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Heat Capacities of 1-Chloroalkanes and 1-Bromoalkanes within the Temperature Range from 284.15 K to 353.15 K. A Group Additivity and Molecular Connectivity Analysis

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The heat capacities at constant pressure of 1-chloropropane, 1-chlorobutane, 1-chloropentane, 1-chlorohexane, 1-chloroheptane, 1-chlorooctane, 1-chlorodecane, and 1-bromoalkanes (1-bromoethane, 1-bromopropane, 1-bromobutane, 1-bromopentane, 1-bromohexane, 1-bromoheptane, 1-bromononane, and 1-bromodecane) were measured within the temperature range from 284 K to 353 K by a DSC III (Setaram) differential scanning calorimeter. These data and data previously reported for α,*ω*-dibromoalkanes and α,*ω*-dichloroalkanes, have been used as input for a group additivity type analysis. The C_p group contributions as a function of temperature of the CH_3 and CH_2 groups and Cl and Br atoms were determined by the group additivity analysis (GAA) method. A molecular connectivity model (MCI) for the calculation of the molar heat capacities of halogenoalkanes is also presented. The given model is based on a set of six molecular connectivity indexes, MCI = $\{D, D^v, {}^0X, {}^0X^v, {}^1X, {}^1X^v\}$. The merits of the additivity scheme are discussed.

Introduction

Knowledge of the thermophysical properties of liquid halogenoalkanes is of high interest on account of their wide usage in science and in industrial processes. One property that is often needed for thermodynamic calculations is the heat capacity of substances in the condensed phase. The heat capacity, C_p, is a key thermophysical quantity. It is crucial for designing chemical processes as well as for the progress of thermodynamic theories. Knowledge of the heat capacities of liquids as a function of temperature renders some insight into their molecular structure and provides information on intermolecular interactions. Thermochemical and thermodynamics calculations depend heavily on the temperature dependencies of the constant pressure heat capacities of liquid phases. Furthermore, enthalpy, entropy, and Gibbs energy changes can be calculated at various temperatures from measurement results obtained at more convenient reference temperatures. Also, the correct group contribution analysis requires precisely determined values of C_p of a series of homologous compounds. Unfortunately, reliable heat capacities of halogen derivatives are rather scarce in the literature. If a measured heat capacity for the compound of interest is not readily available, some estimation technique is frequently used.

This prompted us to continue our earlier study[1,2] on C_p measurements for halogenoalkanes. The purpose of this work is to develop a group contribution method to estimation and predict heat capacities as a function of temperature. The heat capacities of a few 1-chloroalkanes from 1-chloropropane (1-ClPr) to 1-chlorooctane (1-ClOc) and 1-chlorodecane (1-ClDec) and a few 1-bromoalkanes from 1-bromoethane (1-BrEt) to 1-bromoheptane (1-BrHp), 1-bromononane (1-BrNon), and 1-bromodecane (1-BrDec) were determined using a differential scanning calorimeter within the temperature range from 284 K to 353 K.

Experimental Section

Chemicals. The 1-chloropropane (≥98%), 1-chlorobutane (≥99.5%), 1-chloropentane (≥99%), 1-chlorohexane (≥99%), 1-chloroheptane (≥99%), 1-chlorooctane (≥99%), and 1-chlorodecane (≥98%) were purchased from Aldrich, 1-bromoethane (≥99%) was from Fluka, 1-bromopropane (≥99%), 1-bromobutane (≥99%), 1-bromopentane (≥99%), 1-bromohexane (≥98%), and 1-bromoheptane (≥99%) were from Aldrich, and 1-bromononane (≥99%) and 1-bromodecane (≥98%) were from Lancaster. The chemicals were purified before use by fractional distillation, and the middle fraction (∼5%) was collected in every case. The purities of the liquid samples of halogenoalkanes checked by gas−liquid chromatography (GLC) were >99% by mass. Prior to the measurements, all the liquids were dried with molecular sieves (type 3 A, 1−2 mm beads from Lancaster) and degassed in an ultrasonic stream. 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. The differential scanning calorimetry (DSC), applied in this study, is one of the modern analytical techniques often used, since quantitative information can be obtained over a wide range of temperatures from small (1 mL) samples. The heat capacities at constant pressure were measured by means of a Micro DSC III (Setaram) high sensitivity differential scanning calorimeter based on the Tian−Calvet principle. The "continuous with reference" method (heptane as a reference) was applied. Details of the applied procedure and the calorimeter calibration have been described previously.[2] The uncertainty of the absolute temperature value in the measuring cell is estimated to be ±0.05 K.[2] The uncertainty of the C_p values obtained in this work did not exceed ±0.15%.[2]

