Densities and Molal Volumes of *n*-Alkylamines from 15 to 80°C

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Densities of seven *n*-alkylamines from 1-butylamine to 1-decylamine were determined from 15 to 80°C. The density was found to be a linear function of the temperature within this temperature range. At constant temperature, the molal volume was a linear function of the number of methylene units in the chain for the homologous series. A simple equation with four constants correlating the molal volume with the number of methylene units and temperature of the *n*-alkylamines was formulated. Excellent agreement between the calculated, the measured and the literature values were obtained. Accurate molal volumes, and hence the densities of any *n*-alkylamines, other than methylamine, within the temperature range can be calculated from the equation.

KEY WORDS: Density, molal volume, *n*-alkylamines.

Fatty amines are important industrial chemicals in the manufacture of cationic and nonionic surface active agents (1). However, their properties have not been thoroughly studied. Except for the *n*-alkylamines with less than four carbons, the densities of the longer-chain *n*-amines at temperatures other than those near room temperature are difficult to find in the literature.

For organic liquids in a limited range of temperatures, the densities are linear with temperature (2–4). For an extended temperature range, the variation of density with temperature may be expressed in terms of a polynomial equation (5) or the Francis equation (6,7). For aliphatic compounds in a homologous series, the densities at constant temperature can be related linearly to the number of carbon atoms in the chain. Such equations have been developed for alkanes (8), alcohols (9), acids and esters (4).

The densities and molal volumes of the homologous series of fatty alcohols, acids and esters (2–4,9) have been related to temperatures and chainlength by a single equation for each of the series at moderate temperature ranges. This is a continuation of those studies.

EXPERIMENTAL PROCEDURES

Analytical reagent grade *n*-alkylamines from C_4 to C_{10} with 99% purity or better (Fluka, Chemie AG, Buchs, Switzerland) were dried over molecular sieves before use. *n*-Butylamine was dried over potassium hydroxide pellets and fractionally distilled.

A narrow-necked (3-mm i.d.) 10-mL flask-type pycnometer was used for determination of the density. The pycnometer was filled by means of a syringe with a long needle to minimize contact with the atmosphere. Caution was also taken to prevent evaporation. The filled and capped pycnometer was equilibrated for at least 30 min at a temperature controlled to better than 0.05°C. The masses were buoyancy-corrected. The reproducibility of the density measurements was better than 4×10^{-5} g cm^{-3}. The temperature was read from a calibrated thermometer.

RESULTS AND DISCUSSION

The densities of the *n*-alkylamines with 4 to 10 carbon atoms were determined from 15 to 80°C at 5°C intervals. These results are shown in Table 1, together with some literature data at 20 and 25°C (10,11). The differences between the present results and the available literature data are generally less than 0.1%.

TABLE 1

Densities (g cm^{-3}) of *n*-Alkylamines and Coefficients of Equation 1 (k = g cm^{-3}, m = g cm^{-3}C^{-1})

Temperature (°C)	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
15	0.7431	0.7592	0.7705	0.7796	0.7867	0.7925	—
20	0.7386	0.7544	0.7660	0.7754	0.7826	0.7886	0.7933
	0.7392[a]	0.7547[b]	0.7660[b]	0.7754[b]	0.7826[b]	0.7886[b]	0.7936[b]
25	0.7341	0.7496	0.7614	0.7712	0.7785	0.7847	0.7898
	0.7346[a]	0.7505[b]	0.7620[b]	0.7716[b]	0.7790[b]	0.7853[b]	0.7905[b]
30	0.7282	0.7449	0.7570	0.7670	0.7744	0.7808	0.7857
35	0.7231	0.7401	0.7525	0.7627	0.7705	0.7768	0.7817
40	0.7181	0.7353	0.7480	0.7584	0.7660	0.7728	0.7778
45	0.7130	0.7304	0.7434	0.7541	0.7619	0.7689	0.7740
50	0.7079	0.7257	0.7388	0.7499	0.7577	0.7649	0.7701
55	0.7031	0.7211	0.7338	0.7459	0.7536	0.7612	0.7664
60	0.6981	0.7168	0.7304	0.7420	0.7502	0.7577	0.7630
65	0.6929	0.7122	0.7263	0.7381	0.7462	0.7541	0.7595
70	0.6879	0.7076	0.7220	0.7341	0.7423	0.7504	0.7558
75	—	0.7029	0.7176	0.7299	0.7383	0.7465	0.7520
80	—	0.6982	0.7131	0.7257	0.7341	0.7426	0.7483
Constants							
k	0.75867	0.77293	0.78336	0.79174	0.79857	0.80369	0.80806
$m \times 10^4$	−10.117	−9.3635	−8.8167	−8.2752	−8.0756	−7.6558	−7.4989

