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Articles

Heat Capacities of α,ω-Dichloroalkanes at Temperatures from 284.15 K to 353.15 K and a Group Additivity Analysis

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Heat capacities at constant pressure of five α,ω-dichloroalkanes (1,2-dichloroethane, 1,3-dichloropropane, 1,4-dichlorobutane, 1,5-dichloropentane, 1,6-dichlorohexane) were measured at temperatures ranging from 284 K to 353 K by using a highly sensitive Tian−Calvet differential scanning microcalorimeter (DSC). Changes in the standard procedures increased the accuracy of C_p measurements. The influence of the evaporation heat effect on the C_p value is analyzed. In the described method, the uncertainty of the measurements is estimated to be ±0.15% for uncertainties arising solely from the measurement system and method. The group contributions to C_p for CH_2 and Cl and their temperature dependence were determined by a group additivity analysis.

Introduction

Differential scanning calorimetry (DSC) is a frequently applied, modern analytical technique providing quantitative information derived from relatively small samples, over a wide range of temperatures. Due to its very high sensitivity, DSC based on Tian−Calvet's idea is an effective technique for heat capacity (C_p) measurements on both liquid and solid substances. An application of SETARAM Tian−Calvet DSC calorimeters to C_p measurements was analyzed recently by Paramo et al.,[1] Cerdeirina et al.[2] (Micro DSCII), and Becker et al.[3,4] (model BT2.15). In this work on C_p measurements, another model DSC calorimeter was used (Micro DSC III−Setaram). One aim of this study was to define the conditions that give a minimum uncertainty for C_p measurements.

A precise knowledge of heat capacities of liquids as a function of temperature provides insight into their molecular structure and information on intermolecular interactions. Furthermore, changes in enthalpy, entropy, and Gibbs energy at any temperature can be calculated from results obtained at a more convenient reference temperature. Also, the correct group additivity analysis requires precisely determined values of C_p of a series of homologous compounds. Unfortunately, the reliable data on the temperature dependence of heat capacities of many compounds are scarce in the literature. For instance, for the majority of α,ω-dichloroalkanes, the C_p values were determined exclusively at 298 and 303 K, and the temperature dependence of C_p was studied for only 1,2-dichloroethane.[5]

This prompted us to continue our earlier study[6] on C_p measurements for halogenoalkanes. The main objective of this paper was to determine the heat capacities of five α,ω-dichloroalkanes, namely, 1,2-dichloroethane (DClEt), 1,3-dichloropropane (DClPr), 1,4-dichlorobutane (DClBu), 1,5-dichloropentane (DClPe), and 1,6-dichlorohexane (DClHx), in the temperature range from (284.15 to 353.15) K.

Experimental Section

Chemicals. The 1,3-dichloropropane (≥99%), 1,4-dichlorobutane (≥99.5%), 1,5-dichloropentane (≥99%), and 1,6-dichlorohexane (≥98%) were purchased from Aldrich, 1,2-dichloroethane (≥99%) was from Lancaster, and toluene (≥99.8%) and *n*-heptane (≥99.5%) were from Fluka. The substances were purified prior to use by fractional distillation, and the middle fraction (approximately 5%) was collected in every case. The purities of the α,ω-dichloroalkanes checked by gas−liquid chromatography (GLC) were >99.5% by mass, and that of *n*-heptane was >99.8%. Prior to the measurements, all liquids were dried with molecular sieves (type 3A, (1 to 2) mm beads from Lancaster) and degassed by ultrasound. Water used as a standard was deionized and then triple distilled in an atmosphere of argon. The measuring cells were filled in the drybox. The samples were weighed with a SARTORIUS RC 210D balance with an accuracy of 2×10^{-5} g.

Apparatus and Procedure. General principles of C_p measurements by using differential scanning calorimetry were described elsewhere.[3,7−9] The main part of the DSC III (Setaram) is based on Tian−Calvet's idea and consists of the measuring chamber placed in a metal block whose temperature is controlled within ±0.001 °C with a Peltier effect cooler. The actual temperature in the measuring cell during the experiment was determined from the parameters obtained by DSCIII calibration. The calibration (see, e.g., refs 3 and 4) was carried out using three standards with known melting points[12] (water, gallium, and naphthalene) and three different scanning rates: 0.1, 0.5, and 1.0 $K \cdot min^{-1}$. The uncertainty of the absolute temperature value in the measuring cell is estimated to be ±0.05 K. The temperature of the external cooling system is kept

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constant (±0.02 °C) with a HAAKE type DC30 thermostat. The measuring calorimetric chamber contains two separate holes, designed for the measuring and the reference cells. The measuring vessel was the standard "batch" type cell with the volume $\sim$1.0 cm^3. It permitted the C_p measurements at temperatures ranging up to the boiling point of the liquid.

