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Heat capacity of β-alanine in a temperature range between 6 and 300 K

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Abstract Thermodynamic properties of β-alanine in the temperature range 6.3–301 K were studied. No phase transitions were observed for the sample specially prepared to contain no solvent inclusions. At 298.15 K the calorimetric entropy and the difference in the enthalpy values are equal, respectively, to 126.6 $\mathrm{JK^{-1}\,mol^{-1}}$ and 19.220 $\mathrm{Jmol^{-1}}$. The $C_p(T)$ in the temperature range 6–16 K can be well described by Debye equation $C_p = AT^3$. A comparison of the data on the entropies of glycine polymorphs and of β-alanine was used to show, that the empirical Parks–Huffman rule holds in the case of these compounds.

Keywords Adiabatic calorimetry · β-Alanine · Heat capacity · Molecular crystals · Thermodynamic functions

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Introduction

Thermodynamic studies of crystalline amino acids attract much attention, since these systems can be used as molecular materials, drugs and biomimetics [1]. They represent examples of crystals formed by flexible zwitter-ions linked with each other by a network of hydrogen bonds of several types (NH…O, OH…O, SH…O, etc.). The properties of the crystalline amino acids result from an interplay of the intramolecular vibrations with strong dipole-dipole interactions, hydrogen bonds and Van der Waals interactions between the zwitter-ions. In our previous work we have studied in details the thermodynamic properties of several crystalline amino acids: the three polymorphs of glycine, $\mathrm{NH_3^+–CH_2–COO^-}$, to compare the properties of different crystal structures formed by the same molecules [2–5]; D- and DL-serine $\mathrm{NH_3^+–CH–(CH_2OH)–COO^-}$ [6], L- [7, 8] and DL- [9] cysteine, $\mathrm{NH_3^+–CH–(CH_2SH)–COO^-}$, to study the effect of the side chains and to compare the properties of chiral and racemic crystals. To see the effect of the length of a molecule, we have compared the thermodynamic properties of glycine ($\mathrm{NH_3^+–CH_2–COO^-}$, gly), glycilglycine ($\mathrm{NH_3^+–CH_2–CO–NH–CH_2–COO^-}$, glygly) [10], and diglycilglycine ($\mathrm{NH_3^+–CH_2–CO–NH–CH_2–CO–NH–CH_2–COO^-}$, glyglygly) [11]. Another possibility to increase the length of a molecule is to add an extra methylen ($\mathrm{–CH_2–}$) group to it (i.e., to get β-alanine, $\mathrm{NH_3^+–CH_2–CH_2–COO^-}$, instead of glycine, $\mathrm{NH_3^+–CH_2–COO^-}$). The crystals of β-alanine were previously studied in the temperature range 75–320 K by optical birefringence measurements, and by dilatometry, and a phase transition at 204 K on cooling and at 235 K on reverse heating was reported [12]. Calorimetry studies of β-alanine were reported in [13]: heat capacity was measured in the 298–348 K temperature range using the DSC

Table 1 Experimental values of the heat capacity C_p^o of β-alanine in J K^{-1} mol^{-1}

T, K	C_p^o	*T*, K	C_p^o	*T*, K	C_p^o	*T*, K	C_p^o
6.30	0.1535	35.83	15.72	124.10	60.59	245.48	99.34
8.40	0.3456	39.41	18.31	131.07	62.98	250.47	100.93
9.46	0.5230	42.99	20.80	138.13	65.37	255.42	102.50
10.54	0.7521	47.34	23.77	145.20	67.69	260.33	104.06
11.61	0.9936	52.45	27.11	153.70	70.42	265.20	105.63
12.92	1.380	57.53	30.32	163.66	73.61	270.05	107.23
14.49	1.949	62.56	33.33	173.62	76.79	274.93	108.70
16.09	2.629	67.57	36.20	183.60	79.90	279.86	110.27
17.65	3.395	72.55	38.84	193.52	83.12	284.82	111.88
19.20	4.251	77.52	41.35	203.39	86.31	289.75	113.48
20.76	5.154	82.71	43.83	210.86	88.70	294.07	114.73
22.59	6.320	87.80	46.18	215.81	90.08	295.08	115.18
24.63	7.644	92.83	48.39	220.73	91.59	296.56	115.68
26.68	9.007	97.83	50.54	225.68	93.21	298.05	116.17
28.76	10.50	102.86	52.63	230.67	94.75	298.68	116.23
30.88	12.01	110.05	55.46	235.62	96.27	300.98	117.13
32.99	13.55	117.10	58.06	240.53	97.81		

technique. No low-temperature measurements of the $C_p(T)$ have been reported.

The aim of the present contribution was to study the thermodynamic properties of the crystalline β-alanine by adiabatic calorimetry and DSC at low temperatures, in order to compare the results with the data obtained previously for the polymorphs of glycine.

