Heat Capacities of Some Liquid α,ω-Alkanediols within the Temperature Range between (293.15 and 353.15) K

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The heat capacities at constant pressure of 1,2-ethanediol (1,2-EtD), 1,3-propanediol (1,3-PrD), 1,4-butanediol (1,4-BuD), 1,5-pentanediol (1,5-PeD), and 1,7-heptanediol (1,7-HpD) were measured within the temperature range from (293.15 to 353.15) K. The heat capacities of three other compounds, 1,6-hexanediol (1,6-HxD), 1,8-octanediol (1,8-OcD), and 1,9-nonanediol (1,9-NoD), 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 the molar heat capacity shows an additive character, a simple equation was proposed that allows one to describe C_p values of liquid α,ω-alkanediols as a function of temperature and the alkyl chain length with an accuracy below 1 %.

Introduction

Alkanediols are widely used in various fields of life. In the chemical industry, they are used to produce polyurethanes and polyethers; in the cosmetic industry, they serve as skin wetting additives, bactericides, and fungicides; while in the pharmaceutical industry, alkanediols constitute additives to drugs. Diols with short hydrocarbon chains are used as components of operating fluids in refrigerating and thermostatting systems. From this point of view, it is important to know the thermodynamic properties of this group of compounds, among others, their molar heat capacities (C_p) under constant pressure. There are only few experimental data concerning the C_p values of α,ω-alkanediols and their dependence on temperature,[1,2] and some of them are burdened with considerable uncertainty. That is the reason why the predicted values of $C_p = f(T)$ for diols on the basis of group contribution methods usually give results far away (± 10 %) from actual values.[2]

Our previous studies on the temperature dependence of molar heat capacity of homological series of monobromo-, monochloro-, α,ω-dibromo-, and α,ω-dichloroalkanes[3–5] allowed us to state that the molar heat capacity of these compounds could be presented as a sum of group contributions of appropriate functional groups. In the case of bromo-, chloro-, and bromochloro-substituted benzenes (mono-, di-, tri-, tetra-substituted), it has turned out[6] that a precise additive description of heat capacity as a function of temperature and number of substituents requires one to take into account a corrective factor. This factor takes into consideration the "accumulation" of halogen substituents in the ring that change nonadditively the physical and chemical properties of benzene halogen derivatives, including C_p.

The aim of the present study is to determine the specific and molar heat capacities of liquid α,ω-alkanediols within the temperature range (20 to 80) °C, using the DSC method. For diols that are solid at room temperature, the temperature range is (45 to 80) °C (for 1,6-hexanediol and 1,9-nonanediol) or (60 to 80) °C (for 1,8-octanediol). The series under investigation includes all α,ω-alkanediols with hydrocarbon chain lengths $2 \le n \le 9$. It was of interest to check how the presence of strong specific interactions between solvent molecules in a liquid state (H-bonds) influences the additivity of heat capacity. From this point of view, the simplest homologous series was that of α,ω-alkanediols. The molecules of this compounds contain in their structure only two functional groups (CH_2 and OH), and they are subject to both intermolecular and intramolecular hydrogen bonds, which depend on the length of hydrocarbon chain.[7]

The collected C_p data were used to calculate the group contributions of heat capacities of CH_2 and OH groups and to propose a simple mathematical relationship describing the heat capacity of α,ω-alkanediols as a function of temperature and hydrocarbon chain length

$$C_p = f(T, n)$$

Table 1. Comparison of the Experimental and Literature Data of Heat Capacity C_p at $T = 298.15$ K

	C_p/J·mol^{-1}·K^{-1}	
compound	this work	lit.
1,2-ethanediol	149.69	149.7[a]
1,3-propanediol	175.78	176.4[a]; 176.7[b]
1,4-butanediol	203.27	204.2[a]; 203.1[c]; 200.9[d]
1,5-pentanediol	232.49	233.2[a]

[a] Ref 8. [b] Ref 9. [c] Ref 10. [d] Ref 11.