Results and Their Analysis

The measurements of the heat capacity of the studied halogen derivatives of the hydrocarbons were generally

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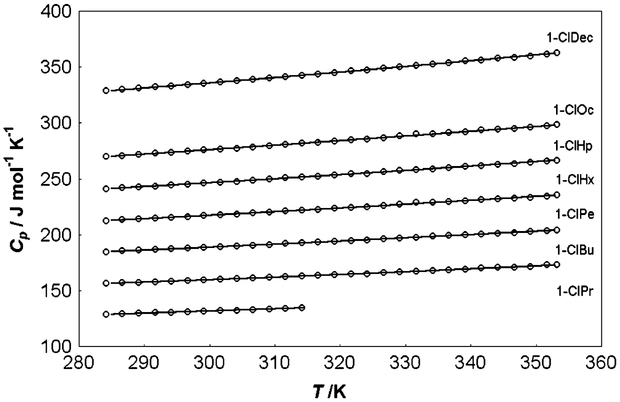

Figure 1. Molar heat capacities of the 1-chloroalkanes as a function of temperature: points, experimental data from Table 1; lines, values calculated from eq 1.

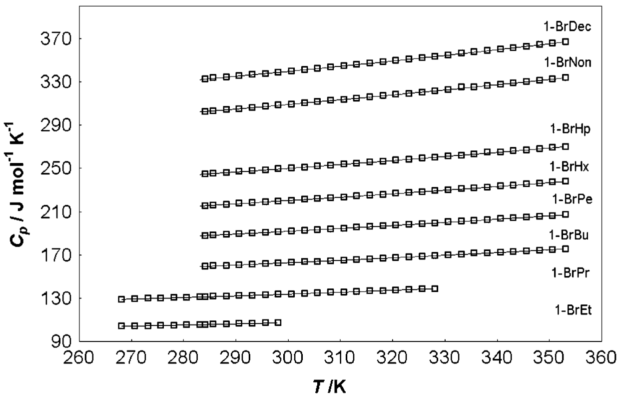

Figure 2. Molar heat capacities of the 1-bromoalkanes as a function of temperature: points, experimental data from Table 2; lines, values calculated from eq 1.

carried out within the temperature range from 284 K to 353 K. Except for the 1-chloropropane, 1-bromoethane, and 1-bromopropane for which the heat capacities were measured within 284 K to 314 K, 269 K to 299 K, and 269 K to 326 K, respectively. The scanning rate was 0.2 K min^{-1}. Thus, with varying temperature, a measuring point is recorded each 0.02 K which results in 3500 data points over the temperature range studied. For clarity, only the values obtained every 2.5 K are presented in Tables 1 and 2. Figures 1 and 2 show that the molar heat capacities of the 1-chloroalkanes and α,ω-dichloroalkanes increase with increasing temperature and length of the hydrocarbon chain.

In Table 3, the molar heat capacity values from our measurements are compared with literature data. Most of the data are in satisfactory agreement. The differences between the literature values of the heat capacity and the experimentally determined ones do not exceed 1.3%. Small differences in heat capacities may result from differences in the purity of the chemicals, measurement techniques, and calibration.

Experimental molar heat capacities, C_p, as a function of temperature were fitted to the following equation:

$$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = \sum_{i=0}^{2} A_i(T/\text{K} - 293.15)^i \qquad (1)$$

where A_i are constants determined by the least-squares method and are collected in Table 4.

Table 1. Molar Heat Capacities, C_p/J·mol^{-1}·K^{-1}, for Some 1-Chloroalkanes in the Temperature Range from 284 K to 353 K