Experimental

Samples

The crystalline sample of β-alanine purchased from Fluka (batch [107-59-9], purity >99%) contained solvent inclusions, which distorted the results of the calorimetry experiments.[1] A sample free from solvent inclusions was prepared by re-crystallization from aqueous solution using ethanol as an antisolvent with a subsequent drying during several hours at ambient temperature. An X-ray diffraction analysis has confirmed the presence of the only crystalline phase in the sample—β-alanine with the crystal structure in space group Pbca [14]. All the data discussed further in the present contribution refer to this re-crystallized inclusions-free sample.

Experimental techniques and the results of the measurements

Heat capacity was measured in the temperature range 6.3–301 K using an automatic vacuum adiabatic calorimeter [15], similarly to the previously described studies of other crystalline amino acids [2–9]. Calorimetry experiments were carried out using the step-wise heating; 67 experimental points were obtained. The measurements results are given in Table 1. Average statistical dispersion of the heat capacity values was 0.4% at temperatures 6–20 K, 0.2% at 20–50 K, and 0.04%—in the range between 50 and 300 K. The experimental $C_p(T)$ curve is plotted in Fig. 1.

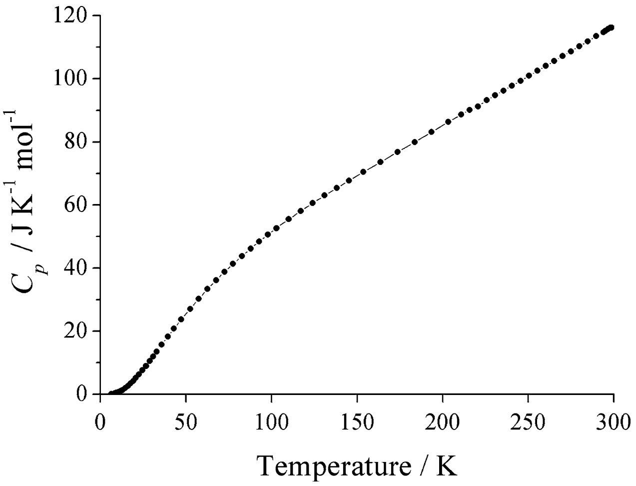

Fig. 1 *Cp(T)* measured for a sample of β-alanine free of solvent inclusions

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[1] The Cp(T) curve measured for the sample with solvent inclusions had a pronounced peak at about 256 K, corresponding to melting of inclusions (about 0.14% of the total sample mass), which could be erroneously taken for a phase transition in β-alanine.

Table 2 Heat capacity and the thermodynamic parameters of β-alanine; $C_p^o(T)$, $S^o(T)^o - S^o(0)$/J K^{-1} mol$^{-1;}$ $H^o(T) - H^o(0)$/J mol^{-1}

T, K	$C_p^o(T)$	$S^o(T)^o - S^o(0)$	$H^o(T)^o - H^o(0)$
6.295	0.1531	0.05104	0.2410
10	0.6277	0.2018	1.513
15	2.156	0.7087	8.017
20	4.700	1.657	24.80
25	7.876	3.039	56.06
30	11.38	4.781	104.1
35	15.02	6.807	170.1
40	18.64	9.050	254.3
45	22.15	11.45	356.3
50	25.52	13.96	475.6
60	31.81	19.18	762.7
70	37.47	24.51	1110
80	42.56	29.86	1510
90	47.19	35.14	1959
100	51.46	40.34	2453
120	59.12	50.41	3560
140	65.99	60.05	4812
160	72.48	69.29	6198
180	78.84	78.19	7711
200	85.17	86.82	9351
220	91.42	95.24	11110
240	97.66	103.5	13010
260	104.0	111.5	15020
280	110.3	119.5	17170
298.15	116.1 ± 0.2	126.6 ± 0.2	19220 ± 20
300	116.7	127.3	19440
300.982	117.1	127.7	19550

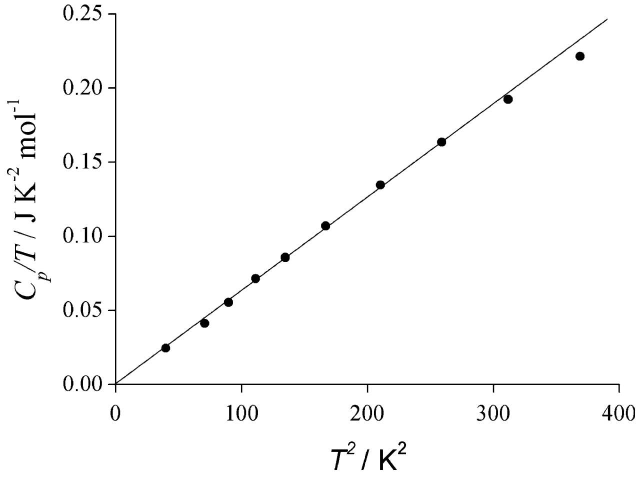

Fig. 2 Approximation of the low-temperature range of $C_p(T)$ curve for crystalline β-alanine by the Debye law

