J. Chem. Eng. Data **2008,** *53,* 1316–1320

Molar Heat Capacity of 1,2-Cyclohexanediol Isomers From (173 to 428) K

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Heat capacities of *cis*-1,2-cyclohexanediol and *trans*-1,2-cyclohexanediol enantiomers have been determined in the solid state in the temperature range $T = (173 \text{ to } 368)$ K for the *cis*-isomer and $T = (173 \text{ to } 373)$ K in the case of the *trans*-isomer and in the liquid state at temperatures up to 428 K. Measurements were carried out by differential scanning calorimetry using the enthalpic method. For the *cis*-isomer, the results show that, before the liquid state is reached, a highly disordered phase is formed. The *trans*-enantiomers show only a one-step fusion process. The values obtained for the solids are quite well predicted by Goodman's power law group contribution method, except for the lower temperatures. The Rûžička method was tested for the prediction of liquid state heat capacity values giving results (15 to 20) % lower than the experimental values.

Introduction

In the present work, the heat capacity of *trans*-1,2-cyclohexanediol enantiomers and of *cis*-1,2-cyclohexanediol in the solid and liquid states are reported at temperatures ranging from $T = (173 \text{ to } 428)$ K using differential scanning calorimetry. Furthermore, a comparison of the experimental data with values calculated using the group contribution methods developed by Goodman et al.[1] for the solid state and by Rûžička et al.[2,3] for the liquid state is made.

The isomers of 1,2-cyclohexanediol are used in the preparation of many high-value compounds, ranging from keto alcohols to polymers.[4–9] In addition, optically active 1,2-diols play an important role as chiral auxiliaries in the syntheses of enantiomerically pure compounds,[10] an increasingly attractive research field for the development of modern drugs and agrochemicals.[11–13]

The molar heat capacity is a fundamental thermodynamic property. In fact, the knowledge of heat capacities at various temperatures is essential for the calculation of the thermodynamic properties, such as enthalpy, entropy, and Gibbs energy, as a function of temperature as well as to assess the effect of temperature on reaction and phase equilibria. Changes in heat capacity are also an indicator of phase transitions and an important tool for understanding modifications in the structure of solids and liquids.

Besides obtaining precise heat capacity values for both 1,2-cyclohexanediol isomers, there is another motivation for studying these systems. From previous work on the 1,2-cyclohexanediol isomers,[14,15] the existence of a mesophase preceding fusion was evidenced for the *cis*-isomer, while for the *trans*-isomer a unique step fusion was observed. Heat capacity values may give a valuable contribution to the characterization of this mesophase.

Experimental Section

Materials. *cis*-1,2-Cyclohexanediol, mass fraction $x \geq 0.99$, was purchased from Aldrich and *trans*-1,2-cyclohexanediol enantiomers, mass fraction $x = 0.99$, from Fluka Chemie. The compounds were purified by sublimation using the coldfinger technique ($T = 353$ K, $p = 10^3$ Pa, freezing fluid: cold water). The purity of the sublimed samples was determined by gas chromatography (column Supelco β-DCX, $d = 0.25$ mm, $l = 30$ m; $T = 373$ K; carrier gas: helium; flame ionization detector; d and l are the internal diameter and the length of the column, respectively) and was better than 99.9 %.

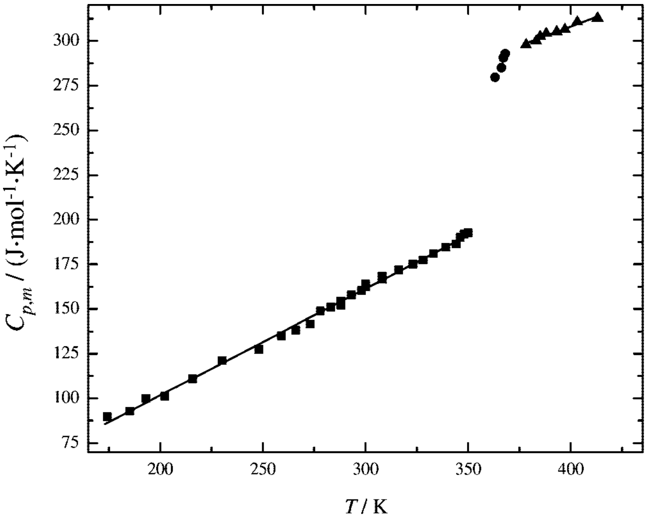

Figure 1. Molar heat capacity of the condensed phases of *cis*-1,2-cyclohexanediol in the temperature range from $T = (173 \text{ to } 413)$ K. ■, crystal II; ●, crystal I; ▲, liquid.

