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
n-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.

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LITERATURE CITED

(1) "Beilstein's Handbuch der Organischen Chemie," Vol. 4, Suppl. 3, Springer-Verlag, Berlin, 1962.
(2) Cowley, E. G., *J. Chem. Soc.*, **1952**, p 3557.
(3) "Dictionary of Organic Compounds," Vol. 5, 4th ed., Oxford Univ. Press, New York, NY, 1965.
(4) Lagowski, J. J., Sienko, M. J., Eds., "Metal-Ammonia Solutions," Proc. of Colloque Weyl II, Cornell Univ., Ithaca, NY, Butterworths, London, 1970.
(5) Le Fevre, R. J. W.,.Russell, P., *Trans. Faraday Soc.*, **43**, 374 (1947).
(6) Lepoutre, G., Sienko, M. J., Eds., "Metal-Ammonia Solutions," Proc. of Colloque Weyl I, Univ. Catholic, Lille, France, W. A. Benjamin, New York, NY, 1964.
(7) Maryott, A. A., Buckley, F., *U. S. Natl. Bur. Std., Circ.* **537**, 1953.
(8) Maryott, A. A., Smith, E. R., *ibid., Circ.* **514**, 1951.
(9) Sayce, L. A., Briscoe, H. V. A., *J. Chem. Soc.*, **127**, 315 (1925).
(10) Schlundt, H., *J. Phys. Chem.*, **5**, 503 (1901).
(11) Smyth, C. P., "Dielectric Behavior and Structure," McGraw-Hill, New York, NY, 1955.
(12) "Solvated Electron," *Advan. Chem. Ser.*, **50**, 1–304 (1965).
(13) Ulich, H., Nespital, W., *Zeit. fur Physikalische Chemie*, **16**, 221 (1932).
(14) von Hipple, A. R., "Dielectric Materials and Applications," MIT Press, Cambridge, MA, 1954.
(15) von Hipple, A. R., "Dielectrics and Waves," MIT Press, Cambridge, MA, 1954.

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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 CS_2, CCl_4, and benzene-d_6 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 CS_2, CCl_4, and benzene-d_6. 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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the weight of the empty pycnometer did not increase in time at lower temperatures.

To ensure that the interior of the cell and the pycnometer had reached thermoequilibrium with the bath, two criteria were used. A thermocouple was placed inside the cell with the measuring point toward the middle of the cell from the walls. The temperature reading from this thermocouple was compared with the temperature of the bath. A temperature difference of 0.1°C could be detected, and the accuracy in temperature measurement was better than ±0.2°C. The thermocouple was calibrated against a set of laboratory thermometers calibrated by the National Bureau of Standards. No measurements were taken until the level of the liquid in the arms of the pycnometer had been constant for at least 10 min. It generally required 45 min to an hour for these two criteria to be met for each change in temperature of the bath.

The pycnometer was calibrated first at 22°C with methanol ($\rho = 0.7894$ g/ml as given in ref. *2*), carbon disulfide ($\rho = 1.2592$ g/ml as given in ref. *3*), and degassed distilled water. Corrections were made to account for the buoyancy of air (*4*).

From the density and weight of the sample, the volume V_o of the pycnometer was obtained at 22°C and was least-square fitted to a straight line

$$V_o = G + F \cdot h \tag{1}$$

Next, the volume of the pycnometer V_t was measured at various temperatures. Methanol and carbon disulfide were used for temperatures below 0°C, and degassed distilled water and benzene were used for temperatures above 0°C. It is then assumed that all the temperature dependence of the volume of the pycnometer is contained in G. This is not strictly true, but since the temperature dependence of the volume does turn out to be quite small, it is felt that no significant error is introduced by this assumption.

Then using the constant F, and the observed volume V_t, G was calculated for each temperature. The data were least-square fitted to a straight line

$$G = E + Ft \tag{2}$$

The final equation for the volume of the pycnometer with the parameters determined by least squares is

$$V_t(\text{ml}) = 0.33664 + 0.0000463\,t \pm 1.007612\,h \tag{3}$$

The density, ρ, of any liquid is then obtained by dividing the weight in grams of the sample in the pycnometer by the volume calculated from Equation 3. Again, a correction for the buoyancy of the air was applied (*4*). The obtained densities are accurate to within ±0.5%. If one neglects the temperature correction in Equation 3, then for $V = 0.4$ ml this would result in a 0.56% error in V.

Viscosities. The Cannon-Manning Ostwald-type viscometer was used for the viscosity measurements with the calibration supplied by the manufacturer.

