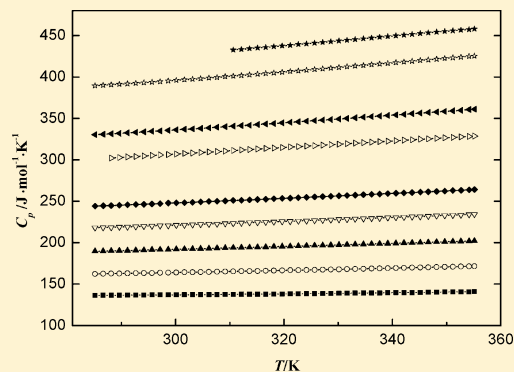


Heat Capacity of α,ω -Bromochloroalkanes and α,ω -Dibromoalkanes: Their Dependence on the Hydrocarbon Chain Length and Temperature (285.15 to 355.15) K

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ABSTRACT: The heat capacities at constant pressure of some α,ω -bromochloroalkanes (from C2 to C6) and α,ω -dibromoalkanes (from C2 to C12, without C7 and C10) were measured within the temperature range of (285.15 to 355.15) K. The measurements were performed by means of a Micro DSC III (Setaram) differential scanning calorimeter. The dependence of molar heat capacity on temperature and hydrocarbon chain length was described by the group additivity method. The densities of α,ω -bromochloroalkanes within the temperature range (288.15 to 318.15) K and their volumetric expansion coefficients at 298.15 K were also determined.



1. INTRODUCTION

The heat capacity (C_p) of chemical compounds is one of the basic quantity used for the thermodynamic description of the state of matter. Numerous application of C_p data and the lack of its values for many common compounds in the literature give rise to the development of methods for theoretical or empirical estimation of C_p values. One of them is a method that uses the group additivity contributions made by the functional groups of the compounds under analysis.^{1–5} A proper determination of group contributions requires an abounding base of C_p data measured within a wide temperature range with as high accuracy as possible. Among others, such data can be obtained by means of differential scanning calorimetry⁶ (DSC). The universality, efficiency, and accuracy of some types of DSC calorimeters have recently caused a considerable extension of the base of reliable experimental C_p data as a function of temperature.⁷

The aim of this study was to determine the C_p values of several liquid α,ω -substituted bromochloroalkanes with a hydrocarbon chain length from C2 to C6 and α,ω -dibromoalkanes (C2–C12, without C7 and C10) within the temperature range of (285.15 to 355.15) K, using the DSC method. In the literature,^{8–11} one can find C_p data of some of the homologue belonging only to the second group of compounds, determined among others in our laboratory.^{8,9} In this study, we wanted to re-examine these data, determining C_p within a wider temperature range (up to 355.15 K) than that used earlier (up to 328.15 K), also increasing the number of C_p data as a function of temperature. Previous measurements were performed at 5 K intervals. The continuous method used in this study provides data at 0.02 K intervals. At the same time, the hydrocarbon chain length of dibromoalkanes investigated now was elongated to 12 carbon atoms in a molecule (previously, only homologues with a length up to 6 carbon atoms were examined). The obtained data allowed one

to verify the correctness of a simple group additivity method previously used to predict the dependence $C_p = f(T, n_i)$ for α,ω -dihalogenoalkanes (n_i , number of carbon atoms in the alkyl chain). The method proposed in this work is a slightly modified version of the simple group additivity method. Thanks to the correction term, it allows a proper description of C_p values as a function of temperature for terminally substituted bromo- and chloroalkanes of an elongated hydrocarbon chain.

2. EXPERIMENTAL SECTION

2.1. Chemicals. The suppliers and the purities of compounds are reported in Table 1.

These compounds were used without further purification. Prior to the measurements, all chemicals were dried with activated molecular sieves (type 4 Å from Lancaster) and degassed in an ultrasonic stream. The samples were stored in a drybox over P_2O_5 .

2.2. Apparatus and Procedure. The saturated specific heat capacities were measured by means of a Tian-Calvet type high sensitivity differential scanning calorimeter Micro DSC III (Setaram). The “continuous with reference” method (n -heptane as a reference) was applied.