The measured $C_p(T)$ dependence was smoothed, in order to calculate the thermodynamic functions (Table 2). The values of C_p in the temperature range 0–6.3 K, which were necessary for the calculations, were obtained by extrapolation of the experimental $C_p(T)$ curve down to $T = 0$ K using the Debye equation $C = AT^3$. This equation was shown to describe well enough the experimental data in the temperature range 6.3–13 K, what makes it possible to approximate a crystal of β-alanine by Debye continuum (Fig. 2). The DSC data were in a good agreement with the results from the adiabatic calorimetry.

Discussion

A comparison of the results obtained in this study with the data published for the C_p of β-alanine at 298 K [13] gives a large (6.5%) dicrepancy, what exceeds the common accuracy of the DSC measurements. The value of the C_p (298.15 K) obtained in this study (116.1 JK^{-1} mol^{-1}) is higher than that published in [13]. In a previous publication [11] we have already noted, that the thermodynamic data for selected amino acids and peptides reported in [13] are about 5–7% lower, than the results published by other authors [16–21]. Possible reasons for this have been discussed elsewhere [11].

The thermodynamic parameters calculated for β-alanine on the basis of the experimental $C_p(T)$ study can be compared with those previously obtained for the three polymorphs of glycine [2–5]. Of special interest is to compare the values of entropy at ambient conditions, S^o (298.15 K). In an earlier publication on normal crystalline alkanes [22], the values of the S^o (298.15 K) for the closest homologues (differing in one CH_2- methylene group) were shown to differ at 24.3 JK^{-1} mol^{-1}. The values of S^o (298.15 K) for the neighbouring members of another homologic series, namely of β-alanine and α-glycine, differ at similar values, i.e. at 22.9 kJ mol^{-1}. This is a very good agreement, taking into account the typical values of the precision and the accuracy of the heat capacity measurements at 298.15 K. The difference between the absolute entropy values at 298.15 K for all the three polymorphs of glycine is less than one percent, indicating that molecular, and not the crystal structure determines these values. Thus, the Parks-Huffman rule [22] can be supposed to hold also for the homologic series of crystalline amino acids. In this respect, it would be interesting to study also the thermodynamic properties of the next members in the same homologic series, namely of the γ-aminobutyric acid.

Comparison of the heat capacity values between series of glycines (alpha-glycine [4], glycylglycine [10], and diglycylglycine [11]), L-alanine [19], and beta-alanine is shown in Fig. 3. Heat capacities are normalized to the average gram-atom, i.e., to the number of oscillators. It is very interesting that the difference between beta- and L-alanine is much greater than that between L-alanine and

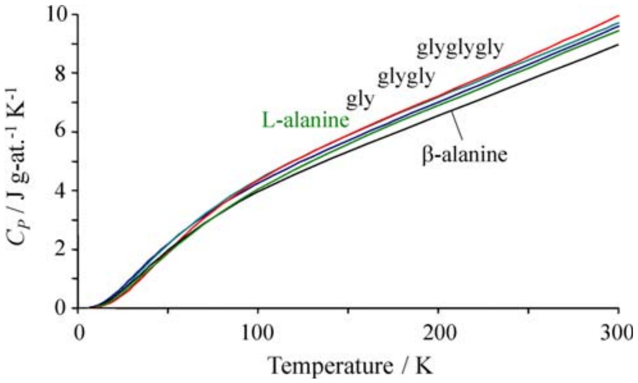

Fig. 3 Heat capacity of alpha-glycine [4], glycylglycine [10], and diglycylglycine [11]), L-alanine [19], and beta-alanine (this work). Beta-alanine has the least heat capacity, differing from L-alanine much greater than L-alanine from all glycines

glycines. This result is very important in the development of the algorithm of estimation of the heat capacity for crystalline amino acids.

Conclusions

As a result of the adiabatic calorimetry measurements in a wide temperature range from 6.3 K up to ambient, thermodynamic parameters for the crystalline β-alanine were calculated. The occurrence of a low-temperature first-order phase transition, which was claimed in [12], was not confirmed by our study. The $C_p(T)$ function in the temperature range 6–16 K was shown to be well approximated by the Debye equation $C_p = \mathrm{AT}^3$. A comparison of the values of absolute entropy for glycine and for β-alanine has shown that the empirical Parks-Huffman rule that was suggested for the homologues of normal alkanes differing in the number of the methylene CH_2 chains holds also for these amino acids.

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