Apparatus. Measurements were carried out in the temperature range between $T = (173 \text{ to } 428)$ K using a Perkin-Elmer DSC7 (CCA7 cooling unit, 20 mL·min^{-1} N$_2$ purge) and a Pyris 1 (Cryofill cooling unit, 20 mL·min^{-1} He purge) power compensation calorimeter. Temperature calibration was performed using indium, $T_{\text{fus}} = 429.75$ K, and cyclohexane, $T_{\text{fus}} = (279.81 \pm 0.04)$ K, or cyclohexane, $T_{\text{fus}} = (279.81 \pm 0.04)$ K, $T_{\text{trs}} = (186.25 \pm 0.02)$ K, and cyclopentane, $T_{\text{trs}} = (138.06 \pm 0.05)$ K, $T_{\text{fus}} = (179.72 \pm 0.05)$ K, depending on the temperature range studied.[16] Indium, $\Delta_{\text{fus}}H = (3286 \pm$

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10.1021/je800047t CCC: $40.75

Table 1. Molar Heat Capacity Values, $C_{p,m}$, for *cis*-1,2-Cyclohexanediol at Different Temperatures T

sample[a]	T K	$C_{p,m}$ $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	PD %[b]	sample[a]	T K	$C_{p,m}$ $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	PD %[b]
A	174.3	89.6 ± 0.8	−18.6	F	323.3	175.0 ± 0.6	0.9
A	185.2	92.7 ± 0.9	−20.3	A	328.2	177.2 ± 0.9	0.9
B	193.1	100 ± 1	−15.2	D	333.2	180.8 ± 0.9	1.7
A	202.2	101.1 ± 0.8	−18.3	F	339.2	184.3 ± 0.8	2.2
C	215.9	111.0 ± 0.9	−13.5	D	344.1	186.2 ± 0.8	2.1
A	230.1	121.1 ± 0.7	−9.4	F	346.3	190.0 ± 0.9	3.6
B	248.1	127.3 ± 0.7	−10.5	F	348.1	191.8 ± 0.8	4.1
C	259.2	134.9 ± 0.5	−7.9	D	350.2	192.5 ± 0.7	4.0
B	266.2	138.2 ± 0.4	−7.6		II→I transition		
D	273.1	141.4 ± 0.8	−7.3	H	363.1	279.6 ± 0.9	
D	278.2	148.8 ± 0.7	−3.5	H	366.2	284.9 ± 0.9	
C	283.0	151.1 ± 0.9	−3.3	C	367.2	290.4 ± 0.9	
E	288.2	152 ± 1	−4.1	H	368.2	292.8 ± 0.9	
C	288.2	154.2 ± 0.8	−2.7		fusion		
E	293.2	157.8 ± 0.7	−1.7	G	378.1	297.9 ± 0.9	15.5
F	293.2	157.6 ± 0.7	−1.8	E	383.2	300.0 ± 0.9	15.4
E	298.1	160.4 ± 0.9	−1.4	H	385.2	302.5 ± 0.8	15.8
G	300.2	162 ± 2	−0.8	H	388.0	304.1 ± 0.7	15.9
C	300.2	163.9 ± 0.7	0.2	H	393.2	305 ± 1	15.5
G	308.2	168 ± 2	0.7	G	397.3	306.3 ± 0.9	15.4
G	308.2	166.4 ± 0.8	−0.4	H	403.1	310.5 ± 0.6	15.8
C	316.0	171.9 ± 0.6	0.9	H	413.2	312.8 ± 0.8	15.3

[a] A, 10.16 mg; B, 16.17 mg; C, 19.82 mg; D, 16.30 mg; E, 12.93 mg; F, 19.24 mg; G, 13.26 mg; H, 14.84 mg. [b] Percent deviation, PD = $[(C_{p,m} - C_{p,m}^{\mathrm{est}})/C_{p,m}]$. $C_{p,m}$ is the experimental molar heat capacity value, and $C_{p,m}^{\mathrm{est}}$ is the estimated heat capacity using group contribution methods by Goodman et al.[1] in the case of solids and Rûžička et al.[3] in the case of liquids.