The procedure used¹² allows one to obtain a better repeatability than 0.1 %, with the total apparatus measurement error being at a level of 0.15 %. The actual experimental uncertainty of the measured C_p is however higher due to the impurities of the compound under investigation. The main impurities occurring in the liquids investigated being difficult to remove by distillation (e.g., isomers) have specific heat capacities that are

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Table 1. Source and Purity of Compounds

chemical name	abbreviation	source	mass fraction purity
1,2-dibromoethane	1,2-DBrEt	Aldrich	≥0.99
1,3-dibromopropane	1,3-DBrPr	Aldrich	≥0.99
1,4-dibromobutane	1,4-DBrBu	Aldrich	≥0.99
1,5-dibromopentane	1,5-DBrPe	Lancaster	0.98
1,6-dibromohexane	1,6-DBrHx	Merck	≥0.97
1,8-dibromooctane	1,8-DBrOc	Aldrich	0.98
1,9-dibromononane	1,9-DBrNo	Aldrich	0.97
1,11-dibromoundecane	1,11-DBrUn	Aldrich	≥0.98
1,12-dibromododecane	1,12-DBrDo	Aldrich	0.98
1-chloro-2-bromoethane	1,2-ClBrEt	Merck	≥0.98
1-bromo-3-chloropropane	1,3-BrClPr	Lancaster	0.99
1-bromo-4-chlorobutane	1,4-BrClBu	Aldrich	0.99
1-bromo-5-chloropentane	1,5-BrClPe	Lancaster	0.98
1-bromo-6-chlorohexane	1,6-BrClHx	Aldrich	0.97
heptane		Fluka	≥0.995

similar to that of the liquid investigated. Therefore we may estimate that the total error of the C_p values determined does not exceed 0.5 %. The samples (about 0.8 g) were weighed with a Sartorius RC 210D balance with an accuracy of $2 \cdot 10^{-5}$ g and stored in a drybox. The comparison of the C_p values obtained with the data available in the literature^{8–11} for 298.15 K is given in Table 2.

Table 2. Comparison of the Experimental and Literature Data of Heat Capacity ($C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) at $T = 298.15 \text{ K}^a$

compound	$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$		
	this work	our earlier data	literature
1,2-DBrEt	136.9	136.4 ^b	136.87 ^d , 134.7 ± 0.2 ^e
1,3-DBrPr	163.8	163.3 ^b	163.7 ± 0.2 ^e
1,4-DBrBu	191.7	191.5 ^b	191.2 ± 0.2 ^e
1,5-DBrPe	220.7	220.7 ^b , 220.84 ^c	

^aStandard uncertainty u is $u(T) = 0.05 \text{ K}$ and the combined expanded uncertainty U_c is $U_c(C_p) = 0.005 \cdot C_p$ (0.95 level of confidence). ^bReference 8. ^cReference 9. ^dReference 10. ^eReference 11.

As is seen, measured C_p data are within the experimental error consistent with both our previous data and those obtained by other authors.

The measurements of the density of α,ω -bromochloroalkanes were carried out within the temperature range of (288.15 to 318.15) K with the use of a vibrating-tube densimeter (Anton Paar, model DMA 5000) operated in the static mode with an uncertainty of $5 \cdot 10^{-5} \text{ g}\cdot\text{cm}^{-3}$ as estimated from the measurement of standard materials for density determinations.

3. RESULTS AND DISCUSSION

The values of the molar C_p of α,ω -dibromoalkanes and α,ω -bromochloroalkanes determined experimentally are listed in Tables 3 and 4. These data are averages of at least three independent runs which differ from each other by not more than $\pm 0.1 \%$. As the continuous method provides C_p values as a function of temperature at 0.02 K intervals, for clarity only C_p data obtained at 1.5 K intervals (and additionally at 298.15 K) are presented in Tables 3 and 4 and Figures 1 and 2.