Two standard procedures of C_p measurements by DSC are usually applied. We used the "continuous with reference" method, which appeared to be superior[2,3] to the "step by step" method, because it is less time-consuming and provided similar accuracy of measurements. In this method, the differential heat flow (HF = dQ/dt) during the experiment is recorded as a function of temperature in three independent steps: (i) for the empty measuring cell (HF$_0$); (ii) for the measuring cell filled with the reference liquid of known specific heat capacity $C_{p,r}$ within the temperature range examined (HF$_r$); and (iii) for the measuring cell filled with the tested liquid (HF$_x$).

The specific heat capacity of the examined substance can be expressed as

$$C_{p,x} = \frac{HF_x - HF_0}{HF_r - HF_0}\frac{m_r}{m_x}C_{p,r} \qquad (1)$$

where $C_{p,x}$ = the specific heat capacity of the examined substance, $C_{p,r}$ = the specific heat capacity of the reference substance r (placed in the measuring cell), m_r = the mass of the reference substance r, and m_x = the mass of the examined substance x.

In published C_p experimental studies using DSC, the reference cell was usually empty[3,11] or filled with the reference liquid[1,2] of known C_p. According to (1), the total heat capacity of the reference cell has no direct impact on a $C_{p,x}$ value. However, our experiments revealed that it markedly affected the accuracy of $C_{p,x}$ measurements. This results from the fact that the level of noise for HF is directly proportional to the HF value, which reflects the difference in heat capacities of both the cells. Better accuracy of the $C_{p,x}$ measurements is achieved when the total heat capacity of the reference cell is comparable to that of the measuring cell, that is, when the HF$_r$ and HF$_x$ values are small as compared to that for HF$_0$. Therefore, it is purposeful to use a filled up (or solid) reference cell with a heat capacity being invariable with time and comparable to that of the filled measuring cell. For this reason, a stainless steel block (the mass of approximately 11 g) providing stable and reproducible heat capacity was used as the reference cell.

The volume of the studied liquids at room temperature was usually 0.92 cm^3, which resulted in 8% "free vapor volume" in the cell during the experiment. Since the "batch" cell is not completely filled with the sample, it is necessary to take into account an evaporation effect on the measured C_p values. At temperatures ranging from 10 to 80 °C, the difference in the evaporation effect for the substances subjected to our investigation and the reference compound (n-heptane) did not exceed 0.02% of the $C_{p,x}$ value, and therefore, it was neglected. For instance, the enthalpy of evaporation corresponding to an increase in temperature of 1 K did not exceed 3×10^{-4} J for n-heptane and 6×10^{-4} J for 1,2-dichloroethane, which was the most volatile compound of all used in our studies, respectively. The result would be an overestimation of C_p values by a maximum of 0.02%. The other sources of C_p uncertainty are the error of sample weight ($\pm 4 \times 10^{-5}$ g), causing the error of the measured C_p to be ±0.005%, and the error of the absolute temperature determination (±0.05 K), causing the C_p error to be ($\pm 1 \times 10^{-4}$)%. According to the earlier studies,[5,10] the influence of an increase in the pressure (up to $\sim$2 bar) on the C_p values may be neglected. Both the calorimeter and method were tested with the use of four liquids regarded to be standards for C_p measurements (water, toluene, n-heptane, and 1-butanol). The measurements repeated three times for each liquid at various scanning rates (0.15, 0.20, and 0.25 K·min^{-1}) provided a set of $C_{p,x}$ data for about 40 individually treated measured liquid−reference liquid pairs within the range from 10 to 80 °C. The calculated average standard deviation of the measured $C_{p,x}$ from literature data[5,12] within this temperature range was about 0.003 $J\cdot g^{1}\cdot K^{-1}$ for water and 0.0015 $J\cdot g^{1}\cdot K^{-1}$ for organic solvents. It corresponds to the relative standard deviation of C_p data ±0.08%.