	C_p/J·mol^{-1}·K^{-1}						
T/K	1-ClPr	1-ClBu	1-ClPe	1-ClHx	1-ClHp	1-ClOc	1-ClDec
284.15	128.63	156.22	184.57	212.36	240.95	269.76	328.57
286.65	128.99	156.75	185.29	213.23	241.75	270.79	329.82
289.15	129.53	157.28	185.95	213.91	242.67	271.83	331.00
291.65	130.10	157.70	186.52	214.63	243.40	272.66	332.01
294.15	130.47	158.27	187.16	215.40	244.29	273.66	333.14
296.65	130.95	158.86	187.66	216.12	245.23	274.53	334.13
299.15	131.33	159.48	188.46	216.95	246.05	275.61	335.39
301.65	131.88	160.05	189.19	217.75	247.03	276.52	336.61
304.15	132.37	160.50	189.81	218.44	247.61	277.29	337.47
306.65	132.94	161.06	190.32	219.22	248.53	278.37	338.66
309.15	133.40	161.59	190.99	219.99	249.54	279.28	339.83
311.65	133.92	162.24	191.89	221.00	250.65	280.50	341.39
314.15	134.38	162.92	192.65	221.78	251.60	281.58	342.42
316.65		163.42	193.22	222.49	252.20	282.47	343.41
319.15		164.11	194.09	223.43	253.36	283.79	345.04
321.65		164.82	194.69	224.31	254.42	284.92	346.36
324.15		165.00	195.06	224.70	254.76	285.45	346.99
326.65		165.97	196.14	226.02	256.19	286.81	348.75
329.15		166.72	196.99	227.13	257.57	288.43	350.01
331.65		167.29	197.64	228.86	258.06	289.95	351.31
334.15		167.78	198.46	228.99	258.84	290.13	352.76
336.65		168.53	199.23	229.44	259.88	291.34	353.39
339.15		169.12	199.92	230.06	261.01	291.91	355.52
341.65		170.01	200.41	231.22	261.55	293.56	356.17
344.15		170.43	201.19	231.83	262.90	294.16	357.74
346.65		170.49	201.73	232.32	263.26	294.82	358.38
349.15		171.50	202.54	233.18	264.30	295.79	359.65
351.65		173.02	203.57	234.56	266.04	297.21	361.49
353.15		173.09	204.24	235.17	266.51	298.14	362.49

Table 2. Molar Heat Capacities, C_p/J·mol^{-1}·K^{-1}, for Some 1-Bromoalkanes at Different Temperatures

	C_p/J·mol^{-1}·K^{-1}							
T/K	1-BrEt	1-BrPr	1-BrBu	1-BrPe	1-BrHx	1-BrHp	1-BrNon	1-BrDec
269.15	104.07	129.02						
271.65	104.37	129.44						
274.15	104.60	129.78						
276.65	104.85	130.10						
279.15	105.14	130.48						
281.65	105.42	130.86						
284.15	105.63	131.20	159.45	187.88	215.54	244.73	302.55	332.6
286.65	105.91	131.64	159.98	188.46	216.29	245.56	303.54	333.65
289.15	106.14	132.01	160.53	189.17	217.08	246.44	304.62	335.00
291.65	106.42	132.46	161.01	189.85	217.78	247.28	305.57	336.08
294.15	106.75	132.78	161.52	190.33	218.54	248.12	306.69	336.90
296.65	107.09	133.20	162.08	190.94	219.26	248.93	307.68	338.20
299.15	107.42	133.64	162.60	191.57	219.99	249.70	308.80	339.29
301.65		134.00	163.08	192.17	220.68	250.38	309.82	340.37
304.15		134.55	163.72	193.01	221.38	251.56	310.95	341.48
306.65		134.93	164.22	193.53	222.22	252.33	311.91	342.74
309.15		135.35	164.78	194.17	222.98	253.19	313.01	343.89
311.65		135.80	165.34	194.86	223.79	254.14	314.10	345.13
314.15		136.23	165.94	195.60	224.63	255.00	315.18	346.34
316.65		136.68	166.49	196.21	225.37	255.97	316.32	347.51
319.15		137.16	167.09	196.98	226.20	256.84	317.44	348.84
321.65		137.60	167.67	197.61	227.01	257.85	318.70	350.10
324.15		138.11	168.29	198.35	227.86	258.76	319.80	351.41
326.65		138.55	168.83	199.09	228.67	259.71	320.96	352.71
329.15			169.45	199.80	229.55	260.68	322.16	354.02
331.65			170.09	200.47	230.39	261.61	323.32	355.32
334.15			170.63	201.48	231.21	262.50	324.63	356.14
336.65			171.00	201.57	231.59	262.97	325.00	357.34
339.15			171.94	202.76	233.25	264.64	326.99	359.30
341.65			172.57	203.58	233.77	265.49	328.13	360.70
344.15			173.26	204.33	234.73	266.52	329.39	362.13
346.65			173.89	205.07	235.64	267.46	330.49	363.37
349.15			174.51	205.89	236.55	268.47	331.79	364.86
351.65			175.19	206.69	237.39	269.51	333.04	366.38
353.15			175.47	207.05	237.85	270.03	333.74	367.07