The temperature dependence of molar heat capacity of α,ω -dihalogenoalkanes may be presented by means of a polynomial

in the following form:

$$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = A_0 + A_1(T/\text{K} - 293.15) + A_2(T/\text{K} - 293.15)^2 + A_3(T/\text{K} - 293.15)^3 \quad (1)$$

where T is temperature and A , A_1 , A_2 , and A_3 are parameters of eq 1. The advantage of such a presentation of the function $C_p = f(T)$ is that the free term A is the value of C_p of the compound examined at a temperature of 293.15 K. Such a way of presenting the temperature dependence of C_p was also used by us previously to analyze the temperature dependence of group contributions to C_p .^{8,12} The coefficients of eq 1, their standard deviation, and mean deviation from the polynomial (δC_p) are given in Table 5.

The molar C_p under a constant pressure is considered to be one of the values performing the additivity rule. In the simplest case, regardless of the number of groups and their vicinity, the molar quantity is presented as a simple sum of contributions made by particular groups (i):

$$C_p = \sum_i n_i C_{p,i} \quad (2)$$

As follows from our previous studies this rule is best fulfilled when: (a) concerning a compounds belonging to one homologous series and (b) intermolecular interactions have only a weak nonspecific character. For the homologous series comprising compounds whose molecules show specific interactions and form intramolecular hydrogen bonds, e.g., α,ω -diols, α,ω -diamines, it was necessary^{13,14} to introduce a corrective factor for the additive description of the function $C_p = f(T, n_i)$. This factor introduces a correction (b/n_{CH_2}) whose value depends on the alkyl chain length n_{CH_2} . Its use appeared to be necessary to properly describe (i.e., with accuracy better than 1 %) C_p values as a function of temperature for compounds of the diol and amine series. In the case of short-chain α,ω -dihalogenoalkanes ($2 \leq n_{\text{CH}_2} \leq 6$), the introduction of the correction term associated with chain length was not necessary.^{8,12} The estimation of C_p values of longer homologues (up to C12) examined in this paper without the correction b/n_{CH_2} appeared however to be unsatisfactory. For instance, for α,ω -dibromododecane at (330 to 350) K the estimation error is 2.4 %. Thus the proper description of $C_p = f(T, n_i)$ with the use of group contributions in the case of α,ω -dibromoalkanes with a chain length of (C2–C12) also requires the introduction of the corrective factor.

Using the multiparameter linear regression, one can obtain an equation correctly describing the molar heat capacity of α,ω -dibromoalkanes as a function of temperature and number of methylene groups:

$$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = n_{\text{CH}_2} \cdot C_p(\text{CH}_2) + 2 \cdot \left(C_p^*(\text{Br}) + \frac{b_{\text{Br}}}{n_{\text{CH}_2}} \right) \quad (3)$$

where $C_p(\text{CH}_2)$ is the molar heat capacity of the CH_2 group, n_{CH_2} is the hydrocarbon chain length, $C_p^*(\text{Br})$ is the molar heat capacity of the Br group for an infinitely long hydrocarbon chain ($n_{\text{CH}_2} \rightarrow \infty$), and b is an adjustable parameter. The

Table 3. Molar Heat Capacities C_p for Series of α,ω -Dibromoalkanes from $T = (285.15 \text{ to } 355.15) \text{ K}^a$