Experimental Section

Chemicals. 1,2-Ethanediol (1,2-EtD) (Aldrich, 99.8 %, anhydrous), 1,3-propanediol (1,3-PrD) (Aldrich, ≥ 99.6 %), 1,4-butanediol (1,4-BuD) (Aldrich, ≥ 99 %), 1,6-hexanediol (1,6-HxD) (Aldrich, 99 %), 1,8-octanediol (1,8-OcD) (Aldrich, ≥ 98 %), and 1,9-nonanediol (1,9-NoD) (Aldrich, ≥ 98 %) were used without further purification. 1,5-Pentanediol (1,5-PeD) (Merck, ≥ 98 %) and 1,7-heptanediol (1,7-HpD) (Merck, ≥ 98 %) were purified by fractional distillation under reduced pressure. The final purity of the compounds used for experiments was determined by the method of thermal analysis using a DSC 111 (Setaram) calorimeter to be ≥ 99 mol %. Prior to the measurements, all chemicals were dried with activated molecular sieves (type 4Å from Lancaster) and degassed in an ultrasonic stream.

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10.1021/je800356x CCC: $40.75

Table 2. Molar Heat Capacities C_p for Series of α,ω-Alkanodiols from T = (293.15 to 353.15) K

	C_p/J·mol^{-1}·K^{-1}							
T/K	1,2-EtD	1,3-PrD	1,4-BuD	1,5-PeD	1,6-HxD	1,7-HpD	1,8-OcD	1,9-NoD
293.15	148.10	173.40	200.51	229.04		292.06		
294.65	148.57	174.11	201.33	230.06		293.40		
296.15	149.05	174.83	202.16	231.10		294.75		
297.65	149.53	175.54	202.99	232.14		296.11		
299.15	150.01	176.26	203.82	233.19		297.48		
300.65	150.48	176.98	204.67	234.25		298.87		
302.15	150.96	177.70	205.51	235.31		300.26		
303.65	151.44	178.42	206.36	236.39		301.67		
305.15	151.92	179.15	207.22	237.47		303.09		
306.65	152.40	179.87	208.08	238.56		304.51		
308.15	152.88	180.59	208.95	239.66		305.95		
309.65	153.36	181.32	209.82	240.77		307.41		
311.15	153.83	182.05	210.70	241.89		308.87		
312.65	154.31	182.78	211.58	243.01		310.34		
314.15	154.79	183.51	212.47	244.14		311.83		
315.65	155.27	184.24	213.36	245.28		313.33		
317.15	155.75	184.97	214.26	246.43		314.83		
318.65	156.23	185.70	215.17	247.59	282.66	316.35		389.02
320.15	156.71	186.44	216.08	248.76	284.25	317.88		391.15
321.65	157.19	187.17	216.99	249.93	285.84	319.43		393.27
323.15	157.67	187.91	217.91	251.11	287.42	320.98		395.39
324.65	158.15	188.65	218.83	252.30	288.99	322.54		397.51
326.15	158.63	189.38	219.76	253.50	290.55	324.12		399.62
327.65	159.11	190.12	220.70	254.70	292.12	325.71		401.73
329.15	159.60	190.87	221.64	255.92	293.67	327.31		403.84
330.65	160.08	191.61	222.58	257.14	295.22	328		405.94
332.15	160.56	192.35	223.53	258.37	296.76	330.54		408.03
333.65	161.04	193.10	224.49	259.61	298.30	332.17	371.35	410.12
335.15	161.52	193.84	225.45	260.86	299.83	333.81	373.24	412.21
336.65	162.00	194.59	226.41	262.11	301.36	335.47	375.13	414.30
338.15	162.49	195.34	227.38	263.38	302.88	337.13	377.03	416.38
339.65	162.97	196.09	228.36	264.65	304.40	338.81	378.93	418.45
341.15	163.45	196.84	229.34	265.93	305.91	340.50	380.83	420.52
342.65	163.93	197.59	230.33	267.22	307.41	342.20	382.74	422.59
344.15	164.42	198.34	231.32	268.51	308.91	343.91	384.65	424.66
345.65	164.90	199.10	232.32	269.82	310.40	345.63	386.56	426.72
347.15	165.38	199.85	233.32	271.13	311.88	347.37	388.48	428.77
348.65	165.86	200.61	234.32	272.45	313.36	349.11	390.40	430.82
350.15	166.35	201.37	235.34	273.78	314.84	350.87	392.32	432.87
351.65	166.83	202.13	236.35	275.12	316.31	352.64	394.24	434.92
353.15	167.32	202.89	237.38	276.46	317.77	354.42	396.17	436.95

