Effect of Temperature and Chainlength on the Densities and Molal Volumes of *n*-Alkyl Chlorides

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ABSTRACT: The densities of *n*-alkyl chlorides from pentyl chloride to hexadecyl chloride were determined at temperatures between 15–80°C at 5°C intervals. The densities increase linearly with temperature and chainlength. A four-constant equation, $V = n/(-3.6640 \times 10^{-5}\ T + 0.07151) + 1/(-5.6526 \times 10^{-5}\ T + 0.04243)$, was formulated. This formula accurately predicted the molal volume and, hence, the density for all the *n*-alkyl chlorides at any temperature within the range.

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KEY WORDS: Density, molal volume, *n*-alkyl chlorides.

The densities of liquids are physical properties that are of practical importance, as well as theoretical interest, in the study of intermolecular interactions. They also can be easily and accurately determined. The densities of *n*-alkyl chlorides have been reported at temperatures of 20 and 25°C (1–6). However, their densities at other temperatures are not easily found. Because *n*-alkyl chlorides are often used as intermediaries in preparation of other, more useful substances, it is advantageous to know their properties at other temperatures.

It is generally true that the density of an organic compound is nearly exactly linearly related to the temperature over a limited range according to the formula:

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

where d is the density, T the temperature, and m and k are constants. More complicated relations may have to be used at wider temperature ranges. The coefficients of the linear equations have been reported for members in the homologous series of *n*-fatty acids and their esters, alcohols, and amines (7–11). For these series of compounds, it has been found that the molal volumes, which are inversely proportional to the densities, are linear functions of the numbers of methylene groups, n, in the hydrocarbon chain. Equation 2 is usually obeyed for members of the series with longer chains:

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

where V is the molal volume, a is a temperature-dependent constant with a value of 16–17 cc per mole corresponding to the contribution from the methylene increments, and b is another temperature-dependent constant, which reflects the contribution from the two end groups of the molecule. For the homologous series where intermolecular interactions are strong, such as the fatty acids and the alcohols, a correction term, which may be a function of the number of methylene groups, may have to be added (7,10). It has been reasoned that, because the density can be expressed as a linear function of the temperature and the molal volume is inversely proportional to the density, the reciprocals of the constants in Equation 1 may be expressed as linear functions of temperatures as follows:

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

and

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

A four-constant empirical equation of the form,

$$V = n/(eT + p) + 1/(fT + q) \qquad [5]$$

where $e, f, p,$ and q are the four constants, was thus formulated and used to calculate the molal volumes of the series of *n*-aliphatic derivatives at temperatures within the range from 15 to 80°C. Accurate molal volumes were obtained. This short communication reports the densities of *n*-alkyl chlorides at temperatures ranging from 15 to 80°C and the empirical constants in Equation 5.

EXPERIMENTAL PROCEDURES

Analytical reagent-grade *n*-alkyl chlorides from C_5 to C_{16} with 99% purity or better (Merck, Schuchardt, Germany) were dried over molecular sieves before use. A narrow-necked (3-mm i.d.), 10-mL, homemade, flask-type pycnometer was used to determine densities. The pycnometer was filled by means of a syringe with a long needle to minimize contact with the atmosphere, and caution was taken to prevent evaporation. The filled and capped pycnometer was equilibrated for at least 30 min at a controlled temperature bath (±0.05°C). The temperature was read from a calibrated thermometer. The masses were buoyancy-corrected. The reproducibility of the density measurements was better than 4×10^{-3} g cm^{-3}.

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TABLE 1
Densities of *n*-Alkyl Chlorides and Coefficients Based on the Equation $d = mT + k$[a]

