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Heat Capacities of Some Liquid α,*ω*-Alkanediamines in the Temperature Range between (293.15 and 353.15) K

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Heat capacities at constant pressure of 1,2-diaminoethane (1,2-DAEt) and 1,3-diaminopropane (1,3-DAPr) were measured within the temperature range from (293.15 to 353.15) K. The heat capacities of four other compounds, 1,4-diaminobutane (1,4-DABu), 1,6-diaminohexane (1,6-DAHx), 1,7-diaminoheptane (1,7-DAHp), and 1,9-diaminononane (1,9-DANo), were also measured between their melting point and 353.15 K. All measurements were performed by means of a DSC III (Setaram) differential scanning calorimeter. Assuming that molar heat capacity shows an additive character, a simple equation was proposed that allows one to describe C_p values of liquid α,*ω*-alkanediamines as a function of temperature and the alkyl chain length with an accuracy below 0.5 %.

Introduction

This work is a continuation of our research on the temperature dependence of molar heat capacity of liquid compounds that form homologous series.[1–4] The use of a standard DSC apparatus, employed in the thermal analysis, fails to provide highly precise results. One can estimate that despite carefully performing the experiment the apparatus uncertainty of these measurements is from (1 to 3) %. However, high precision of C_p measurements is still possible with the use of Tian-Calvet type microcalorimeters, including DSC III (SETARAM). The use of appropriate procedures allows one to obtain a better reproducibility 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 nature of these impurities plays a dominating role. Some impurities (e.g., isomers, other compounds of the same homologous series) can have specific heat capacities that are very similar to that of the investigated liquid. This does not cause any error that could result from a high percentage of impurity content. It seems that one should lay the greatest stress on the removal of traces of water, whose heat capacity considerably departs from that of the majority of organic liquids.

Compounds of the α,*ω*-alkanediamines series have found a wide application in pharmaceutical and cosmetic industries as well as in the production of polymers. From this point of view, it is of importance to know the thermodynamic properties of these compounds, including their molar heat capacities under constant pressure. Only a few experimental data concerning heat capacities of α,*ω*-alkanediamines are available in the literature.[5–9] The temperature dependence of C_p has been examined only in the case of 1,2-diaminoethane[6–8] and 1,3-diaminopropane.[9] In turn, the values of C_p estimated on the basis of group contributions[10–13] depart from the real values by several to a dozen percent. The basic aim of this study was to create a C_p database for α,*ω*-alkanediamines that would comprise a wide range of temperatures and considerable variation of hydrocarbon chain length. The additional objective was to calculate the group contributions of C_p that would make it possible to estimate the heat capacities of liquid diamines as a function of temperature, for compounds that have not been investigated as of yet.

Experimental Section

Chemicals. 1,2-Diaminoethane (1,2-DAEt) (Aldrich, ≥ 99.5 % in mass fraction), 1,3-diaminopropane (1,3-DAPr) (Aldrich, 99 % in mass fraction), 1,4-diaminobutane (1,4-DABu) (Aldrich, 99 % in mass fraction), 1,6-diaminohexane (1,6-DAHx) (Fluka, ≥ 99 % in mass fraction), 1,7-diaminoheptane (1,7-DAHp) (Aldrich, 98 % in mass fraction), and 1,9-diaminononane (1,9-DANo) (Aldrich, 98 % in mass fraction) 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 the drybox over P_2O_5.

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. Details of the applied procedure and the calorimeter calibration have been described previously.[1] Due to some changes[4] made in relation to the standard measurement technique, the uncertainty of the C_p values obtained in this work did not exceed ± 0.15 %. The samples (about 0.8 g) were weighed with a Sartorius RC 210D balance with an accuracy of $2 \cdot 10^{-5}$ g and were filled in a drybox.

The comparison of obtained values of C_p with the data available in the literature[5,8,9] for 298.15 K is given in Table 1.

Results

The measured molar heat capacity of α,*ω*-diamines as a function of temperature are listed in Table 2 and illustrated in Figure 1.

The continuous method was used in this work,and the values of C_p were obtained at 0.02 °C intervals. For clarity,only the C_p values obtained every 1.5 °C (and additionally at 298.15 K)

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Table 1. Comparison of the Experimental and Literature Data of Heat Capacity

	C_p/J·mol^{-1}·K^{-1}	
compound	this work	lit.
1,2-diaminoethane	172.7	172.6 ± 0.1[a]; 172.6[b]
1,3-diaminopropane	203.6	203.8 ± 0.2[a]; 204.0[c]
1,4-diaminobutane	236.3	236.3 ± 0.2[a]

[a] Ref 5. [b] Ref 8 (interpolated value). [c] Ref 9 (interpolated value).