On the basis of an analysis of the applied procedure and the use of a solid reference cell, we estimate that the uncertainty of the C_p measurements with the Micro DSCIII is ±0.15%, excluding the effects of sample impurities. A similar level of uncertainty of C_p data obtained by DSCII (Setaram) is reported by Paramo et al.[1] and Carderina et al.[2,16] Some values of C_p, either derived from our measurements (n-heptane used as a reference) or reported in the literature, are compared in Table 1.

Table 1. Comparison of the Experimental and Recommended C_p/J·mol^{-1}·K^{-1} Data of Water, Toluene, and 1-Butanol

	water C_p/J·mol^{-1}·K^{-1}		toluene C_p/J·mol^{-1}·K^{-1}		1-butanol C_p/J·mol^{-1}·K^{-1}	
T/K	exptl	lit.[12]	exptl	lit.[5]	exptl	lit.[5]
283.15	75.47	75.573	152.85	153.07	153.00	153.07
293.15	75.29	75.377	155.56	155.74	155.71	155.74
303.15	75.29	75.308	158.38	158.53	181.16	180.62
313.15	75.34	75.304	161.47	161.42	188.39	188.26
323.15	75.32	75.339	164.51	164.41	196.66	196.48
333.15	75.33	75.381	167.63	167.49	205.33	205.10
343.15	75.38	75.472	170.85	170.67	214.22	213.93

Results

The heat capacity measurements of the studied α,ω-dichloroalkanes were carried out at temperatures from 284 to 353 K with a scanning rate of 0.2 K·min^{-1}. The results were recorded at each 0.02 K, thus giving 3500 data points over the temperature range studied. For clarity, only the values obtained every 2.5 K are shown in Table 2 and compared with literature data at 298.15 K.

The molar heat capacities, C_p, as a function of temperature were fitted to the equation

$$C_p = \sum_{i=0}^{2} A_i (T - 293.15)^i \qquad (2)$$

where A_i are constants determined by a least-squares method and presented in Table 2.

Results presented in Figure 1 show that, in the studied temperature range, the molar heat capacities of the α,ω-dichloroalkanes are virtually linearly proportional to temperature (A_2 constants are relatively small) and increase with the alkyl chain length.

Group Additivity Analysis. The nonexperimental methods of estimation of the heat capacities of liquids can be divided[10] into four categories, such as the theoretical ones, the methods of corresponding states, Watson's thermodynamic cycle, and estimates with group contributions. The last method is based upon the concept that various groups of the molecule contribute definite values to the total molar

Table 2. Molar Heat Capacities, C_p/J·mol^{-1}·K^{-1}, for Some α,ω-Dichloroalkanes in the Temperature Range 284 K to 353 K, Coefficients, A_i, and Standard Deviation, δ_{C_p}, for Eq 2

	C_p/J·mol^{-1}·K^{-1}				
T/K	DClEt	DClPr	DClBu	DClPe	DClHx
284.16	128.02	154.94	181.25	209.50	236.57
286.66	128.21	155.40	181.71	210.04	237.13
289.15	128.39	155.76	182.15	210.65	237.89
291.66	128.58	156.11	182.62	211.20	238.51
294.15	128.75	156.39	182.99	211.70	239.26
296.65	128.94	156.76	183.49	212.19	239.89
298.15	129.06	157.03	183.76	212.63	240.39
	129.4,[13] 128.81[14]	157.0[13]	184.0,[13] 183.59[15]	213.4[13]	239.58[5]
299.16	129.11	157.20	183.89	212.96	240.68
301.65	129.39	157.65	184.47	213.55	241.35
304.16	129.47	157.89	184.80	214.12	242.00
308.56	129.86	158.63	185.71	215.36	243.00
309.15	129.86	158.67	185.83	215.26	243.48
311.66	130.16	159.23	186.41	215.96	244.27
314.15	130.40	159.54	186.88	216.61	245.06
316.65	130.55	159.89	187.38	217.17	245.79
319.16	130.88	160.47	187.89	217.92	246.57
321.65	131.09	160.93	188.52	218.56	247.24
324.16	131.20	161.01	188.85	219.00	247.78
326.65	131.56	161.59	189.48	219.91	248.95
329.15	131.87	162.11	190.01	220.61	249.58
331.66	132.06	162.48	190.54	221.16	250.36
334.15	132.24	162.96	190.99	221.76	251.24
336.66	132.59	163.33	191.48	222.43	252.00
339.16	132.82	163.82	192.00	223.10	252.72
341.65	132.96	164.10	192.36	223.58	253.70
344.16	133.32	164.44	193.05	224.70	254.49
346.65	133.59	165.10	193.63	225.01	255.12
349.15	133.83	165.38	194.00	225.75	255.75
351.66	134.22	165.81	194.70	226.41	257.00
353.14	134.46	166.22	195.12	227.13	257.47
A_0	128.68 ± 0.00	156.31 ± 0.00	182.86 ± 0.00	211.52 ± 0.01	238.83 ± 0.01
10^2A_1	7.40 ± 0.03	15.13 ± 0.04	18.58 ± 0.04	23.39 ± 0.05	27.82 ± 0.06
10^3A_2	0.338 ± 0.005	0.213 ± 0.007	0.288 ± 0.007	0.403 ± 0.009	0.493 ± 0.011
δ_{C_p}/J·mol^{-1}·K^{-1}	0.11	0.14	0.15	0.19	0.23