Table 2. Molar Heat Capacity Values, $C_{p,m}$, for (1*R*,2*R*)-*trans*-Cyclohexanediol at Different Temperatures T

sample[a]	T K	$C_{p,m}$ $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	PD %[b]	sample[a]	T K	$C_{p,m}$ $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	PD %[b]
B	176.5	100.6 ± 0.8	−6.7	C	293.2	156.4 ± 0.8	−2.6
A	183.2	105.6	−4.7	B	293.2	157.4 ± 0.9	−2.0
B	189.1	109.5 ± 0.8	−3.5	A	303.2	167.0 ± 0.8	1.3
C	198.9	115.4 ± 0.8	−2.3	B	308.1	168.1 ± 0.8	0.7
B	206.9	115.6 ± 0.8	−5.3	A	308.1	169.9 ± 0.7	1.7
D	215.0	121 ± 2	−3.6	C	313.2	173 ± 2	2.3
A	222.2	124.6 ± 0.6	−3.4	B	323.3	174 ± 1	0.4
E	230.2	127.3 ± 0.8	−4.1	B	333.1	177.4 ± 0.7	−0.1
B	238.3	135.4 ± 0.9	−0.6	A	343.2	181.4 ± 0.8	−0.2
C	258.3	142.2 ± 0.7	−2.1	C	343.2	183.9 ± 0.9	1.1
A	273.2	145.6 ± 0.9	−4.2	A	353.1	187.1 ± 0.7	0.6
C	278.1	148.8 ± 0.9	−3.4	B	363.2	190.5 ± 0.9	0.2
A	278.1	150.6 ± 0.8	−2.2	B	373.2	198 ± 1	1.9
B	278.1	149 ± 1	−3.2		fusion		
A	283.2	151 ± 1	−3.4	D	393.1	310.7 ± 0.7	20.0
B	283.2	151.1 ± 0.8	−3.3	D	403.2	313 ± 2	19.8
B	288.2	154 ± 1	−2.8				

[a] A, 13.24 mg; B, 11.24 mg; C, 8.94 mg; D, 7.12 mg; E, 12.34 mg. [b] Percent deviation, PD = $[(C_{p,m} - C_{p,m}^{\mathrm{est}})/C_{p,m}]$. $C_{p,m}$ is the experimental molar heat capacity value, and $C_{p,m}^{\mathrm{est}}$ is the estimated heat capacity using group contribution methods by Goodman et al.[1] in the case of solids and Rûžička et al.[3] in the case of liquids.

13) $\mathrm{J \cdot mol^{-1}}$, or cyclohexane, $\Delta_{\mathrm{trs}}H = (6713 \pm 74)\ \mathrm{J \cdot mol^{-1}}$, were also used for enthalpy calibration.[16] A standard deviation equal to 0.1 K is obtained for temperature.

Experimental Procedure. The methodology followed for heat capacity determination has been described as the enthalpic method.[17–19] The calorimeter was stabilized at the initial temperature at least for 5 min, and then the temperature was raised by 3 K at a scanning rate $\beta = 2\ \mathrm{K \cdot min^{-1}}$. As the final temperature was reached, a 5 min stabilization period was maintained. For each $C_{p,m}$ determination, three different experiments, using this temperature program, were performed. First of all, a baseline was run with empty pans and the calibration factor determined with an appropriate standard substance. The sample was then studied using the same temperature program. These operations, several runs for each, were always performed in the same day. The calculated $C_{p,m}$ values were assigned to the temperature corresponding to the mean of the scanned temperature range. Heat capacity calibration was made using synthetic sapphire, NIST-RM 720,[16,20,21] and benzoic acid, SRM LGC 2606,[16,21,22] was used to verify the uncertainty of the experimental procedure. Uncertainty better than 1.5 % was achieved.

