

The rapidly deteriorating precision at the highest temperatures is attributable mostly to those density tubes which contained the least AlCl_3 . That this is so was demonstrated by using Equation 1 to calculate V_i at various temperatures, using T_i and m_i from Table I and D and d from Equation 5. Appropriate corrections for thermal expansion were made. This procedure reproduced the 11 liquid volumes in Table II at 197°C with a $\pm 0.2\%$ average deviation, the nine volumes from 197–337°C with a $\pm 0.7\%$ average deviation, and the eight volumes over the temperature range 197–345°C with an average deviation of $\pm 2.6\%$. The maximum expected error arising from the uncertainties in the calibration data and cathetometer readings was about $\pm 0.5\%$ to $\pm 1.0\%$. At the higher temperature it was evident that the tubes with the least AlCl_3 , and most especially tubes IV and V, were the sources of most of the uncertainty. On the other hand, the liquid volume in tube III, whose overall density of AlCl_3 was very nearly the critical density, could be calculated to within $\pm 1.5\%$ of the observed value at temperatures as high as 355°C.

There were three likely contributors to this observation. Any temperature gradients or temperature uncertainties in the bath would affect most the location of the meniscus of tubes with the least AlCl_3 . Any impurities in the AlCl_3 would become more and more concentrated as the liquid volume decreased and therefore most profoundly affect the vapor densities of these tubes. Finally, as a meniscus would approach either end of a density tube it would eventually enter a region where the volume of capillary per unit length would deviate from the calibration value.

Nisel'son and Sokolova (4) obtained a critical temperature of 354.0°C from plots of orthobaric densities and the mean density. They reported a critical density of 0.505 g/cm³. Denisova and Baskova (1) reported 352.5°C as the critical temperature and a critical density of 0.510 g/cm³. Our critical temperature was an adjustable parameter in Equation 3 and had the value 355.2 \pm 0.3°C. Equation 4 yields a critical density of 0.5073 \pm 0.0004 g/cm³.

NOMENCLATURE

- a_i, b_i = empirical coefficients
 d = density of AlCl_3 vapor
 D = density of AlCl_3 liquid
 m_i = mass of AlCl_3 in i th tube
 n = number of pairs of equations solved for density
 N = number of density tubes used at each temperature
 t = temperature in degrees centigrade
 t_c = empirical coefficient; critical temperature
 T_i = total enclosed volume in i th tube
 V_i = volume of liquid in i th tube
 z_i = residual in mass
 δ_D, δ_a = standard deviation in calculated liquid or vapor density
 ρ = orthobaric density
 ρ_m = mean density
 σ = standard deviation in mass
 σ_D, σ_a = estimated error in calculated liquid or vapor density

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RECEIVED for review January 3, 1972. Accepted March 2, 1972.

Low-Frequency Dielectric Constant of Methylamine, *n*-Propylamine, and Isopropylamine

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The dielectric constants of liquid methylamine, *n*-propylamine, and isopropylamine have been measured at 0.1 MHz over a wide range of low temperatures. The data are accurate to 3%. The dielectric constants at 0°C and the linear temperature coefficients are computed for each amine by least-squares analysis.

Recent studies of solvation effects in ammonia and ammonia-like solvents have produced a need for low-frequency dielectric constant data for liquid alkyl amines over a wide temperature range (4, 6, 12). Currently available data do not allow accurate extrapolation to low temperatures. The present work reports measurements of the low-frequency dielectric constants of methylamine, *n*-propylamine, and isopropylamine over an extended range of low temperatures and presents linear temperature coefficients computed for each amine.

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METHOD

The dielectric constants of the liquids were measured by a conventional liquid substitution procedure using an all-glass capacitance cell and a Boonton 74C-S8 capacitance bridge operating at 0.1 MHz (11, 14, 15).