The viscometer was filled as prescribed by the manufacturer. Both sides of the viscometer were connected through a T stopcock to a nitrogen supply. To raise the liquid into the measuring arm of the viscometer, slight nitrogen pressure was applied to the other arm, since using vacuum would result in a loss of the most volatile components. For the measurements, both arms were opened to atmospheric pressure through a drying tube. The times for the liquid to fall were measured to 0.1 sec with a timer from Precision Scientific, whose accuracy was checked against standard digital timers. The viscosity values obtained for purified components were in good agreement with literature values (*2*, *3*) (for viscosity of C_6D_6, see ref. *1*); the average deviation was ±0.5%. The precision of our viscosity measurements for any one sample was better than 0.5%. However, mainly due to the sample preparation errors involved, the accuracy over the whole temperature range was only better than 1%. At least three timing measurements were done at each temperature. An average reproducibility of better than 0.1 sec was obtained.

The viscosities thus obtained are kinematic viscosities (i.e., in centistokes). To convert these values to centipoise, the kinematic viscosities were multiplied by the appropriate densities determined from Equations 4–6 below, before the viscosity data were fitted to Equations 7–9 below.

Materials. 2,4-Hexadiyne and 2-butyne were obtained from Farchan Research Laboratories. Before use, 2,4-hexadiyne was sublimed, under vacuum, onto a Dry Ice–acetone finger; 90% of the material was recovered. When not in use, 2-butyne was stored at −24°C in sealed ampuls previously cleaned with chromic acid and sodium hydroxide solutions.

Carbon disulfide (CS_2) was obtained from Merck and Co., Inc. It was twice distilled before solutions were prepared with it; at each distillation, approximately 80% of the material was recovered. All solutions were used within the shortest possible time after preparation so as to reduce error due to decomposition of CS_2. When not in use, solutions were stored at −24°C or in a Dry-Ice–acetone bath.

Carbon tetrachloride (CCl_4) was obtained from J. T. Baker Chemical Co.; benzene-*d*$_6$ (C_6D_6)(isotopic purity = 99.5%) from Stohler Isotope Chemicals. All compounds were twice distilled before use.

Solution Preparation. All solutions were prepared under dry nitrogen atmosphere to minimize any contamination. Since 2-butyne boils just above room temperature (+27°C), all its solutions were prepared in a cold room at −24°C. The solutions were made by volume in the desired mole fractions of 2-butyne using syringes. The syringes used for sample preparation were calibrated by weighing degassed distilled water (accuracy 2%); reproducibility of sample preparation was better than 0.5%. The preparation of the samples introduces the largest errors. However, because of the limited quantities of materials available, we feel that the technique used was justified.

For the viscosity and density measurements, only one solution was made at a time and used immediately. A different solution was made for viscosity and density measurements. For the 2-butyne solutions, the pycnometer and viscometer were filled in the cold room and immediately placed in the constant-temperature Dewar which had already been thermostated at the starting temperature of the measurements.

RESULTS

The densities of 2-butyne and 2,4-hexadiyne in the three solvents CS_2, CCl_4, and benzene-*d*$_6$ were measured as a function of concentration and temperature. For each concentration X (= mole fraction of 2,4-hexadiyne or 2-butyne), the density, ρ, was determined as a linear function of temperature t, and the data were least-square fitted to the straight line

$$\rho = A - Bt \tag{4}$$

Four different concentrations were measured, and the least-square parameters A and B were then fitted to a cubic equation as a function of X

$$A = a_1 + a_2X + a_3X^2 + a_4X^3 \tag{5}$$

$$B = b_1 + b_2X + b_3X^2 + b_4X^3 \tag{6}$$

The results are summarized in Table I, giving the a_i's, b_i's, and the temperature range of measurements. The densities thus calculated from Equations 4–6 are accurate within ± 0.5%.

For each concentration, X, the viscosity, η, was determined as an exponential function of $1/T$(K), and the data were least-square fitted to the equation

$$\eta = C \cdot \exp(D/T) \tag{7}$$

Four different concentrations were measured and the least-square parameters, $\ln(C)$ and D were fitted to a cubic equation as a function of X

$$\ln(C) = c_1 + c_2X + c_3X^2 + c_4X^3 \tag{8}$$

Table I. Coefficients in Equations 5 and 6 for 2-Butyne (I) and 2,4-Hexadiyne (II) in the Solvents CS_2, CCl_4, and Benzene-d_6 (C_6D_6)

Solute[a]	Solvent	a_1	a_2	a_3	a_4	$b_1 \times 10^3$	$b_2 \times 10^3$	$b_3 \times 10^3$	$b_4 \times 10^3$	Temp range, °C
I	CS_2	1.2916	−0.7304	0.2378	−0.0855	1.450	−0.287	−0.840	0.657	−45 ~ +20
	CCl_4	1.6328	−0.4785	−0.8967	0.4559	1.945	−1.625	2.132	−1.472	−30 ~ +20
	C_6D_6	0.9724	−0.1871	−0.1058	0.3397	1.181	−2.065	4.310	−2.446	−30 ~ +30
II	CS_2	1.2916	−0.7706	0.0898	1.1895	1.450	2.584	−26.67	55.95	+10 ~ +45
	CCl_4	1.6328	−0.7735	−0.0334	−0.0413	1.945	1.275	−9.864	10.87	+10 ~ +65
	C_6D_6	0.9724	−0.1573	0.1004	−0.1746	1.181	0.0367	−3.700	7.333	+10 ~ +75

[a] Concentration range in mole fraction of solute 0–1.0 except for: II in CS_2 (0–0.3); II in CCl_4 (0–0.4); II in C_6D_6 (0–0.4).