Some techniques of estimation of the liquid heat capacity are presented in the literature. They can be classified[7] into two groups, the QPPR (quantity property−property relationship) and QSPR (quantity structure−property relationship) methods. The first group of methods (QPPR) uses the correlation between the different physicochemical properties as the base of their estimation. The second one (QSPR) correlates the physicochemical properties of liquids with its molecular structure. QSPR methods are based on statistical correlations between molecular structure and measurable properties. In this case, the structures of

Table 3. Heat Capacities, C_p, of 1-Chloroalkanes and 1-Bromoalkanes at 298.15 K

	C_p/J·mol^{-1}·K^{-1}	
compound	this work	lit.
1-ClPr	131.30	132.2[3]
1-ClBu	159.24	159.64,[4] 158.9[5]
1-ClPe	188.12	187.7[5]
1-ClHx	216.73	216.2[5]
1-ClHp	245.71	245.4[5]
1-ClOc	275.03	274.7[5]
1-ClDec	334.75	335.27[6]
1-BrEt	107.28	105.8[5]
1-BrPr	133.46	134.6[5]
1-BrBu	162.37	162.2[5]
1-BrPe	191.33	191.0[5]
1-BrHx	219.64	219.7[5]
1-BrHp	249.34	247.9[5]
1-BrNon	308.39	
1-BrDec	338.73	

Table 4. Coefficients of eq 2 and Their Standard Deviations for the Heat Capacities, C_p, of 1-Chloroalkanes and 1-Bromoalkanes within the Temperature Range from 284 K to 353 K (for 1-Chloropropane, 1-Bromoethane, and 1-Bromopropane, 284 K to 314 K, 268 K to 298 K, and 268 K to 328 K, Respectively) and Mean Deviations from the Regression Line, δC_p

	A_0	$A_1 \times 10^2$	$A_2 \times 10^3$	δC_p
compound	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-2}	J·mol^{-1}·K^{-3}	J·mol^{-1}·K^{-1}
1-ClPr	130.29 ± 0.00	18.86 ± 0.02	0.446 ± 0.015	0.05
1-ClBu	158.12 ± 0.01	21.58 ± 0.04	0.475 ± 0.008	0.18
1-ClPe	186.90 ± 0.01	26.23 ± 0.04	0.353 ± 0.008	0.17
1-ClHx	215.12 ± 0.01	30.92 ± 0.06	0.404 ± 0.010	0.22
1-ClHp	244.01 ± 0.01	34.47 ± 0.06	0.455 ± 0.010	0.22
1-ClOc	273.24 ± 0.01	38.96 ± 0.07	0.402 ± 0.012	0.26
1-ClDec	332.63 ± 0.01	45.65 ± 0.07	0.675 ± 0.013	0.27
1-BrEt	106.65 ± 0.00	11.66 ± 0.03	0.450 ± 0.013	0.04
1-BrPr	132.65 ± 0.00	16.16 ± 0.00	0.433 ± 0.002	0.03
1-BrBu	161.31 ± 0.00	21.04 ± 0.02	0.449 ± 0.003	0.07
1-BrPe	190.09 ± 0.00	24.97 ± 0.03	0.561 ± 0.004	0.10
1-BrHx	218.16 ± 0.00	29.49 ± 0.03	0.567 ± 0.005	0.12
1-BrHp	247.71 ± 0.00	33.70 ± 0.04	0.598 ± 0.006	0.15
1-BrNon	306.21 ± 0.01	41.55 ± 0.04	0.742 ± 0.007	0.16
1-BrDec	336.56 ± 0.01	44.82 ± 0.05	0.991 ± 0.008	0.20

organic compounds allow the estimation of the properties. Most QSPR methods make use of the group additivity concept.