The capacitance cell was made of concentric thin-walled glass cylinders with cylindrical electrodes plated on the inside surfaces in contact with the dielectric fluid after the design of Sayce and Briscoe (9). An alternative design used electrodes plated on the outside of the glass surface. End-effect correction expressions were computed by calibration with analytical grades of benzene, carbon tetrachloride, chloroform, and

Table I. Low-Frequency Dielectric Constant of Alkyl Monoamines

Dielectric constant	Temp, °C	Dielectric constant	Temp, °C	Dielectric constant	Temp, °C
Methylamine (Aminomethane)		<i>n</i> -Propylamine (1-Aminopropane)		Isopropylamine (2-Aminopropane)	
12.7	-15.0	5.08	23.0	5.11	23.0
13.1	-19.5	5.08	23.0	5.54	7.0
13.7	-27.0	5.26	14.0	5.64	0.0
14.2	-30.0	5.46	7.5	6.01	-7.0
14.3	-38.0	5.54	2.0	6.41	-17.0
14.9	-38.0	5.91	-5.0	6.83	-25.0
15.6	-46.5	5.94	-10.5	7.16	-33.0
15.5	-50.0	6.21	-16.0	7.41	-40.0
15.9	-50.0	6.26	-20.0	7.66	-44.5
16.1	-52.0	6.56	-27.0	8.24	-53.0
16.4	-54.0	6.60	-31.0	7.79	-54.5
16.5	-56.0	6.89	-36.0	7.85	-58.0
16.5	-56.0	6.99	-41.0	8.44	-61.5
16.7	-58.0	7.01	-43.0	8.45	-65.0
16.8	-60.0	7.37	-54.0	8.98	-71.0
17.0	-62.0	7.48	-59.0	9.12	-74.0
16.6	-62.0	7.91	-67.0	9.21	-76.5
17.3	-64.0	8.00	-69.0		
17.6	-66.0				
17.5	-69.0				
17.7	-69.0				
17.5	-71.0				
18.4	-73.0				
17.9	-75.0				

acetone using the data of Maryott and Smith (8).

Analytical-grade Matheson methylamine was distilled into a glass vacuum line, dried with sodium, and outgassed by cycles of freezing, pumping, and thawing (4, 6, 12). The dry sample was then distilled into the capacitance cell, frozen, and sealed under vacuum.

Analytical-grade Eastman propylamines were outgassed as above without drying, frozen and sealed, and transferred to the capacitance cell by tipping.

The calibration liquids were dried, outgassed, frozen, and sealed with the same care as the amines. The accuracy of the measurements is 3%, limited by random variations in the parasitic capacitance of cables, lead wires, and the mounting of the capacitance cell.

RESULTS AND DISCUSSION

The data are tabulated in Table I and are compared with all published measurements of the first three alkyl monoamines in Figure 1.

Methylamine. A linear least-squares curve fit to the present data is in agreement with the datum points of Le Fevre and Russell (5) within the precision of the measurement. The reported values of Schlundt (10) and Ulich and Nespital (13) lie 10% above and below this line, respectively. Schlundt states explicitly that his methylamine sample was impure and that his value is suspect and should be considered only as an upper limit.

The linear temperature coefficient corresponding to the methylamine line of Figure 1 based on our data is slightly higher than the coefficients defined by either the three datum points of Ulich and Nespital or the two of Le Fevre and Russell. In view of the number of measured points, however, it is more reasonable to attach the greater significance to this coefficient.

***n*- and Isopropylamine.** Linear least-squares curves fit to all data pass slightly below the points of Cowley (2) and Schlundt (10). However, these points lie within the precision of the measurement. The dielectric constant of isopropylamine is higher than that of *n*-propylamine at low temperatures and has a greater temperature coefficient. These properties are