T/K	$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$								
	1,2-DBrEt	1,3-DBrPr	1,4-DBrBu	1,5-DBrPe	1,6-DBrHx	1,8-DBrOc	1,9-DBrNo	1,11-DBrUn	1,12-DBrDo
285.15	136.3	162.2	189.6	218.0	244.1		330.4	389.4	
286.65	136.4	162.4	189.9	218.3	244.5		330.9	390.0	
288.15	136.4	162.6	190.1	218.6	244.8	302.2	331.4	390.6	
289.65	136.5	162.7	190.3	218.9	245.2	302.8	332.0	391.2	
291.15	136.6	162.9	190.6	219.2	245.6	303.4	332.6	391.8	
292.65	136.6	163.1	190.8	219.5	246.0	304.0	333.1	392.5	
294.15	136.7	163.3	191.0	219.9	246.4	304.6	333.7	393.1	
295.65	136.8	163.4	191.3	220.2	246.8	305.2	334.3	393.8	
297.15	136.8	163.6	191.5	220.5	247.2	305.8	334.9	394.5	
298.15	136.9	163.7	191.7	220.7	247.5	306.2	335.3	394.9	
298.65	136.9	163.8	191.8	220.8	247.6	306.4	335.5	395.2	
300.15	137.0	164.0	192.0	221.2	248.0	307.0	336.1	395.9	
301.65	137.1	164.2	192.3	221.5	248.4	307.6	336.7	396.6	
303.15	137.2	164.3	192.5	221.8	248.8	308.2	337.3	397.3	
304.65	137.2	164.5	192.8	222.2	249.2	308.8	338.0	398.0	
306.15	137.3	164.7	193.0	222.5	249.6	309.4	338.6	398.8	
307.65	137.4	164.9	193.3	222.8	250.1	310.0	339.2	399.5	
309.15	137.5	165.1	193.5	223.2	250.5	310.6	339.9	400.3	
310.65	137.6	165.3	193.8	223.5	250.9	311.2	340.5	401.0	432.6
312.15	137.7	165.5	194.0	223.8	251.3	311.8	341.2	401.8	433.4
313.65	137.8	165.7	194.3	224.2	251.7	312.4	341.8	402.6	434.2
315.15	137.8	165.9	194.6	224.5	252.2	313.0	342.5	403.4	435.0
316.65	137.9	166.0	194.8	224.9	252.6	313.6	343.2	404.2	435.8
318.15	138.0	166.2	195.1	225.2	253.0	314.2	343.8	404.9	436.6
319.65	138.1	166.4	195.4	225.6	253.4	314.8	344.5	405.8	437.5
321.15	138.2	166.6	195.6	225.9	253.9	315.4	345.2	406.6	438.3
322.65	138.3	166.8	195.9	226.3	254.3	315.9	345.9	407.4	439.2
324.15	138.4	167.0	196.2	226.6	254.7	316.5	346.5	408.2	440.0
325.65	138.5	167.2	196.4	227.0	255.2	317.1	347.2	409.0	440.9
327.15	138.6	167.4	196.7	227.3	255.6	317.7	347.9	409.8	441.8
328.65	138.7	167.7	197.0	227.7	256.0	318.3	348.6	410.7	442.7
330.15	138.9	167.9	197.3	228.1	256.5	318.9	349.3	411.5	443.6
331.65	139.0	168.1	197.6	228.4	256.9	319.5	350.0	412.3	444.5
333.15	139.1	168.3	197.8	228.8	257.4	320.1	350.7	413.2	445.4
334.65	139.2	168.5	198.1	229.1	257.8	320.6	351.4	414.0	446.3
336.15	139.3	168.7	198.4	229.5	258.3	321.2	352.1	414.8	447.2
337.65	139.4	168.9	198.7	229.9	258.7	321.8	352.8	415.7	448.0
339.15	139.5	169.1	199.0	230.2	259.2	322.4	353.5	416.5	448.9
340.65	139.7	169.4	199.3	230.6	259.6	323.0	354.2	417.4	449.8
342.15	139.8	169.6	199.6	231.0	260.1	323.6	354.9	418.2	450.7
343.65	139.9	169.8	199.8	231.4	260.5	324.1	355.6	419.0	451.6
345.15	140.0	170.0	200.1	231.7	261.0	324.7	356.3	419.9	452.4
346.65	140.2	170.2	200.4	232.1	261.5	325.3	357.0	420.7	453.3
348.15	140.3	170.5	200.7	232.5	261.9	325.9	357.7	421.6	454.1
349.65	140.4	170.7	201.0	232.9	262.4	326.5	358.4	422.4	455.0
351.15	140.6	170.9	201.3	233.3	262.9	327.0	359.1	423.2	455.8
352.65	140.7	171.1	201.6	233.6	263.3	327.6	359.8	424.0	456.6
354.15	140.8	171.4	201.9	234.0	263.8	328.2	360.5	424.9	457.4
355.15	140.9	171.5	202.1	234.3	264.1	328.6	361.0	425.4	457.9