Table II. Coefficients in Equations 8 and 9 for 2-Butyne (I) and 2,4-Hexadiyne (II) in the Solvents CS_2, CCl_4, and Benzene-d_6 (C_6D_6)

Solute[a]	Solvent	c_1	c_2	c_3	c_4	d_1	d_2	d_3	d_4	Temp range, °C
I	CS_2	−3.0114	−1.5324	0.2409	+0.0920	590.14	262.02	46.378	−15.127	−45 ~ +20
	CCl_4	−4.5933	1.9797	−3.9211	2.1400	1337.6	−808.17	662.01	−307.92	−10 ~ +20
	CCl_4	−5.0704	4.1076	−6.7271	3.2948	1463.7	−1429.7	1607.7	−758.25	−30 ~ −10
	C_6D_6	−4.7494	2.5123	−4.0857	1.9280	1287.1	−107838.	1296.6	−621.89	−30 ~ +20
II	CS_2	−3.2075	−6.8035	67.338	−156.89	646.53	2314.4	−20500.	48355.	+10 ~ +45
	CCl_4	−4.3113	−2.2438	11.499	−16.436	1255.7	771.06	−4272.8	6322.2	+10 ~ +65
	C_6D_6	−4.7494	1.9563	−9.6528	18.943	1287.1	−287.19	1151.4	−2552.1	+10 ~ +75

[a] Concentration range in mole fraction of solute 0–1.0 except for: II in CS_2 (0–0.3); II in CCl_4 (0–0.4); II in C_6D_6 (0–0.375).

$$D = d_1 + d_2X + d_3X^2 + d_4X^3 \qquad (9)$$

The results are summarized in Table II, giving the c_i's, d_i's, and the temperature range of measurements. The viscosities thus calculated from Equations 7–9 are accurate within 1%.

NOMENCLATURE

h = sum of the scales of both arms of the pycnometer
V_t = vol, ml of the liquid in the pycnometer corresponding to liquid height, h
t = temp, °C
ρ = density of liquid, g/ml
V_o = vol, ml of the liquid in the pycnometer at 22°C
$A, B, C, D, E, F, G,$ = least-square determined parameters
a_i, b_i, c_i, d_i
η = viscosity of liquid, cP

LITERATURE CITED

(1) Dixon, J. A., Schiessler, R. W., *J. Phys. Chem.*, **58**, 430 (1954).
(2) Egloff, G., "Physical Constants of Hydrocarbons," Rheinhold, 1939.
(3) International Critical Tables, Vol. 3, p 23, McGraw-Hill, New York, NY, 1930.
(4) Lipkin, M. R., Davison, J A., Harvey, W. T., Kurtz, S. S., Jr., *Ind. Eng. Chem. Anal. Ed.*, **16**, 55 (1944).
(5) Parker, R. G., Jonas, J. J., *Magn. Resonance*, **6**, 106 (1972).

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Solubility of 16 Gases in $(C_4F_9)_3N$ and CS_2

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The solubility of the following gases was measured in $(C_4F_9)_3N$ and CS_2 at 1 atm and over ranges of approximately 30°: He^3, He^4, Ne, Ar, Kr, Xe, H_2, D_2, N_2, CH_4, C_2H_6, c-C_3H_6, CF_4, C_2F_6, c-C_4F_8, and SF_6.

Dymond and Hildebrand (*4*) in 1967 described an apparatus that gave rapid, accurate values of the solubility of gases in liquids. Dymond (*3*) published values of the mole fraction, x_2, of nine gases at 1 atm in c-C_6H_{12} over ranges of temperature of ~40°. Points for log x_2 vs. log T for each gas fell upon straight lines whose slopes, $\Delta \log x_2/\Delta \log T$, multiplied by the gas constant, R, give the entropy of solution, since $\bar{S}_2 = S_2^g = R(\partial \ln x_2/\partial \ln T)_{\Delta F=0}$. The points for the entropy of solution plotted against the solubility expressed as $-R \ln x_2$ gave a straight line whose slope was 1.64 and whose intercept at $-R \ln x_2 = 0$ was −21.0 cal/mol deg. The points for CF_4 and SF_6 were just off the line. Miller (*10*) later added points for C_2F_6, C_3F_8, c-C_4F_8, and $CClF_3$.

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