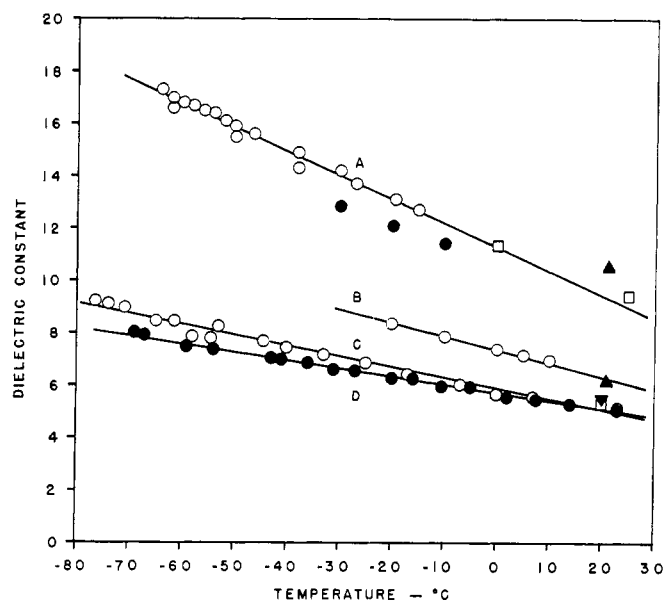


Figure 1. Low-frequency dielectric constant of alkyl monoamines vs. temperature

A. Methylamine		C. Isopropylamine	
Present work	○	Present work	○
Schlundt	▲	Schlundt	▼
Ulich and Nespital	●	D. <i>n</i> -Propylamine	
Le Fevre and Russell	□	Present work	●
B. Ethylamine		Cowley	□
Schlundt	▲		
Ulich and Nespital	○		

consistent with the dielectric behavior of other substituted propane isomers (7, 8) and with the more rapid change of density of isopropylamine with temperature in comparison to *n*-propylamine (1, 3).

The temperature coefficients and the dielectric constant at 0°C derived from the curves of Figure 1 are presented in Table II. Both the dielectric constant and the temperature coefficient

Table II. Temperature Coefficient of Dielectric Constant of Alkyl Monoamines

Amine	Dielectric constant at 0°C	Temp Coeff, °C ⁻¹
Methylamine	11.3	-0.0919
Ethylamine	7.34	-0.0514
<i>n</i> -Propylamine	5.73	-0.0309
Isopropylamine	5.87	-0.0407

decrease monotonically with increasing length of the alkyl radical in the normal fashion of a homologous series. The ethylamine values are computed from a linear least-squares curve fit to the measurements of Ulich and Nespital and Schlundt.

ACKNOWLEDGEMENT

The authors wish to acknowledge the assistance of Robert M. White.

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RECEIVED for review January 20, 1972. Accepted April 7, 1972.

Densities and Viscosities of 2-Butyne and 2,4-Hexadiyne in Several Solvents

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The concentration and temperature dependences of the densities and viscosities of 2-butyne and 2,4-hexadiyne in CS₂, CCl₄, and benzene-d₆ are reported. Experimental techniques used to measure small volumes of volatile liquids are briefly discussed.

In connection with our nmr study (5) of molecular motions in 2-butyne and 2,4-hexadiyne, we needed densities and viscosities of these solutes in several solvents to be able to attempt a meaningful interpretation of the nmr data. Therefore, we measured the temperature and concentration dependences of densities and viscosities of 2-butyne and 2,4-hexadiyne in CS₂, CCl₄, and benzene-d₆. In this work we report the results of our measurements with a detailed description of the calibration procedure for a small volume pycnometer (<0.5 ml). While the accuracy of the results presented here is not so good as with conventional techniques, the justification for the use of the method is that only small sample sizes are required. This is important when large quantities of samples are not available.

EXPERIMENTAL

Densities. The densities were determined using the pycnometer described by Lipkin et al. (4). This particular

pycnometer was chosen as it is well suited for small volume samples (<1 ml). The pycnometer was made from two 1/10-ml pipets with 1/1000-ml calibration marks. The charge of the pycnometer was approximately 0.4 ml. The charged pycnometer was placed in a stainless steel cell (13 × 3 1/2 × 2 1/2 in.) with Plexiglas windows front and back. The cell was subsequently placed in the constant-temperature Dewar. The temperature was maintained to within ±0.5°C using a constant-temperature circulator, Lauda model NBS (Brinkmann Instruments, Inc., New York, NY). The pycnometer was suspended in the cell from a double-beam chain-o-matic balance located above the Dewar with the cell.

The pycnometer was filled and then weighed in the cell in the temperature bath. At each temperature, the level in both arms of the pycnometer and its weight were obtained. The weight of the filled pycnometer changes slightly (a few milligrams) with temperature. This was attributed to two factors—one is the slight evaporation of the solvent and/or solute and the other is the change in buoyancy of the air with temperature. The system was flushed with dry nitrogen, and the measuring cell also contained a drying agent. Our experiments show that

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