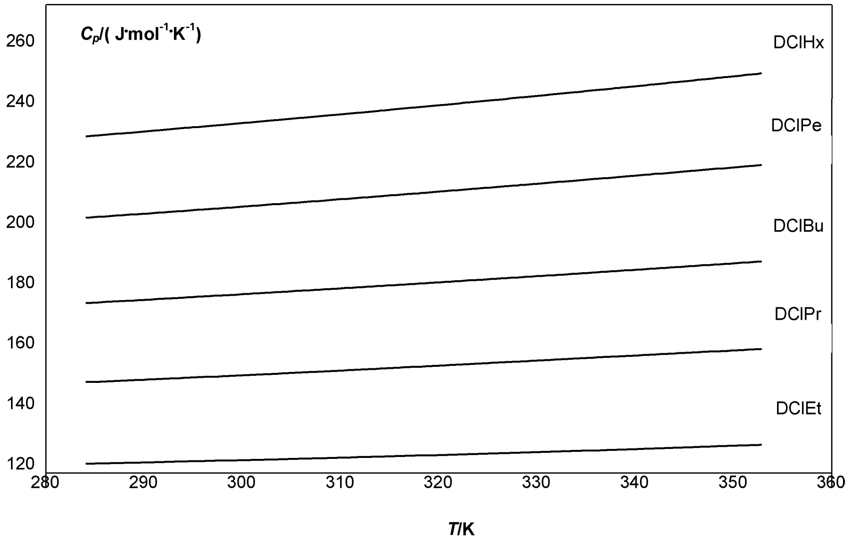

Figure 1. Molar heat capacities of the α,ω-dichloroalkanes as a function of temperature: —, values calculated from eq 2.

heat capacity. In the case of halogeno derivatives, the temperature dependences of group contributions to C_p are only given by Missenard[17] and Ruzicka and Domalski.[18,19] The methods of Chueh and Swanson,[20,21] Shehatta,[22] and Chickos at al[23,24] can be applied only at one temperature.

Our measurements of C_p data of a series of α,ω-dichloroalkanes enable calculation of the temperature dependence of the C_p contribution of the CH_2 and Cl groups by using a group additivity analysis. The molar heat capacity of a given halogenated hydrocarbon can be presented as

$$C_p = 2C_p(\mathrm{Cl}) = n_{\mathrm{CH_2}}C_p(\mathrm{CH_2}) \tag{3}$$

where $n_{\mathrm{CH_2}}$ is the number of CH_2 groups in the molecule and $C_p(CH_2)$ and $C_p(Cl)$ are the corresponding molar heat capacity contributions.