^aStandard uncertainty u is $u(T) = 0.05 \text{ K}$ and the combined expanded uncertainty Uc is $Uc(C_p) = 0.005 \cdot C_p$ (0.95 level of confidence).

corrective factor b/n_{CH_2} has the same form as that previously introduced for diols and diamines. Considering the lack of strong specific interactions, the necessity of its introduction results from the so-called "proximity effect" determined and defined for the first time by Kehiajan.¹⁵ This effect is connected with the change in the properties (e.g., heat capacity) of the given group induced by mutual approach of functional groups as the alkyl chain is shortened.

The temperature dependence of C_p of particular groups is presented in the following form:

$$C_{p,i}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = \sum_j A_j(T/\text{K} - 293.15)^j \quad (4)$$

The values of coefficients A_j of eq 4 for parameters $C_p(\text{CH}_2)$, $C_p^*(\text{Br})$, and b_{Br} of α,ω -dibromoalkanes are listed in Table 6.

Table 4. Molar Heat Capacities C_p for Series of α,ω -Bromochloroalkanes from $T = (285.15 \text{ to } 355.15) \text{ K}^a$

T/K	$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$				
	1,2-BrClEt	1,3-BrClPr	1,4-BrClBu	1,5-BrClPe	1,6-BrClHx
285.15	136.3	162.2	189.6	218.0	244.1
286.65	136.4	162.4	189.9	218.3	244.5
288.15	136.4	162.6	190.1	218.6	244.8
289.65	136.5	162.7	190.3	218.9	245.2
291.15	136.6	162.9	190.6	219.2	245.6
292.65	136.6	163.1	190.8	219.5	246.0
294.15	136.7	163.3	191.0	219.9	246.4
295.65	136.8	163.4	191.3	220.2	246.8
297.15	136.8	163.6	191.5	220.5	247.2
298.15	136.9	163.7	191.7	220.7	247.5
298.65	136.9	163.8	191.8	220.8	247.6
300.15	137.0	164.0	192.0	221.2	248.0
301.65	137.1	164.2	192.3	221.5	248.4
303.15	137.2	164.3	192.5	221.8	248.8
304.65	137.2	164.5	192.8	222.2	249.2
306.15	137.3	164.7	193.0	222.5	249.6
307.65	137.4	164.9	193.3	222.8	250.1
309.15	137.5	165.1	193.5	223.2	250.5
310.65	137.6	165.3	193.8	223.5	250.9
312.15	137.7	165.5	194.0	223.8	251.3
313.65	137.8	165.7	194.3	224.2	251.7
315.15	137.8	165.9	194.6	224.5	252.2
316.65	137.9	166.0	194.8	224.9	252.6
318.15	138.0	166.2	195.1	225.2	253.0
319.65	138.1	166.4	195.4	225.6	253.4
321.15	138.2	166.6	195.6	225.9	253.9
322.65	138.3	166.8	195.9	226.3	254.3
324.15	138.4	167.0	196.2	226.6	254.7
325.65	138.5	167.2	196.4	227.0	255.2
327.15	138.6	167.4	196.7	227.3	255.6
328.65	138.7	167.7	197.0	227.7	256.0
330.15	138.9	167.9	197.3	228.1	256.5
331.65	139.0	168.1	197.6	228.4	256.9
333.15	139.1	168.3	197.8	228.8	257.4
334.65	139.2	168.5	198.1	229.1	257.8
336.15	139.3	168.7	198.4	229.5	258.3
337.65	139.4	168.9	198.7	229.9	258.7
339.15	139.5	169.1	199.0	230.2	259.2
340.65	139.7	169.4	199.3	230.6	259.6
342.15	139.8	169.6	199.6	231.0	260.1
343.65	139.9	169.8	199.8	231.4	260.5
345.15	140.0	170.0	200.1	231.7	261.0
346.65	140.2	170.2	200.4	232.1	261.5
348.15	140.3	170.5	200.7	232.5	261.9
349.65	140.4	170.7	201.0	232.9	262.4
351.15	140.6	170.9	201.3	233.3	262.9
352.65	140.7	171.1	201.6	233.6	263.3
354.15	140.8	171.4	201.9	234.0	263.8
355.15	140.9	171.5	202.1	234.3	264.1

^aStandard uncertainty u is $u(T) = 0.05 \text{ K}$ and the combined expanded uncertainty Uc is $Uc(C_p) = 0.005 \cdot C_p$ (0.95 level of confidence).