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

		coefficients of eq 1			
	temperature range	A	B_1	B_2	
compound	K	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-2}	J·mol^{-1}·K^{-3}	δC_p
1,2-EtD	293.15 to 353.15	148.10 ± 0.005	0.3181 ± 3.4E-04	3.70E-05 ± 5.0E-06	0.045
1,3-PrD	293.15 to 353.15	173.40 ± 0.005	0.4759 ± 3.8E-04	2.60E-04 ± 5.6E-06	0.050
1,4-BuD	293.15 to 353.15	200.51 ± 0.005	0.5455 ± 3.6E-04	1.15E-03 ± 5.4E-06	0.048
1,5-PeD	293.15 to 353.15	229.04 ± 0.007	0.6812 ± 4.8E-04	1.82E-03 ± 7.2E-06	0.064
1,6-HxD	318.15 to 353.15	254.76 ± 0.13	1.127 ± 5.9E-03	−1.28E-03 ± 6.4E-05	0.124
1,7-HpD	293.15 to 353.15	292.06 ± 0.011	0.8887 ± 7.8E-04	2.51E-03 ± 1.2E-05	0.104
1,8-OcD	333.15 to 353.15	321.58 ± 0.71	1.199 ± 2.7E-02	7.4E-04 ± 2.5E-04	0.086
1,9-NoD	318.15 to 353.15	352.22 ± 0.13	1.466 ± 6.0E-03	−8.95E-04 ± 6.7E-05	0.167

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

group	coefficients	
$C_p(CH_2)$	A/J·mol^{-1}·K^{-1}	31.13 ± 0.09
	B/J·mol^{-1}·K^{-2}	0.1598 ± 0.0007
$C_p(OH)$	$C_p{}^{*}{}_{OH}$/J·mol^{-1}·K^{-1}	32.02 ± 0.35
	b/J·mol^{-1}·K^{-1}	0.694 ± 0.027

Apparatus and Procedure. The saturated specific heat capacities were measured by means of a high sensitivity differential scanning calorimeter Micro DSC III (Setaram) based on the Tian−Calvet principle. 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.[4] 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 were weighed with a Sartorius RC 210D balance with an accuracy of $2 \cdot 10^{-5}$g and were filled in the drybox.

The comparison of obtained values of C_p with the data available in the literature for 298.15 K is given in Table 1.

Results

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

In the continuous method, the values of C_p were obtained with a step of 0.02 °C. For clarity, only the C_p values obtained

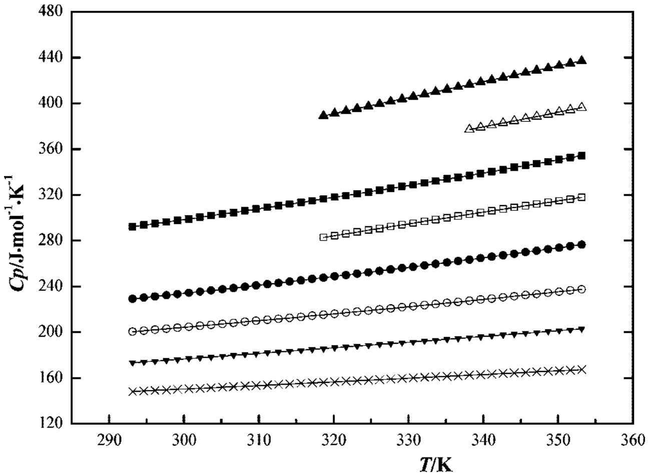

Figure 1. Molar heat capacities of α,*ω*-alkanediols as a function of temperature: ×, 1,2-EtD; ▼, 1,3-PrD; ○, 1,4-BuD; ●, 1,5-PeD; □, 1,6-HxD; ■, 1,7-HpD; △, 1,8-OcD; ▲, 1,9-NoD (experimental data from Table 2).

every 1.5 °C 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 %.