Temperature (°C)	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{12}	C_{14}	C_{16}
15	0.8867	0.8828	0.8797	0.8772	0.8754	0.8735	0.8709	0.8698	0.8675
20	0.8819	0.8778	0.8750	0.8730	0.8715	0.8696	0.8672	0.8658	0.8640
	0.8818[b]	0.8785[b]	0.8758[b]	0.8737[b]	0.8720[b]	0.8705[b]	0.8682[b]	0.8665[b]	0.8652[b]
25	0.8768	0.8732	0.8708	0.8688	0.8671	0.8657	0.8636	0.8622	0.8605
	0.8769[b]	0.8739[b]	0.8715[b]	0.8695[b]	0.8679[b]	0.8666[b]	0.8644[b]	0.8628[b]	0.8615[b]
	0.87682[c]	0.87327[c]	0.87108[c]	0.86872[c]					
	0.87692[d]	0.87333[d]	0.87098[f]	0.86865[d]					
	0.87696[e]	0.87307[e]	0.8715[g]	0.86872[e]					
30	0.8718	0.8685	0.8660	0.8644	0.8631	0.8618	0.8597	0.8586	0.8569
35	0.8668	0.8641	0.8620	0.8602	0.8593	0.8577	0.8560	0.8550	0.8534
40	0.8619	0.8593	0.8574	0.8561	0.8551	0.8537	0.8523	0.8513	0.8499
45	0.8565	0.8545	0.8530	0.8519	0.8510	0.8497	0.8484	0.8474	0.8460
50	0.8514	0.8498	0.8486	0.8474	0.8466	0.8455	0.8444	0.8437	0.8425
55	0.8460	0.8448	0.8438	0.8431	0.8426	0.8416	0.8407	0.8402	0.8390
60	0.8413	0.8404	0.8397	0.8390	0.8388	0.8376	0.8368	0.8365	0.8354
65	0.8358	0.8353	0.8348	0.8345	0.8343	0.8336	0.8331	0.8328	0.8318
70	0.8305	0.8305	0.8304	0.8303	0.8302	0.8296	0.8294	0.8292	0.8283
75	0.8250	0.8259	0.8258	0.8257	0.8256	0.8254	0.8253	0.8251	0.8246
80	0.8200	0.8210	0.8212	0.8216	0.8216	0.8215	0.8217	0.8217	0.8211
k	1.1837	1.1560	1.1380	1.1240	1.1139	1.1048	1.0900	1.0824	1.0737
$m \times 10^{-4}$	−10.29	−9.48	−8.97	−8.56	−8.27	−8.02	−7.60	−7.38	−7.16

[a]Where d is density; T, temperature; and m and k are constants. [b]Reference 1. [c]Reference 2. [d]Reference 3. [e]Reference 4. [f]Reference 5. [g]Reference 6

RESULTS AND DISCUSSION

The densities of nine *n*-alkyl chlorides, from pentyl chloride to hexadecyl chloride, were determined at temperatures between 15 to 80°C at 5°C intervals. These data are shown in Table 1 together with some literature data determined at 20 and 25°C. The present values are comparable to the literature values, which differ slightly from one another. The accuracies of these values were further demonstrated when we plotted the densities as a function of the temperature according to Equation 1. Straight lines with correlation coefficients of better than 0.9999 were obtained in all cases. The values of the constants evaluated by linear least squares also are shown in Table 1.

The molal volumes of these chlorides were calculated and are shown in Table 2. As mentioned previously, the molal volume of some series of homologous compounds may be correlated by Equation 2, although an additional term may be required for some other series. When we tested the linearity of the equation for the *n*-alkyl chlorides by plotting $V - (an + b)$ against n with some suitable values for the constants, no systematic deviations from linearity were observed at any of the temperatures studied. That linearity was observed, as opposed to the fatty acids and alcohols, may be because, although the

TABLE 2
Molal Volumes of *n*-Alkyl Chlorides from Experiments and Coefficients Based on Equation $V = an + b$[a]

Temperature	Number of methylene group, n = N-1									
(°C)	4	5	6	7	8	9	11	13	15	a	b
15	120.22	136.64	153.06	169.49	185.86	202.32	235.14	267.69	300.74	16.4017	54.6475
20	120.87	137.41	153.88	170.30	186.69	203.23	236.14	268.92	301.96	16.4539	55.1103
25	121.57	138.14	154.63	171.13	187.64	204.14	237.13	270.05	303.18	16.5019	55.6068
30	122.27	138.88	155.48	172.00	188.51	205.07	238.20	271.18	304.46	16.5522	56.1086
35	122.98	139.59	156.20	172.84	189.34	206.05	239.23	272.32	305.71	16.6049	56.5641
40	123.67	140.37	157.04	173.66	190.27	207.02	240.27	273.51	306.96	16.6551	57.0750
45	124.45	141.16	157.85	174.52	191.19	207.99	241.37	274.76	308.38	16.7147	57.5473
50	125.20	141.94	158.67	175.45	192.18	209.02	242.52	275.97	309.66	16.7658	58.0979
55	126.00	142.78	159.57	176.34	193.10	209.99	243.58	277.12	310.95	16.8079	58.7123
60	126.70	143.53	160.35	177.20	193.97	210.99	244.72	278.34	312.29	16.8684	59.1501
65	127.54	144.40	161.29	178.16	195.02	212.01	245.81	279.58	313.64	16.9129	59.8048
70	128.35	145.24	162.15	179.06	195.98	213.03	246.90	280.80	314.97	16.9611	60.3905
75	129.20	146.05	163.05	180.06	197.07	214.11	248.13	282.19	316.38	17.0198	60.9665
80	130.00	146.92	163.96	180.96	198.03	215.13	249.22	283.36	317.73	17.0653	61.5793