Estimated on the basis of these coefficients, C_p values are consistent with experiment with an average deviation (avg dev = $100/n \cdot |C_p^{\text{calc}} - C_p^{\text{exp}}|/C_p^{\text{exp}}$) of 0.25 %. A similar value of estimation (0.23 %) was obtained previously¹² for short-chain (C2–C6) α,ω -dichloroalkanes.

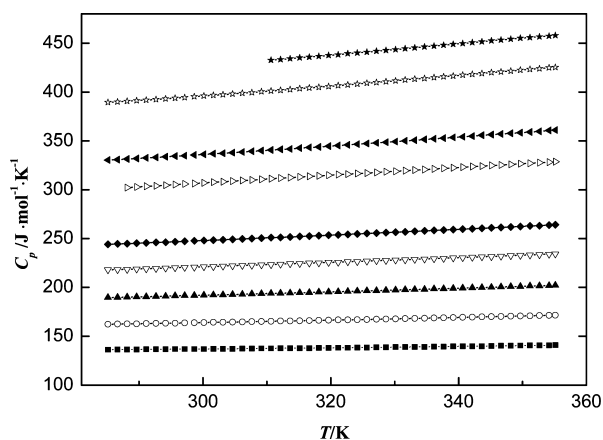


Figure 1. Molar heat capacities ($C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) of α,ω -dibromoalkanes as a function of temperature: ■, 1,2-DBrEt; ○, 1,3-DBrPr; ▲, 1,4-DBrBu; ▽, 1,5-DBrPe; ◆, 1,6-DBrHx; ▷, 1,8-DBrOc; ◀, 1,9-DBrNo; ☆, 1,11-DBrUn; ★, 1,12-DBrDo.

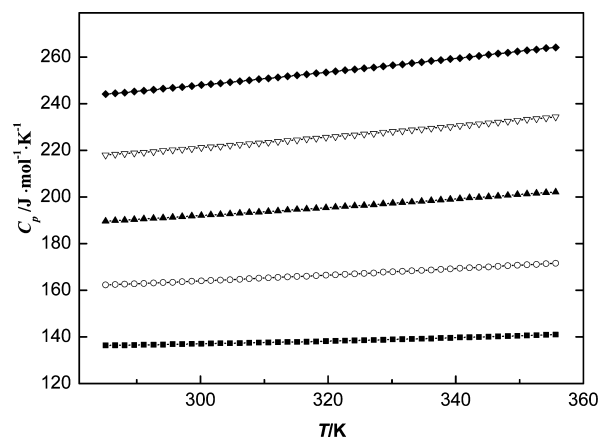


Figure 2. Molar heat capacities ($C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) of α,ω -bromochloroalkanes as a function of temperature: ■, 1,2-ClBrEt; ○, 1,3-BrClPr; ▲, 1,4-BrClBu; ▽, 1,5-BrClPe; ◆, 1,6-BrClHx.

The homologous series containing bromo- and chloroalkanes substituted in terminal positions examined so far by us comprise: 1-chloroalkanes¹⁶ (C3–C10, without C9), 1-bromoalkanes¹⁶ (C2–C10, without C8), α,ω -dichloroalkanes¹² (C2–C6), α,ω -dibromoalkanes (C2–C12, without C7 and C10), and α,ω -bromochloroalkanes (C2–C6). The C_p values of these compounds within the temperature range of (285.15 to 353.15) K can constitute a database for the calculation of group contributions according to the equation:

$$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = n_{\text{CH}_3}C_p(\text{CH}_3) + n_{\text{CH}_2}C_p(\text{CH}_2) + n_{\text{Br}}\left(C_p^*(\text{Br}) + \frac{b_{\text{Br}}}{n_{\text{CH}_2}}\right) + n_{\text{Cl}}\left(C_p^*(\text{Cl}) + \frac{b_{\text{Cl}}}{n_{\text{CH}_2}}\right) \quad (5)$$

where n_{CH_3} , n_{CH_2} , n_{Br} , n_{Cl} are the numbers of relevant groups in the compound, respectively; $C_p(\text{CH}_3)$, $C_p(\text{CH}_2)$, heat capacities of methyl and methylene groups, respectively; $C_p^*(\text{Br})$, $C_p^*(\text{Cl})$, heat capacities of Br and Cl groups, respectively, for an infinitely long hydrocarbon chain ($n_{\text{CH}_2} \rightarrow \infty$), and b is an adjustable

Table 5. Coefficients of the Polynomial (Equation 1) and Mean Deviation from the Regression Line

compound	temperature range/K	coefficients of eq 1			
		$A_0/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$A_1\cdot 10^2/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}$	$A_2\cdot 10^4/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-3}$	$A_3\cdot 10^5/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-4}$
α,ω -Dibromoalkanes					
1,2-DBrEt	285.15–355.15	136.65 ± 0.02	4.592 ± 0.02	3.663 ± 0.03	
1,3-DBrPr	285.15–355.15	163.15 ± 0.03	11.59 ± 0.04	3.072 ± 0.03	
1,4-DBrBu	285.15–355.15	190.87 ± 0.05	15.98 ± 0.05	3.531 ± 0.03	
1,5-DBrPe	285.15–355.15	219.64 ± 0.03	21.39 ± 0.04	3.571 ± 0.04	
1,6-DBrHx	285.15–355.15	246.14 ± 0.02	26.34 ± 0.03	4.290 ± 0.03	
1,8-DBrOc	291.15–355.15	304.23 ± 0.04	40.07 ± 0.04	-1.296 ± 0.06	
1,9-DBrNo	285.15–355.15	333.33 ± 0.02	38.52 ± 0.04	16.64 ± 0.18	-1.12 ± 0.02
1,11-DBrUn	285.15–355.15	392.69 ± 0.02	43.41 ± 0.08	27.41 ± 0.04	-1.99 ± 0.04
1,12-DBrDo	309.15–355.15	425.26 ± 0.09	31.68 ± 0.21	69.41 ± 0.42	-5.74 ± 0.87
α,ω -Bromochloroalkanes					
1,2-BrClEt	285.15–355.15	131.44 ± 0.01	7.036 ± 0.022	3.406 ± 0.036	
1,3-BrClPr	285.15–355.15	159.98 ± 0.01	12.29 ± 0.014	3.803 ± 0.023	
1,4-BrClBu	285.15–355.15	187.22 ± 0.01	16.29 ± 0.013	4.915 ± 0.022	
1,5-BrClPe	285.15–355.15	216.31 ± 0.01	21.89 ± 0.012	4.196 ± 0.020	
1,6-BrClHx	285.15–355.15	242.98 ± 0.01	27.13 ± 0.014	4.345 ± 0.024	

Table 6. Coefficients of Equations 4 and 5 and Their Standard Deviations

database of C_p values	estimation avg dev % ^b	$C_p(\text{CH}_3)$		$C_p(\text{CH}_2)$		$C_p(\text{Br})$		$C_p(\text{Cl})$	b
		$A_0/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$A_1/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}$	$A_0/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$A_1/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}$	$A_0/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$A_1/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}$	$A_0/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
α,ω -dibromoalkanes (C2–C12)	0.27	36.38 ± 0.06	0.083 ± 0.002	29.21 ± 0.01	0.048 ± 0.0002	34.71 ± 0.06		31.29 ± 0.06	7.74 ± 0.13
+ α,ω -dichloroalkanes (C2–C6)	0.38								
+ α,ω -bromochloroalkanes (C2–C6)	0.47								
+monochloroalkanes (C3–C10)	0.18								
+monobromoalkanes (C2–C10)	0.24								
α,ω -dibromoalkanes (C2–C12) only	0.25			29.20 ± 0.02	0.051 ± 0.001	34.48 ± 0.12	-0.0128 ± 0.001		9.24 ± 0.23
α,ω -dichloroalkanes (C2–C6) only ^a	0.23			27.56 ± 0.02	0.051 ± 0.003			36.65 ± 0.04	