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

$$C_p/\mathrm{J\cdot mol^{-1}\cdot K^{-1}} = A + B_1\cdot(T/\mathrm{K} - 293\cdot 15) + B_2\cdot(T/\mathrm{K} - 293\cdot 15)^2 \quad (1)$$

where T is temperature and A, B_1, and B_2 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.[3–6]

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

Analyzing the changes in C_p values in the homological series of α,*ω*-alkanediols, it is seen that the increment in the C_p value per CH_2 group increases with an increase of the hydrocarbon chain length. Thus, a simple additivity model assuming that the contribution of a given functional group in the measured C_p value should be constant is not satisfied. A simple group additivity of C_p was observed by us previously in the case of the series 1-halogenoalkanes[5] and α,*ω*-halogenoalkanes.[3,4] The lack of analogous additivity in the case of α,*ω*-alkanediols is not surprising if one takes into account the inter- as well as intramolecular hydrogen bonds being formed in the liquid. Particularly, the intramolecular bonds are sensitive to changes in the hydrocarbon chain length of α,*ω*-alkanediols. According to Klein's opinion,[7] the maximum density of intramolecular hydrogen bonds is shown in $n,(n+3)$-diols, in which hydroxyl groups are separated by four CH_2 groups (e.g., 1,4-butanediol). The diols under our investigation include both compounds with a shorter chain from 1,4-butanediol (1,2-EtD, 1,3-PrD) and with long chains (1,8-OcD and 1,9-NoD).

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

$$C_p/\mathrm{J\cdot mol^{-1}\cdot K^{-1}} = n_{\mathrm{CH_2}}\cdot C_p(\mathrm{CH_2}) + 2\cdot\left(C_p^*(\mathrm{OH}) + \frac{b}{n_{\mathrm{CH_2}}}\right) \quad (2)$$

where $n_{\mathrm{CH_2}}$ is hydrocarbon chain length; C_p*(OH) is molar heat capacity of the OH group for an infinitely long hydrocarbon chain ($n_{\mathrm{CH_2}} \rightarrow \infty$), and b is the adjustable parameter. The term $b/n_{\mathrm{CH_2}}$ is a correction of heat capacity of the hydroxyl group connected with the nonadditivity of C_p, due to all the changes in inter- and intramolecular H-bond interactions as well as to the proximity effect.

The parameter $C_p(\mathrm{CH_2})$ is a molar heat capacity of the methyl group linearly depending on temperature, and for α,*ω*-alkanediols, it has the following form

$$C_p(\mathrm{CH_2}) = A + B\cdot(T/\mathrm{K} - 298\cdot 15) \quad (3)$$

The values of appropriate parameters of eqs 2 and 3 and their standard deviations are listed in Table 4.

Equation 2 correctly describes the molar heat capacity of all examined diols as a function of temperature and the average deviation from the experimental data (av.dev = $100/n\cdot\Sigma|C_p^{\mathrm{calcd}} - C_p^{\mathrm{exptl}}|/C_p^{\mathrm{calcd}}$) is 0.42 %. The highest average deviation (0.75 %) was observed for 1,3-propanediol, but it does not exceed 1 % for any of the temperatures used.

It seems that the presented relationships (eqs 2, 3) can be useful for the estimation of C_p values of liquid α,*ω*-alkanediols at temperatures exceeding the examined range (293 K to 353 K) and chain length ($n < 9$).

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Received for review May 16, 2008. Accepted June 14, 2008.

JE800356X