[a]Where V is the molal volume; a is a temperature-dependent constant with a value of 16–17 cc/mole; b, another temperature-dependent constant; and n represents the methylene groups.

molecules are highly polar, interactions between molecules are still not strong enough to be observable in terms of the density, or that the number of intercepting methylene groups between the ends were too large. We thus correlated the molal volumes with the number of methylene groups by simply using Equation 2 by linear least squares. The values of the constants, together with the correlation coefficients, also are shown in Table 2. The values of a, which correspond to the contribution from the methylene increment, are between 16–17 cc mol^{-1}, similar to the values obtained for the other homologous series. The values of b, which correspond to the contribution from the two end groups of CH_3 and Cl, are in the range of 54–61 cc mol^{-1}. These values are larger than the values determined for the end group contributions by alcohols and amines, which are 43–48 cc mol^{-1} and 48–57 cc mol^{-1} (10,11), respectively. That the hydroxyl and the amine groups are bulkier than the chloride and yet have smaller contributions to the molal volume is likely a manifestation of the formation of hydrogen bonding in the alcohols and amines.

The linear plots of $1/a$ and $1/b$ vs. the temperature in °C, according to Equations 3 and 4, are shown in Figure 1. The values of the four constants were evaluated by linear least square. The correlation coefficients are better than −0.9997 in both cases. When these values were substituted into Equation 5, Equation 6 is obtained:

$$V = n/(-3.6640 \times 10^{-5}\, T + 0.07151) + 1/(-5.6526 \times 10^{-5}\, T + 0.04243) \qquad [6]$$

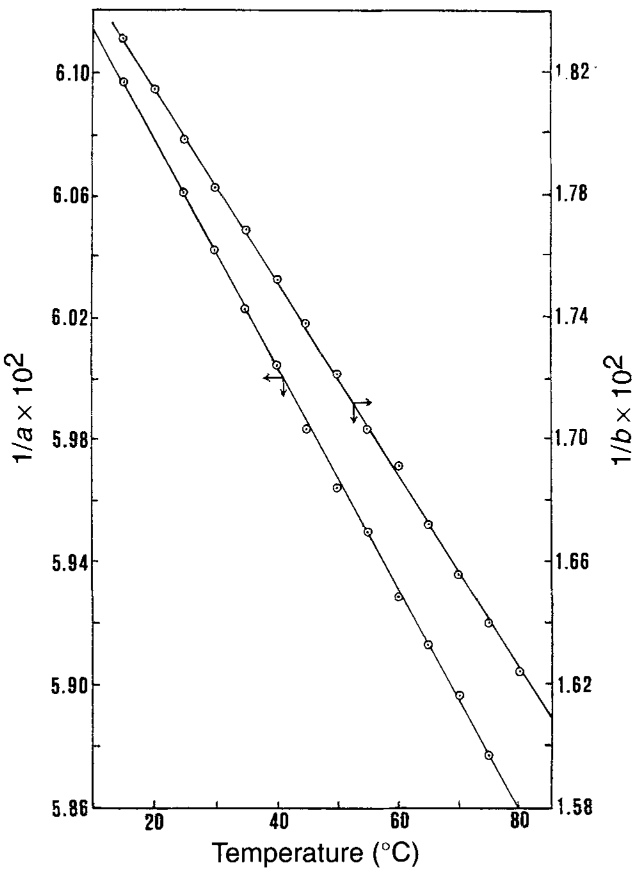

FIG. 1. Plots of $1/a$ and $1/b$ against temperature for n-alkyl chlorides, where a and b are constants.

This equation was used to calculate the molal volumes of the n-alkyl chlorides at different temperatures within the range of temperatures studied and compared with the values calculated from the experimental densities. Average absolute deviation of less than 0.1% was obtained for the available data. A convenient empirical equation is thus obtained for the calculation of accurate molal volumes and, hence, the densities for the chlorides at any temperature within the range.

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