The first QSPR method applied in this work, *the group additivity analysis* (GAA) method, assumes that various groups of the molecule contribute definite values to the total molar heat capacity. In the case of halogenoderivatives, the temperature dependence of group contributions to C_p was taken into consideration only by Misserand[8] and Ruzicka and Domalski.[9,10] The data of Chueh and Swanson,[11,12] Shehatta,[5] and Chickos et al.[13,14] can be applied only at one temperature, usually 298.15 K. In the present study, the group additivity analysis method has been applied to the 1-chloroalkanes, 1-bromoalkanes, α,ω-dichloroalkanes, and α,ω-dibromoalkanes under study. The heat capacities of the α,ω-dibromoalkanes and α,ω-dichloroalkanes were taken from our earlier study.[1,2] In the present analysis, our attention is restricted only to four structural groups: CH_3, CH_2, Cl, and Br. Thus, the molar heat capacity of a given halogenated hydrocarbon can be described by the following equation:

$$C_p = n_{CH_3}C_p(CH_3) + n_{CH_2}C_p(CH_2) + n_{Cl}C_p(Cl) + n_{Br}C_p(Br) \quad (2)$$

where n_{CH_3} and n_{CH_2} are the number of CH_3 and CH_2 groups in the molecule, n_{Cl} and n_{Br} are the number of Cl and Br atoms in the molecule, and $C_p(CH_3)$, $C_p(CH_2)$, $C_p(Cl)$, and $C_p(Br)$ are the corresponding molar heat capacity contributions of the CH_3 and CH_2 groups and of the Cl and Br atoms.

Table 5. Coefficients of eqs 3 and 9 and Their Standard Deviations

GAA method, eq 3		MCI method, eq 9	
a_0/J·mol^{-1}·K^{-1}	37.86 ± 0.10	B_0/J·mol^{-1}·K^{-1}	−43.294 ± 0.743
a_1/J·mol^{-1}·K^{-2}	0.077 ± 0.004	B_1/J·mol^{-1}·K^{-1}	40.519 ± 0.602
b_0/J·mol^{-1}·K^{-1}	28.67 ± 0.02	B_2/J·mol^{-1}·K^{-1}	28.131 ± 0.255
b_1/J·mol^{-1}·K^{-2}	0.044 ± 0.001	B_3/J·mol^{-1}·K^{-2}	0.088 40 ± 0.000 53
b_2/J·mol^{-1}·K^{-3}	0.000 10 ± 0.000 02	B_4/J·mol^{-1}·K^{-1}	2.938 ± 0.818
c_0/J·mol^{-1}·K^{-1}	34.58 ± 0.04		
d_0/J·mol^{-1}·K^{-1}	38.42 ± 0.06		
d_1/J·mol^{-1}·K^{-2}	−0.011 ± 0.003		

The degree of polynomials approximating properly the temperature dependence of the heat capacity is seldom higher than 3. Consequently, eq 2 may be written in the following form:

$$C_p/\mathrm{J\cdot mol^{-1}\cdot K^{-1}} = n_{CH_3}\sum_{i=0}^{2} a_i(T/\mathrm{K} - 293.15)^i + n_{CH_2}\sum_{i=0}^{2} b_i (T/\mathrm{K} - 293.15)^i + n_{Cl}\sum_{i=0}^{2} c_i(T/\mathrm{K} - 293.15)^i + n_{Br}\sum_{i=0}^{2} d_i (T/\mathrm{K} - 293.15)^i \quad (3)$$

where a_i, b_i, c_i, and d_i are constants found by a multiple regression method using a backward stepwise rejection procedure and the F-test. This led to eight nonzero coefficients, a_0, a_1, b_0, b_1, b_2, c_0, d_0, and d_1, which are given in Table 5. The standard deviation of the fit was 1.6 J·mol^{-1}·K^{-1} with a maximum deviation of 2.9 J·mol^{-1}·K^{-1}.

According to the results of the GAA method, $C_p(CH_3)$ and $C_p(Br)$ depend linearly on temperature: $C_p(CH_3)/\mathrm{J\cdot mol^{-1}\cdot K^{-1}} = a_0 + a_1(T/\mathrm{K} - 293.15)$ and $C_p(Br)/\mathrm{J\cdot mol^{-1}\cdot K^{-1}} = d_0 + d_1(T/\mathrm{K} - 293.15)$. Contrary to them, $C_p(Cl)$ is independent of temperature within the investigated temperature range (c_1 and c_2 are equal to zero), while $C_p(CH_2)$ depends on temperature as follows: $C_p(CH_2)/\mathrm{J\cdot mol^{-1}\cdot K^{-1}} = b_0 + b_1(T/\mathrm{K} - 293.15) + b_2(T/\mathrm{K} - 293.15)^2$.