^aReference 12. ^bavg dev/% = $100/n\cdot\sum|C_p^{\text{calc}} - C_p^{\text{exp}}|/C_p^{\text{exp}}$.

parameter. The temperature dependence of $C_{p,i}$ of particular groups was described by eq 4, and parameters A_j of this equation are given in Table 6, which contains also the average deviation of calculated C_p values from the experimental data for each of the homologous series.

The C_p dependence of the methyl or methylene group on temperature is linear, while the C_p of the chloro substituent can be treated as independent of temperature. Parameters b_{Br} and b_{Cl} appeared to be the same for both halogen substitutes. Despite a simple description of the temperature dependence of C_p of particular groups, the average estimation error for a particular homologous series is low, always below 0.5 %. For dihalogen-substituted alkanes, the estimation is not much worse (0.27 %, dibromoalkanes and 0.38 %, dichloroalkanes) than that obtained on the basis of the group contributions calculated separately for each series (0.23 % and 0.25 %, respectively, Table 6).

The least satisfactory results of estimation were obtained for 1-bromoethane (avg dev = 1.29 %) and 1,3-dichloropropane (avg dev = 0.84 %), which did not considerably affect the average estimation error of the whole series of 1-bromoalkanes

(0.24 %) and α,ω -dichloroalkanes (0.38 %). In the case of compounds of long chains, the estimated C_p values are very similar to experimental data (the estimation error is below 0.3 %). Thus the equation proposed by us makes it possible to precisely predict C_p values of the homologues with longer chains than examined (extrapolation) or compounds omitted in heretofore studies (interpolation).

In the literature, one can find only few data concerning the density of α,ω -bromochloroalkanes and they are limited to a temperature of 298.15 K. This has prompted us to perform additional measurements of the density of compounds belonging to this series (from C2 to C6). Measurements were carried out within the temperature range of (288.15 to 318.15) K at 10 K intervals. The values obtained by us, their comparison with available literature data at 298.15 K, and the calculated coefficients of volumetric expansion $\alpha = -1/d (d/dT)_p$ at this temperature are presented in Table 7. Values of thermal expansion coefficients of α,ω -bromochloroalkanes decrease with the increase of hydrocarbon chain length. This behavior seems to be typical for different homologue series of

Table 7. Densities of α,ω -Bromochloroalkanes from $T = (288.15 \text{ to } 318.15) \text{ K}$ and Its Thermal Expansion Coefficients at 298.15 K^a

compound	288.15 K	298.15 K		308.15 K	318.15 K
	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\alpha\cdot 10^4/\text{K}^{-1}$	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\rho/\text{kg}\cdot\text{m}^{-3}$
1,2-BrClEt	1742.45	1726.56 1726.33 ^b	9.51	1710.57	1693.61
1,3-BrClPr	1601.96	1588.17 1588.37 ^b	8.72	1574.87	1560.65
1,4-BrClBu	1496.19	1485.12 1485.77 ^b	7.98	1473.33	1460.96
1,5-BrClPe	1409.70	1399.37	7.62	1388.77	1377.96
1,6-BrClHx	1345.17	1336.47	7.20	1327.17	1316.45

^aStandard uncertainty u is $u(T) = 0.02 \text{ K}$ and the combined expanded uncertainties U_c are $U_c(\rho) = 0.5 \text{ kg}\cdot\text{m}^{-3}$, $U_c(\alpha) = 0.5 \text{ K}^{-1}$ (0.95 level of confidence). ^bReference 17.

substituted alkanes,¹⁸ e.g., primary n -amines, tertiary n -amines, or chloroalkanes. As well, it is observed for isothermal compressibilities coefficients (κ_T).

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