Table 2. Molar Heat Capacities (C_p/J·mol^{-1}·K^{-1}) for Series α,ω-Alkanediamines from T = (293.15 to 353.15) K

	C_p/J·mol^{-1}·K^{-1}					
T/K	1,2-DAEt	1,3-DAPr	1,4-DABu	1,6-DAHx	1,7-DAHp	1,9-DANo
293.15	172.34	203.05				
294.65	172.43	203.21				
296.15	172.53	203.37				
297.65	172.63	203.53				
298.15	172.66	203.59	236.33			
299.15	172.73	203.70	236.45			
300.65	172.84	203.86	236.61			
302.15	172.95	204.03	236.77		332.76	
303.65	173.06	204.19	236.94		332.93	
305.15	173.17	204.36	237.09		333.11	
306.65	173.29	204.53	237.25		333.29	
308.15	173.41	204.70	237.41		333.48	
309.65	173.53	204.87	237.56		333.67	
311.15	173.66	205.04	237.72		333.86	398.93
312.65	173.79	205.21	237.87		334.06	399.04
314.15	173.92	205.38	238.03	301.08	334.27	399.17
315.65	174.05	205.56	238.18	301.25	334.48	399.32
317.15	174.18	205.73	238.34	301.42	334.70	399.47
318.65	174.31	205.91	238.49	301.59	334.92	399.64
320.15	174.45	206.08	238.65	301.77	335.15	399.82
321.65	174.59	206.26	238.81	301.95	335.38	400.02
323.15	174.72	206.43	238.97	302.14	335.62	400.22
324.65	174.86	206.61	239.13	302.33	335.87	400.44
326.15	175.00	206.79	239.29	302.53	336.12	400.67
327.65	175.15	206.96	239.46	302.74	336.38	400.92
329.15	175.29	207.14	239.63	302.95	336.64	401.17
330.65	175.43	207.32	239.80	303.17	336.91	401.44
332.15	175.58	207.50	239.98	303.40	337.18	401.72
333.65	175.72	207.67	240.15	303.64	337.47	402.02
335.15	175.86	207.85	240.34	303.88	337.76	402.32
336.65	176.01	208.03	240.52	304.13	338.05	402.64
338.15	176.15	208.20	240.71	304.40	338.35	402.97
339.65	176.30	208.38	240.91	304.67	338.66	403.32
341.15	176.44	208.56	241.11	304.95	338.98	403.67
342.65	176.59	208.73	241.32	305.25	339.30	404.04
344.15	176.73	208.91	241.53	305.55	339.63	404.43
345.65	176.87	209.08	241.74	305.87	339.97	404.82
347.15	177.02	209.26	241.97	306.20	340.31	405.23
348.65	177.16	209.43	242.20	306.54	340.66	405.65
350.15	177.30	209.60	242.43	306.89	341.02	406.08
351.65	177.44	209.78	242.68	307.26	341.39	406.52
353.15	177.58	209.95	242.93	307.64	341.76	406.98

are presented. The values given in Table 2 are averages of three independent runs, which differ from each other by not more than 0.1 %.

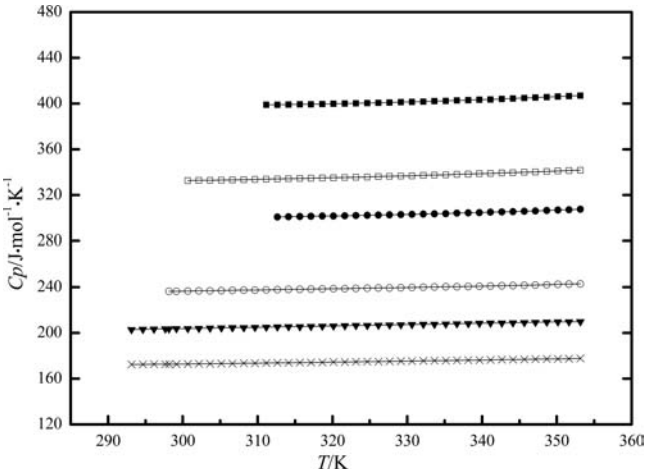

Figure 1. Molar heat capacities of α,ω-alkanediols as a function of temperature. ×, 1,2-DAEt; ▼, 1,3-DAPr; ○, 1,4-DABu; ●, 1,6-DAHx; □, 1,7-DAHp; ■, 1,9-DANo.

The temperature dependence of molar heat capacity of α,ω-diamines is presented by means of a polynomial in the following form

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

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 function $C_p = f(T)$ is that the free term A is the value of C_p of the examined compound 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.[1–4]

The coefficients of eq 1, their standard deviation, and mean deviation from polynomial (δC_p) are given in Table 3.