[a]Reference 10.
[b]Reference 11.

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We further evaluated the accuracy of our experimental data by plotting them as a function of temperature by using Equation 1:

$$d = mT + k \quad [1]$$

where d is the density, T is the temperature in Celsius, and m and k are constants. Good straight lines with correlation coefficients better than 0.9998 were obtained for all n-alkylamines studied. The least-square values of the constants are shown in Table 1.

Empirical equations (12–14) as well as semi-empirical methods (8) have been proposed to correlate the molal volumes, and hence the density, of homologous series of compounds at constant temperature with the number of carbon atoms. One of the equations that has been used frequently is Equation 2:

$$V = an + b \quad [2]$$

where V is the molal volume, n is the number of methylene units in the chain, and a and b are constants characteristic of the series. The constant b is the contribution to the molal volume by the end groups while the constant a is the contribution from each methylene unit. It has been observed that for compounds with short chains, deviation from linearity occurred. For hydrocarbons, the slope of the plot decreased, while for alcohols, acids and esters, the slope increased as the chain shortened. Thus, correction terms have been proposed (4,15,16) to account for these deviations.

The molal volumes of the n-alkylamines were calculated from the experimental densities at all temperatures studied. These are shown in Table 2. Additional molal volumes for the methyl, ethyl, propyl and longer-chain n-alkylamines at 20°C were calculated from literature densities (11). From these values, the differences in molal volumes ($V_n - V_{n-1}$) between adjacent n-alkylamines at 20°C were obtained. There was hardly any systematic deviation from the mean value of 16.49 ± 0.07 up to n = 20, excluding $V_1 - V_0$, which has a value of 19.25. For n-alkylamines, the interactions between end groups, in this case CH_3 and NH_2, are not effective in reducing the molal volumes once the end groups are separated by more than one methylene unit.

We thus correlated the molal volumes of the n-alkylamines with the number of methylene units according to Equation 2. Correlation coefficients of better than 0.9999 were obtained at all temperatures. The least-square values of the slopes and the intercepts are shown in Table 2. The molal volumes were calculated from these constants and compared with the experimentally obtained values. The average absolute deviations were less than 0.04% for all temperatures.

Because the molal volumes are reciprocally proportional to the densities and because the densities are linear functions of temperature in a moderate temperature range, we related the constants a and b with the reciprocal of the temperatures according to Equations 3 and 4:

$$1/a = eT + p \quad [3]$$

$$1/b = fT + q \quad [4]$$

These linear plots are shown in Figure 1. The values of e, f and p, q were obtained by least-square fit, and their correlation coefficients were better than 0.9980.

When Equations 3 and 4 were substituted in Equation 2, Equation 5 with four empirical constants was obtained:

$$V_n = \frac{n}{-3.1101x10^{-5}T + 0.06108} + \frac{1}{-4.2872x10^{-5}T + 0.02108} \quad [5]$$

From equation 5, the molal volumes of the n-alkylamines at temperatures ranging from 15 to 80°C were calculated and compared with the values obtained from the measured densities. The average absolute deviation between the calculated values and the measured values is less than 0.06%. Excellent agreement is thus obtained.