Masses between m = (7 and 20) mg were used in sealed Perkin-Elmer 40 μL aluminum pans. The results presented at each temperature are the mean of at least three runs. Different samples for each substance under study were used to confirm the reliability of data. $C_{p,m}$ determinations at equal or adjacent temperatures were always performed on different days.

In this work, the uncertainties are expressed by one standard deviation.

Table 3. Molar Heat Capacity Values, $C_{p,m}$, for (1*S*,2*S*)-*trans*-Cyclohexanediol at Different Temperatures *T*

sample[a]	T / K	$C_{p,m}$ / $\text{J·mol}^{-1}\text{·K}^{-1}$	PD / %[b]
A	180.1	103.2	−5.7
C	248.2	134.5	−4.6
A	278.1	149.0 ± 0.6	−3.3
B	288.0	153.7 ± 0.7	−3.0
A	298.2	163.2 ± 0.9	0.3
B	303.2	165.4 ± 0.7	0.3
C	308.1	168.1 ± 0.9	0.7
D	308.1	169 ± 1	1.2
A	313.2	169 ± 1	−0.1
D	318.2	172.3 ± 0.9	0.6
B	318.2	170.4 ± 0.7	−0.5
E	323.1	175 ± 1	0.9
C	333.0	177 ± 1	−0.3
E	343.2	184 ± 1	1.2
C	353.2	188.8 ± 0.8	1.5
E	363.2	194.0 ± 0.9	2.0
E	373.2	198 ± 1	1.9
		fusion	
F	393.1	313 ± 1	20.6
F	403.2	318 ± 1	21.1
G	413.1	321 ± 2	21.3
F	423.2	327 ± 1	22.1
G	428.2	331 ± 2	22.9

[a] A, 14.32 mg; B, 15.41 mg; C, 2.67 mg; D, 11.01 mg; E, 12.74 mg; F, 8.18 mg; G, 6.85 mg. [b] Percent deviation, PD = $[(C_{p,m} - C_{p,m}^{\text{est}})/C_{p,m}]$. $C_{p,m}$ is the experimental molar heat capacity value, and $C_{p,m}^{\text{est}}$ is the estimated heat capacity using group contribution methods by Goodman et al.[1] in the case of solids and Růžička et al.[3] in the case of liquids.

Results and Discussion

In Table 1, the results obtained for the heat capacities of *cis*-1,2-cyclohexanediol are given, and Tables 2 and 3 contain the results for the enantiomers of *trans*-1,2-cyclohexanediol. For better visualization, the values found for heat capacity are plotted against temperature in Figures 1 and 2.

The temperature dependence of the heat capacity of 1,2-cyclohexanediol isomers both in the solid and in the liquid phases, in the range of temperatures considered, is well described by linear functions

$$C_{p,m}/(\text{J·mol}^{-1}\text{·K}^{-1}) = a + b(T/\text{K}) \qquad (1)$$

whose coefficients, a and b, together with their respective standard deviations, determined by the least-squares method, are given in Table 4.

The *cis*-isomer presents three phases on heating: a crystalline phase, stable below $T = 360$ K, crystal II, an intermediate phase, crystal I, between $T = 360$ K and $T = 372$ K, and the liquid phase for temperatures above $T = 372$ K.[14,15] The transition between phases II and I ($T_{\text{trs}} = 360.4$ K, $\Delta_{\text{trs}}H = 19.9$ kJ·mol^{-1})[14] is accompanied by an increase in $C_{p,m}$ of about 80 $\text{J·mol}^{-1}\text{·K}^{-1}$, while the transition between phase I and the liquid ($T_{\text{fus}} = 371.6$ K, $\Delta_{\text{fus}}H = 3.3$ kJ·mol^{-1})[14] gives rise to the increase of $C_{p,m}$ of only 5 $\text{J·mol}^{-1}\text{·K}^{-1}$. From these data, a clear conclusion may be drawn about phase I: it is evident that phase I has a highly disordered structure, not far from that of the liquid. A typical DSC curve obtained in heating runs at $\beta = 2$ K·min^{-1} is given as Supporting Information.