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

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

where $C_p(\text{CH}_2)$ is molar heat capacity of the CH_2 group; n_{CH_2} is hydrocarbon chain length; $C_p(\text{NH}_2)$ is molar heat capacity of the NH_2 group for an infinitely long hydrocarbon chain ($n_{\text{CH}_2} \to \infty$); and b is the adjustable parameter.

The term b/n_{CH_2} is a correction of heat capacity of the amine group connected with the nonadditivity of C_p, increasing with the approach of NH_2 groups to each other in diamine. Parameters

Table 3. Coefficients of the Polynomial (1) and Mean Deviation from the Regression Line

		coefficients of eq 1				
		A	A_1·10^2	A_2·10^4	A_3·10^6	
compound	temp. range/K	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-2}	J·mol^{-1}·K^{-3}	J·mol^{-1}·K^{-4}	δC_p
1,2-DAEt	293.15 to 353.15	172.34 ± 0.02	6.12 ± 0.20	7.92 ± 0.71	−5.93 ± 0.70	0.149
1,3-DAPr	293.15 to 353.15	203.05 ± 0.01	10.54 ± 0.07	3.30 ± 0.24	−2.85 ± 0.24	0.032
1,4-DABu	298.15 to 353.15	235.75 ± 0.01	11.97 ± 0.10	−8.34 ± 0.33	13.9 ± 0.33	0.044
1,6-DAHx	314.15 to 353.15	298.88 ± 0.05	10.90 ± 0.40	−6.74 ± 1.10	21.4 ± 0.88	0.052
1,7-DAHp	302.15 to 353.15	331.82 ± 0.01	9.65 ± 0.10	8.77 ± 0.34	4.72 ± 0.34	0.043
1,9-DANo	311.15 to 353.15	398.49 ± 0.02	−2.57 ± 0.10	27.9 ± 0.14		0.073

Table 4. Coefficients of Equations 2 and 3 and Their Standard Deviations

group	coefficients	
$C_p(CH_2)$	$A_0/J\cdot mol^{-1}\cdot K^{-1}$	32.05 ± 0.04
	$A_1/J\cdot mol^{-1}\cdot K^{-2}$	0.0142 ± 0.0007
$C_p(NH_2)$	$A_0/J\cdot mol^{-1}\cdot K^{-1}$	52.85 ± 0.15
	$A_1/J\cdot mol^{-1}\cdot K^{-2}$	0.032 ± 0.002
	$b/J\cdot mol^{-1}\cdot K^{-1}$	2.23 ± 0.25

$C_p(CH_2)$ and $C_p(NH_2)$ depend linearly on temperature, and for α,*ω*-diamines they have the following form

$$C_p = A_0 + A_1(T/K - 293.15) \tag{3}$$

The values of appropriate parameters of eqs 2 and 3 and their standard deviations are listed in Table 4. An analogous to eq 2 relationship $C_p = f(n_{CH_2}, T)$ was obtained when describing the molar heat capacity of several liquid α,*ω*-alkanediols as a function of temperature.[4] The necessity taking into account the correcting term b/n_{CH_2} was justified by the formation of various intramolecular and intermolecular hydrogen bonds, whose quantity depends on the hydrocarbon chain length. In the case of α,*ω*-diamines, the tendency to form hydrogen bonds is considerably smaller and their energy lower. The average energy of hydrogen bond formation between hydroxyl groups of alcohols amounts to −26.7 $kJ\cdot mol^{-1}$, while between amine groups it is only −8.7 $kJ\cdot mol^{-1}$.[14] Certainly, this is why the value of the correction for nonadditivity of C_p is considerably lower for α,*ω*-diamines than for α,*ω*-dioles. However the total omission of this correction deteriorates the mathematical description of $C_p = f(n_{CH_2}, T)$.

Equation 2 correctly describes the molar heat capacity of all investigated diamines as a function of temperature. The average deviation from the experimental data

$$\text{avg dev.} = \frac{100}{n}\cdot\sum|C_p^{calc} - C_p^{exptl}|/C_p^{exptl} \tag{4}$$

amounts only to 0.12 %. The highest average deviation (0.29 %) was observed for 1,6-diaminohexane, but it does not exceed 0.4 % at any of the temperatures used for this compound. It seems that the presented relationships (eqs 1 and 2) can be useful for the estimation of the C_p values of liquid α,*ω*-alkanediamines at temperatures exceeding the investigated range (293 to 353) K as well as of those compounds of this series that have not been examined as of yet: 1,5-diaminopentane, 1,8-diaminooctane, or other diamines with a chain length of $n > 9$.

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