The second QSPR method for the estimation of the C_p values applied in this work is *molecular connectivity indexes* (MCI) analysis. The MCI method employ structural descriptors, that is, parameters derived from molecular structure, to develop correlations between the molecular structures of substances and their physical properties. Up to now, the molecular connectivity model has been applied to the estimation and prediction of numerous physicochemical properties,[15−17] for example, the molar refraction and volume, solubility data, heats of atomization and vaporization, isoelectric points, relaxation times, and crystal densities. Some authors have also attempted to use this model for the molar heat capacities.[18] In this study, we analyze the applicability of this method for correlating and predicting the heat capacities of pure halogenoalkanes.

The following set of molecular connectivity indexes was chosen to describe the heat capacities of halogenoalkanes, MCI = $\{D, D^v, {}^0X, {}^0X^v, {}^1X, {}^1X^v\}$. These indexes are defined using two cardinal numbers:[15,16,18] the delta index, δ_i, is the number of the non-hydrogen sigma electrons contributed by atom i, and the valence delta index, δ_i^v, is the number of all non-hydrogen valence electrons contributed

Table 6. Molecular Connectivity Index Values of Some Halogenoderivatives of Hydrocarbons

compound	D	D^v	${}^0X$	${}^0X^v$	${}^1X$	${}^1X^v$
1-BrC2	4	3.260	2.707	3.668	1.414	2.094
1-BrC3	6	5.260	3.414	4.375	1.914	2.594
1-BrC4	8	7.260	4.121	5.082	2.414	3.094
1-BrC5	10	9.260	4.828	5.790	2.914	3.594
1-BrC6	12	11.260	5.536	6.497	3.414	4.094
1-BrC7	14	13.260	6.243	7.204	3.914	4.594
1-BrC9	18	17.260	7.657	8.618	4.914	5.594
1-BrC10	20	19.260	8.364	9.325	5.414	6.094
1-ClC3	6	5.780	3.414	3.546	1.914	2.008
1-ClC4	8	7.780	4.121	4.254	2.414	2.508
1-ClC5	10	9.780	4.828	4.961	2.914	3.008
1-ClC6	12	11.780	5.536	5.668	3.414	3.508
1-ClC7	14	13.780	6.243	6.375	3.914	4.008
1-ClC8	16	15.780	6.950	7.082	4.414	4.508
1-ClC10	20	19.780	8.364	8.496	5.414	5.508
α,ω-diBrC2	6	4.520	3.414	5.337	1.914	3.274
α,ω-diBrC3	8	6.520	4.121	6.044	2.414	3.774
α,ω-diBrC4	10	8.520	4.828	6.751	2.914	4.274
α,ω-diBrC5	12	10.520	5.536	7.458	3.414	4.774
α,ω-diBrC6	14	12.520	6.243	8.165	3.914	5.274
α,ω-diClC2	6	5.560	3.414	3.679	1.914	2.101
α,ω-diClC3	8	7.560	4.121	4.386	2.414	2.601
α,ω-diClC4	10	9.560	4.828	5.093	2.914	3.101
α,ω-diClC5	12	11.560	5.536	5.800	3.414	3.601
α,ω-diClC6	14	13.560	6.243	6.507	3.914	4.101

by atom i. A general expression for this valence delta index emerges:

$$\delta_i^v = Z_i^v - h_i \tag{4}$$

where Z_i^v is the number of valence electrons of atom i and h_i is the number of hydrogen atoms attached to this atom. For heteroatoms, the δ_i^v values are defined as

$$\delta_i^v = \frac{Z_i^v - h_i}{Z_i - Z_i^v - 1} \tag{5}$$

where Z_i is the total number of electrons.

The connectivity indexes were calculated using the Kier and Hall method.[15−17] The simple molecular connectivity index and the valence molecular connectivity index of the zero and first order are described as

$${}^0X = \sum(\delta_i)^{-0.5} \quad \text{and} \quad {}^0X^v = \sum(\delta_i^v)^{-0.5} \tag{6}$$

$${}^1X = \sum(\delta_i\delta_j)^{-0.5} \quad \text{and} \quad {}^1X^v = \sum(\delta_i^v\,\delta_j^v)^{-0.5} \tag{7}$$

where i and j denote adjacent atoms forming a bond, other than hydrogen, and the summation is run over the nonhydrogen atoms of the entire molecule.