The enantiomers of the *trans*-isomer exhibit only one solid phase, stable for temperatures below $T = 383$ K.[15,23] Fusion ($T_{\text{fus}} = 382.6$ K, $\Delta_{\text{fus}}H = 21.0$ kJ·mol^{-1})[23] gives rise to an increase of $C_{p,m}$ of about 100 $\text{J·mol}^{-1}\text{·K}^{-1}$. No significant differences between the pure enantiomers were observed, as expected. A typical DSC curve obtained in heating runs at $\beta = 2$ K·min^{-1} is given as Supporting Information.

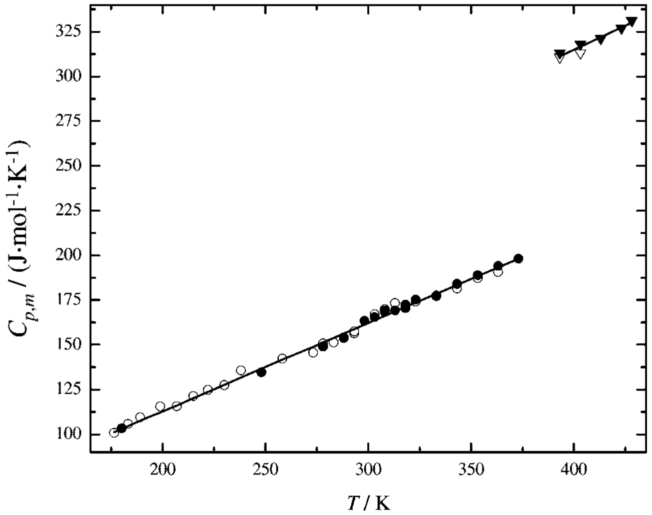

Figure 2. Molar heat capacity of the condensed phases of the enantiomers of *trans*-1,2-cyclohexanediol in the temperature range from $T = (176$ to $428)$ K. ○, solid (1*R*, 2*R*)-*trans*-cyclohexanediol; ●, solid (1*S*, 2*S*)-*trans*-cyclohexanediol; ▽, liquid (1*R*,2*R*)-*trans*-cyclohexanediol; ▼, liquid (1*S*,2*S*)-*trans*-cyclohexanediol.

Table 4. Parameters *a* and *b* of the Equation $C_{p,m}/(\text{J·mol}^{-1}\text{·K}^{-1}) = a + b(T/\text{K})$

	temp range/K	a	b
cis-1,2-cyclohexanediol	173 to 350	−17.6 ± 1.9	0.5964 ± 0.0064
	378 to 413	137 ± 12	0.426 ± 0.032
trans-1,2-cyclohexanediol enantiomers	176 to 373	15.2 ± 1.6	0.4896 ± 0.0056
	393 to 428	100 ± 24	0.537 ± 0.059

To our knowledge, there is only one work dealing with the heat capacity of 1,2-cyclohexanediols.[24] The measurements were made above room temperature, and the values reported for the *trans*-1,2-isomer concern the racemic mixture. The enantiomers and the racemic substance may have distinct thermodynamic properties in the solid phase, depending on the (solid + liquid) phase diagram of the enantiomer mixture.[23,25] This is the case for *trans*-1,2-cyclohexanediol, so no comparison between our values and Cairong's will be carried out. Cairong and co-workers[24] report heat capacity values for *cis*-1,2-cyclohexanediol in the solid state for $T = (310$ to $355)$ K and in the liquid state for $T = (375$ to $470)$ K. The values presented are systematically higher than those found in the present work. The differences are quite large, ranging in the solid from 45 % at the lower temperature up to 100 % for the higher temperature. For temperatures between $T = 325$ K and $T = 355$ K, the values reported by Cairong et al. are higher than those of the liquid at 375 K. In the liquid at $T = 380$ K, our values and Cairong's are not significantly different, but at $T = 413$ K, a divergence of about 34 % is observed. It is worthy to note that the authors of ref 24 also did not detect the solid−solid phase transition in the *cis*-isomer.