Table 3. Coefficients of Eq 4 and Their Standard Deviations

	C_p(Cl)	C_p(Br)	C_p(CH$_2$)	
group of compds	a_0	a_0	b_0	b_1
α,ω-dichloroalkanes	36.65 ± 0.04		27.56 ± 0.02	0.051 ± 0.003
α,ω-dibromoalkanes[6]		39.71 ± 0.14	27.90 ± 0.7	0.044 ± 0.002

Table 4. Comparison of the Average Deviations between the Results of Group Contribution Methods[17−24] and Experimental C_p Values of α,ω-Dichloroalkanes

method ref	temp range	avg deviation DClEt	DClPr	DClBu	DClPe	DClHx
this work	284−319	0.2[a]	−0.2	+0.4	−0.2	0.1[a]
	320−353	+0.2	−0.5	+0.4	−0.2	0.1[a]
18, 19	284−319	+0.5	+1.5	+3.0	+3.0	+3.0
	320−353	+1.6	+1.9	+3.5	+3.4	+4.3
17	284−319	−10.2	−8.3	−6.2	−5.7	−4.8
	320−353	−9.5	−8.5	−6.6	−6.3	−5.2
20, 21	293.15	+3.2	+4.4	+5.9	+5.9	+6.5
23, 24	298.15	−2.6	+0.6	+3.4	+4.5	+5.9
22	298.15	−2.4	−1.6	−0.5	−0.7	−0.2

[a] avg dev = $(100/n)\sum|c_p^{calc} - c_p^{exp}|/c_p^{exp}$. In other cases all the deviations were only positive (+) or negative (−) and avg dev = $(100/n)\sum(c_p^{calc} - c_p^{exp})/c_p^{exp}$.

The degree of polynomials that approximate the temperature dependence of the molar heat capacity is seldom higher than three. Consequently, eq 3 can be written for the α,ω-dihalogeno derivatives in the form

$$C_p(T,n_{CH_2}) = 2\sum_{i=0}^{3} a_i(T - 293.15)^i + n_{CH_2}\sum_{i=0}^{3} b_i(T - 293.15)^i \quad (4)$$

where a_i and b_i are constants found by a multiple regression method, using a backward stepwise rejection procedure and the F-test. Seventy values of C_p (determined every 1 K) were taken into consideration for every compound. The nonzero coefficients (a_0, b_0, and b_1) are collected in Table 3 and compared with corresponding values calculated earlier[6] for α,ω-dibromoalkanes. The standard deviation of the fit was 0.5 J·mol^{-1}·K^{-1} with a maximum deviation of 1.0 J·mol^{-1}·K^{-1}.

According to the results of group additivity analysis, the C_p(CH$_2$) depends linearly on temperature: $C_p(CH_2) = b_0 + b_1(T - 293.15)$. The b_0 and b_1 constants for α,ω-dichloro- and α,ω-dibromoalkanes have very close values. In contrast to C_p(CH$_2$), the values of C_p(Cl) and C_p(Br) are independent of temperature within the investigated temperature range.

The measured heat capacities were compared with heat capacities predicted by other group contribution methods. The average deviations of predicted and measured C_p values are shown in Table 4. These comparisons indicate that C_p values estimated by Missenard's method give systematic negative average deviations of (5 to 10)% throughout the whole temperature range from (284 to 353) K. The decrease in negative deviation with an increase in alkyl chain length presumably arises from an underestimation of the C_p(Cl) group. According to Missenard,[17] C_p(Cl) is 29.7 J·mol^{-1}·K^{-1} at 298.15 K and is lower than that calculated in this work (35.9 J·mol^{-1}·K^{-1}) or those calculated by Shehatta[22] (34.59 J·mol^{-1}·K^{-1}) and Chueh-Swanson[20,21] (36.0 J·mol^{-1}·K^{-1} at 293 K). The C_p values predicted from the group contributions presented by Ruzicka and Domalski are from 0.5% (DClEt at (284 to 319) K) to 4.3% (DClHx at (320 to 353) K) higher than experimental measurements. The problem arose from the fact that a sparse number of reliable C_p data for halogenoalkanes was available to Ruzicka and Domalski in 1993. The estimations based on Chueh−Swanson, Shehatta, and Chickos group contributions are limited only to a single (usually 298.15 K) temperature.

The C_p values of α,ω-dichloroalkanes predicted from group contributions calculated in this work are consistent with the experiment within 0.4% (for (284 to 319) K) and 0.5% (for (320 to 353) K). Very low (0.1 to 0.2)% standard deviations corresponding to the longest homologues of α,ω-dichloroalkanes (DClPe and DClHx), in this study, suggest that a prediction of C_p values is possible for homologues with $n_{CH_2} > 6$.

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