The sum-delta and sum-delta valence indexes are described as

$$D = \sum\delta_i \quad \text{and} \quad D^v = \sum\delta_i^v \tag{8}$$

The calculated values of the molecular connectivity indexes are collected in Table 6. Sets of higher order molecular connectivity indexes were also investigated, but their description of the heat capacity was very poor.

Several models for the linear and square temperature dependence of heat capacities were checked; however, the following equation provides the best fit.

$$C_p/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = B_0D + B_1D^v + B_2\,{}^0X^v + B_3\,{}^1XT/\text{K} + B_4\,{}^1X^v \tag{9}$$

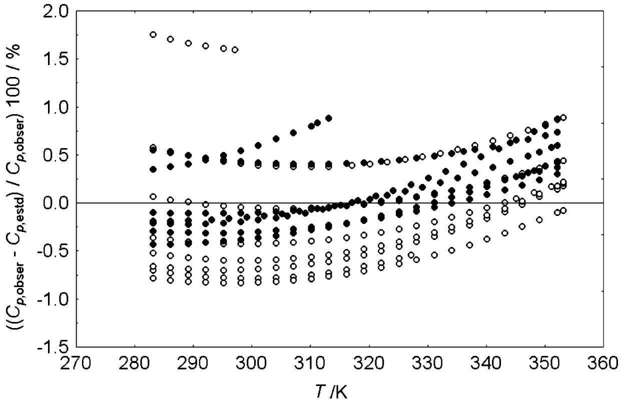

Figure 3. Relative errors of C_p for halogenoalkanes obtained from the MCI method: ○, 1-bromoalkanes; ●, 1-chloroalkanes.

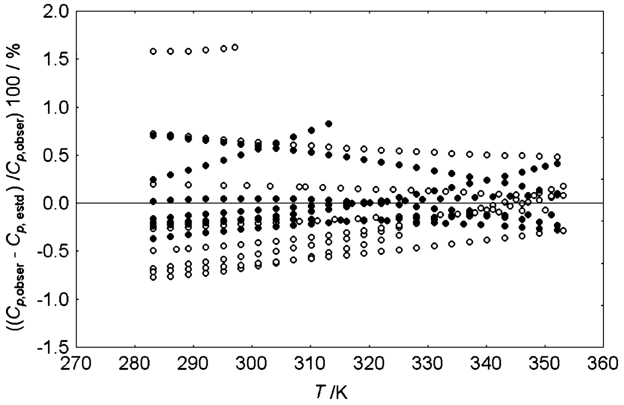

Figure 4. Relative errors of C_p for halogenoalkanes obtained from the GAA method: ○, 1-bromoalkanes; ●, 1-chloroalkanes.

The parameters B_i have been obtained by means of multiple stepwise regressions and the F-test and are reported with their standards errors in Table 5. The standard deviation of the fit was 1.4 J·mol^{-1}·K^{-1} with a maximum deviation of 4.9 J·mol^{-1}·K^{-1}.

Discussion

In this study, we show the applicability of the GAA and MCI methods for correlating the heat capacities of pure halogenoalkanes.

The comparisons of the experimental data of the heat capacities with the respective estimated values using the MCI and GAA methods are shown in Figures 3 and 4, respectively. In both cases, the comparison was performed for the two homologous series, that is, 1-chloroalkanes and 1-bromoalkanes. As can be see in Figure 3, the agreement of the experimental values of the heat capacities with the values calculated on the basis of the MCI model is in the range of ±1.7%.

The classical group additivity analysis (GAA) method seems to be a more useful method for predicting the value of the heat capacity. As can be see in Figure 4, the agreement of the experimental values of the heat capacities with the values calculated on the basis of the GAA model is in the range of ±1.6%. The error of the estimation in most cases of 1-halogenoalkanes is judged to be ±1%.

It is interesting that both methods give similar results. These results confirmed the utility of the molecular connectivity approach in estimating the heat capacities of structurally similar compounds.

