar tube.[4] The thermometers were standardized against two Bureau of Standards calibrated thermometers and at the sodium sulfate transition point and the ice-point.[4] It is probable that the temperatures recorded were within 0.03° of the corresponding true temperatures, which is equivalent to an error of 0.005% in density at the greatest.

Measurements of Densities.—The densities of the compounds were found by measuring the volume of a known weight of liquid in a 20-ml. pycnometer with a calibrated tube. The diameter of this tube was about 5 mm., and the height of the meniscus could be read to about 0.02 mm. corresponding to an error of 0.002% in the volume.

For each series of measurements the pycnometer was sealed to the vacuum system, evacuated, and the amine slowly distilled in to the zero mark. The vessel was then sealed off and weighed to the nearest 0.1 mg., and measurements of the volume at each temperature taken. The weight of the liquid was found by opening the vessel without loss of glass, drying and weighing again. Calibrated weights were used throughout. The pycnometer was tested for expansion due to excess internal pressure and corrections applied when necessary, the greatest correction being only 0.015%.

The weight of the amine was corrected to vacuum, the space in the pycnometer above the liquid also being taken into account. The volume of this space was measured and a correction applied for the amount of vapor present.[5] This correction amounted to 0.06% at the greatest.

Two separate samples of each amine were measured as a check, except in the case of diethylamine, where, due to lack of material, the same sample was dried again and distilled into the pycnometer.

Results.—The values of the densities of the liquids under their own vapor pressures are given in Table I. They have not been converted to atmospheric pressure since data on the compressibilities and the effect of dissolved air on the densities are not available. The reported densities refer to water as weighed in vacuum at the temperature of maximum density. Using the method of least squares, the data were fitted into equations of the form[6]

$$d_t = d_s + 10^{-3}\alpha(t - t_s) + 10^{-6}\beta(t - t_s)^2$$

Higher terms were found to be unnecessary to give an adequate expression of the data. In each case, t_s was taken as 0° and d_s as the density at that temperature. The resulting values of α and β are given in Table II.

These values have been compared with those found in the literature, only those values which appear to be of a precision of better than 0.1% being taken into account.

(1) J. H. Yoe, *Chem. News*, **130**, 340 (1925).
(2) H. E. Bent and H. M. Irwin, THIS JOURNAL, **58**, 2072 (1936).
(3) E. Swift, Jr., *ibid.*, **61**, 199 (1939).
(4) E. E. Roper, *ibid.*, **60**, 866 (1938).
(5) C. S. Cragoe and D. R. Harper, *Bur. Stds. Sci. Paper*, No. **420**, 287 (1921).
(6) "International Critical Tables," McGraw-Hill Book Company, New York, N. Y., 1928, Vol. III, p. 27.

TABLE I

MEASURED DENSITIES OF AMINES UNDER SATURATION CONDITIONS

	0°	Approximate vapor press., atm.	15°	Approximate vapor press., atm.	25°	Approximate vapor press., atm.	35°	Approximate vapor press., atm.
Dimethylamine	0.67862		0.66159		0.64968		0.63738	
	.67862	0.75	.66156	1.4	.64961	2.0	.63726	2.9
Trimethylamine	.65659		.63903		.62705		.61466	
	.65687	1	.63922	2	.62714	3	.61478	4
Ethylamine	.70562		.68859		.67682		.66485	
	.70569	0.5	.68858	0.95	.67691	1.4	.66478	2
Diethylamine	.72514		.70942		.69891		.68819	
	.72512	.1	.70945	.2	.69897	0.3	.68812	0.5
Triethylamine	.74555		.73193		.72271		.71340	
	.74567	.02	.73204	.06	.72276	0.1	.71351	.15

TABLE II

CONSTANTS FOR DENSITY EQUATIONS

	d_s	α	β	Av. dev. obs.—calcd. values
Dimethylamine	0.67862	−1.1042	−2.171	0.004%
Trimethylamine	.65673	−1.1537	−1.312	.013
Ethylamine	.70565	−1.1153	−1.464	.004
Diethylamine	.72513	−1.0375	−0.481	.002
Triethylamine	.74561	−0.9044	− .396	.006

Values of d^0_4 for dimethylamine (0.6804) and for trimethylamine (0.6709) have been reported by Jaeger,[7] but are considerably higher than those presented here.

Considerable work has been done on ethylamine. The most reliable values are those given in the "International Critical Tables," Vol. III, p. 28, which lie slightly below the values found here, and those reported by Pohland and Mehl,[8] which are slightly higher. For diethylamine, the values found by Perkin[9] and by Oudemans[10] are about 0.2% higher than those presented in this paper, and appear to be fairly reliable. Perkin's values[9] for triethylamine lie about 0.1% higher than the values in Table I.

Because of the fact that all of these compounds are hygroscopic, it is probable that many of the higher values cited in the literature are in error because of the presence of a small precentage of water. Diethyl and triethyl amines are readily oxidized in contact with the atmosphere, and unless due precautions are taken, this reaction may also lead to error.

The author wishes to thank Mr. Andrew Kasper, Mr. Harry Miller, Dr. Leonard Rosen and Dr. E. R. Coburn for their work in the purification of the compounds. He also wishes to express his appreciation for a grant from the Chemical Research Fund of Harvard University.

Summary

The densities under saturation pressure of five carefully purified aliphatic amines have been determined with a precision of 0.01% from 0 to 35°.

APPLETON, WISCONSIN RECEIVED AUGUST 14, 1941

(7) F. M. Jaeger, *Z. anorg. Chem.*, **101**, 86 (1917).
(8) E. Pohland and W. Mehl, *Z. physik. Chem.*, **164**, 48 (1933).
(9) W. H. Perkin, *J. Chem. Soc.*, **55**, 691 (1889).
(10) A. C. Oudemans, Jr., *Rec. trav. chim.*, **1**, 59 (1882).