The power law group contribution method developed by Goodman and co-workers[1] for organic solids was applied to assess heat capacity values of the 1,2-cyclohexanediols. This method, which does not distinguish between isomers, uses the following equation to estimate $C_{p,m}$

$$C_{p,m}/(\text{J·mol}^{-1}\text{·K}^{-1}) = \frac{A}{1000}(T/\text{K})^{0.79267} \qquad (2)$$

A is given by

$$A = \exp\left(6.7796 + \sum_{i}^{k} a_i n_i + \sum_{i}^{k} b_i n_i^2\right) \qquad (3)$$

a_i and b_i are parameters characteristic of group i, and n_i is the number of each type of group making up the molecule. For 1,2-cyclohexanediol, the following equation is obtained

$$C_{p,m}/(\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}) = \frac{1777.71}{1000}(T/\mathrm{K})^{0.79267} \qquad (4)$$

Deviations between experimental and calculated values are presented in Tables 1 to 3. The predictions made by the Goodman method are quite satisfactory, with deviations ranging from (−7 to 2) % for *trans*-1,2-cyclohexanediol and from (−20 to 4) % in the case of the *cis*-isomer. The highest deviations are registered for *cis*-1,2-cyclohexanediol for temperature values below 250 K. The crystalline structures of *cis*-1,2-cyclohexanediol and of (1*S*,2*S*)-*trans*-cyclohexanediol were determined by X-ray diffraction and are different. The *cis*-isomer crystallizes in the orthorhombic *Pbca* space group[26] and the *trans*-isomer in the hexagonal $P3_121$.[27] Consequently, it is not unexpected that they have different heat capacity values, and naturally, the Goodman method cannot predict with similar precision the heat capacity for both isomers.

The heat capacity of pure organic liquids, from the normal melting temperature to the normal boiling point, can be estimated by the Rûžička et al.[2,3] group contribution method as follows

$$\frac{C_{p,m}}{R} = \sum_{i}^{k} n_i \Delta c_i \qquad (5)$$

n_i has the meaning given above, and Δc_i is the dimensionless value of the contribution of group i which the authors express as a function of temperature. For *cis*-1,2-cyclohexanediol, the following equation is obtained

$$\frac{C_{p,m}}{R} = -7.234046 + 0.1489962(T/\mathrm{K}) - 1.31617 \cdot 10^{-4}(T/\mathrm{K})^2 \qquad (6)$$

and for the *trans*-isomer

$$\frac{C_{p,m}}{R} = -9.68424 + 0.17200235(T/\mathrm{K}) - 1.813786 \cdot 10^{-4}(T/\mathrm{K})^2 \qquad (7)$$

The values obtained in the present work are higher than those estimated by the Rûžička method for both compounds, with the differences, presented in Tables 1 to 3, being of the order of 20 % for the *trans*-isomer and about 15 % for the *cis*-one. In their work, Zabransky and Rûžička[3] stress some problems in the prediction of heat capacity values for diols, namely, high uncertainty or inadequate temperature dependence.

Concluding Remarks

Heat capacity gives evidence for the structural differences accompanying the fusion process of 1,2-cyclohexanediol isomers. The fusion of the *cis*-isomer takes place in two steps, and a disordered solid phase resulting from the crystalline phase is obtained before the isotropic liquid. The (1*R*,2*R*)- and (1*S*,2*S*)-enantiomers of the *trans*-isomer show a one-step fusion process.

Comparison of heat capacity group contribution predictions with experimental data shows that the Goodman et al.[1] power law method for organic solids gives quite satisfactory results, except for the *cis*-isomer for temperatures below 250 K, where deviations rise up to −20 %, whereas the estimates resulting from the Rûžička et al. method for liquids are systematically lower by (15 to 20) % than the results obtained in the present work.

Supporting Information Available:

Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review January 17, 2008. Accepted March 26, 2008.

JE800047T