For the majority of the studied compounds, the values of $(C_{p,\text{obsd}} - C_{p,\text{estd}})/C_{p,\text{obsd}}$ are independent of the temperature and the estimation errors are $< \pm 1\%$. Thus, it appears

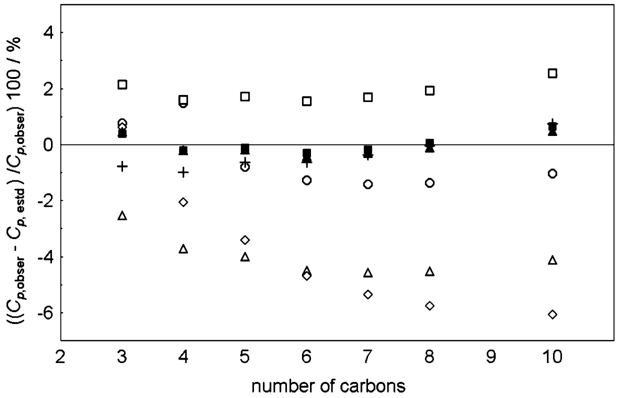

Figure 5. Comparison of the relative error of the molar heat capacities of 1-chloroalkanes calculated in this work with methods reported in the literature[5,8−15] (temperature 293.15 K): ○, Ruzicka and Domalski;[9,10] □, Missenard;[8] Δ, Chueh and Swanson;[11,12] ◇, Chickos;[13,14] +, Shehatta;[5] ■, this work, GAA; ▲, this work, MCI.

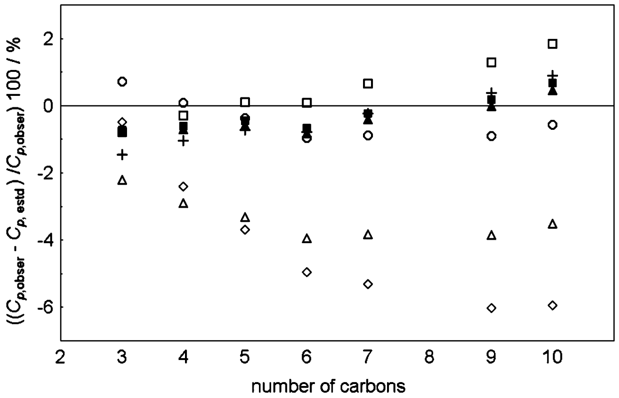

Figure 6. Comparison of the relative error of the molar heat capacities of 1-bromoalkanes calculated in this work with methods reported in the literature[5,8−15] (temperature 293.15 K): ○, Ruzicka and Domalski;[9,10] □, Missenard;[8] Δ, Chueh and Swanson;[11,12] ◇ Chickos;[13,14] +, Shehatta;[5] ■, this work, GAA; ▲, this work, MCI.

that the method may be used to estimate the values of C_p for the compounds with longer alkyl chains ($n > 10$), and at the temperatures beyond the range of 284 K to 354 K. The only halogenoalkane that was not considered in these analyses was 1-bromooctane, since the data for the value of C_p as a function of temperature for the compound already exist in the literature.[19] For this compound, the deviation between the experimental[19] value of C_p and the value estimated using the GAA method varies between 0.9% at 295.4 K and 0.4% at 360.0 K. While using the MCI method, the deviations are 0.7% at 295.4 K and 0.9% at 360.0 K.

The prediction capabilities of the present methods have been compared with the results obtained from some of the methods described in the literature[5,8−14] for the calculation of liquid heat capacity. As can be seen from Figures 5 and 6, the values of C_p estimated by different methods and the experimentally determined values are in agreement within the range of +3% to −6%. In general, as the number of CH_2 groups increases, the error of the estimation also increases.

The estimation errors for the 1-chloroalkanes and for the 1-bromoalkanes are up to 2.5% and 1.8%, respectively, based on the Missenard method; the respective values based on the Chueh and Swanson method are up 4.6% and 4%. Estimation errors based on the Chickos method are up to 6% for both series of compounds and are 1.5% and 0.9% based on the Ruzicka and Domalski method.

The group contribution methods reported by Missenard, Chueh and Swanson, and Chickos have been determined for a variety of compounds of different categories (hydrocarbons, alcohols, amines, etc.). Therefore, the agreement of the C_p values calculated from their group contributions with those obtained from experiment is usually not better than 2−6%. Additionally, the data of Chueh and Swanson and Chickos refer only to 293 K and/or 298 K, which further limits their use in the prediction of heat capacities. The estimated values of C_p by the Shehatta method have smaller deviations from the experimentally determined ones (up to 1.5%) due to its limitation only to the halogenated alkanes.

In summary, one can state that the two group contribution methods analyzed in this work can be useful for calculating the molar heat capacities with relatively good precision, even if up to now it is limited only to halogenated alkanes.

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