Equation 5 was also used to calculate the molal volumes of ethyl and propyl amines as well as the n-alkylamines with carbon numbers between 13 and 30 at 20 and 25°C, for which density data are available, and they show good agreement. Equation 5 can thus be utilized to obtain

TABLE 2

Experimental Molal Volumes of n-Alkylamines and Coefficients of Equation 2

Temperature (°C)	Carbon number (n = N − 1)							Constants	
	3	4	5	6	7	8	9	a	b
15	98.42	114.81	131.34	147.79	164.29	180.79	—	16.4783	48.9428
20	99.02	115.53	132.10	148.59	165.15	181.68	198.29	16.5414	49.3743
25	99.63	116.27	132.89	149.41	166.02	182.58	199.15	16.5825	49.9264
30	100.43	117.01	133.67	150.23	166.91	183.50	200.20	16.6261	50.5221
35	101.14	117.77	134.47	151.07	167.74	184.43	201.22	16.6725	51.0850
40	101.85	118.54	135.29	151.92	168.72	185.38	202.23	16.7232	51.6507
45	102.58	119.33	136.12	152.79	169.64	186.34	203.24	16.7686	52.2514
50	103.31	120.11	136.96	153.65	170.57	187.31	204.25	16.8154	52.8450
55	104.02	120.87	137.89	154.48	171.50	188.21	205.26	16.8575	53.4593
60	104.76	121.59	138.55	155.27	172.28	189.10	206.15	16.8900	54.0457
65	105.55	122.39	139.33	156.11	173.21	190.00	207.12	16.9218	54.7136
70	106.32	123.17	140.15	156.96	174.12	190.94	208.11	16.9600	55.3500
75	—	124.00	141.01	157.85	175.07	191.91	209.17	17.0220	55.8587
80	—	124.84	141.90	158.77	176.06	192.92	210.22	17.0643	56.5338

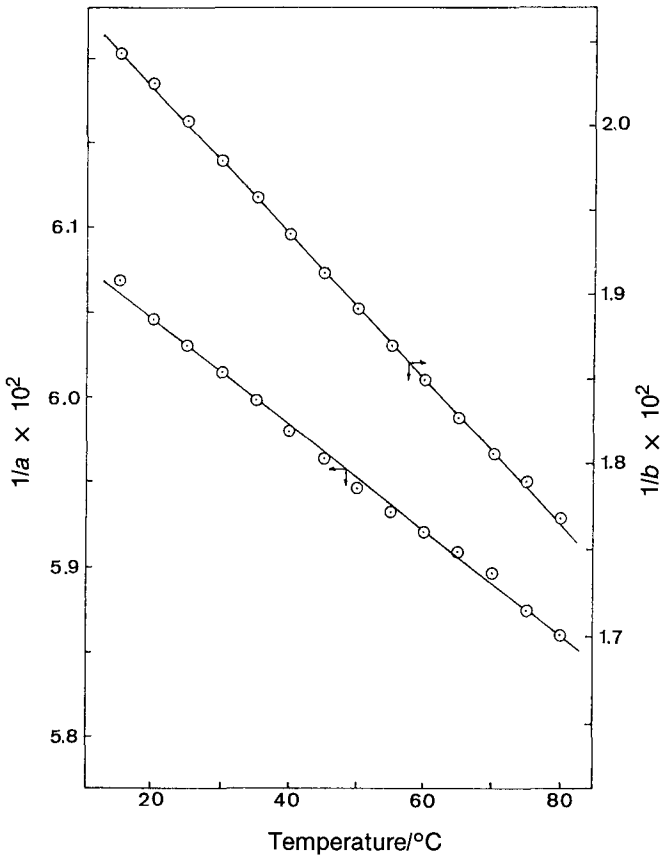

FIG. 1. Plots of $1/a$ and $1/b$ against temperature for *n*-alkylamines where a and b are constants.

accurate molal volumes and hence the density for any *n*-alkylamine, except methylamine, at any temperature within the range.

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