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HEAT CAPACITY OF *D*- AND *DL*-SERINE IN A TEMPERATURE RANGE OF 5.5 TO 300 K

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Heat capacity of *D*- and *DL*-serine was measured using adiabatic calorimetry in a temperature range of 5.5 to 300 K, and then thermodynamic functions were calculated. The difference in heat capacity (C_{PD}–C_{PDL}) between two species indicates a small anomaly in *D*-serine near 15 K and a systematic excess over *DL* for temperatures >30 K. This is much larger, than a difference in thermodynamic functions measured so far for the polymorphs of organic molecular crystals. The excess is fitted well to Einstein contribution with characteristic temperature of 185 K which is equivalent to vibrational mode at 129 cm^{-1}.

Keywords: *adiabatic calorimetry, enantiomorph, heat capacity, molecular crystals, racemate, serine*

Introduction

The problem of comparing the properties of racemic crystals and of their chiral counterparts attracts attention, at least, since the end of the 19th century. In 1895, on the basis of eight pairs of compounds Wallach has supposed crystal structures of racemic compounds to be denser, than those of the corresponding chiral ones [1]. This hypothesis is now termed as a 'Wallach's rule', although more recent studies based on much larger statistical surveys did not confirm this 'rule' [2]. The problem of relative densities of chiral/racemic crystals was usually considered in relation to the problem of their relative thermodynamic stability, what is of importance for crystal engineering of molecular materials (e.g., NLO compounds) and pharmaceuticals, and for control of their properties. Racemic crystals were stated to be more stable, than their chiral counterparts [3].

Despite the large importance of comparing relative thermodynamic stability of racemic *vs.* chiral compounds, to the best of our knowledge, almost no reliable thermodynamic data are available in the literature. The conclusions on relative stability of racemic and enantiomeric crystals made on the basis of comparing relative densities, packing coefficients, heats of fusing or melting points can be considered as preliminary hypothesis only, requiring further testing [2]. Adiabatic calorimetry is known to be the best appropriate technique for a direct comparison of the thermodynamic functions of compounds. Thermodynamic and thermoanalytic measurements are carried out usually only with enantiomeric forms, not racemic [4, 5]. Very restricted data on heat capacity of racemic amino acids are available. The data are scarce in the number of substances and short in the temperature range of measurements: *DL*-alanine (85 to 298 K) and *DL*-leucine (86 to 297 K) [6], *DL*-citrulline and *DL*-ornithine (90 to 298 K) [7]. Therefore, we have initiated a project aimed at comparative studies of chiral/racemic pairs of the same compounds using adiabatic calorimetry. As the priority systems to study, we have selected amino acids, due to the obviously large importance of these compounds not as molecular materials and drugs only, but also in relation to biological and cosmological problems.

The first compound to be considered in the present work is serine, $C_3H_7NO_3$, – one of the smallest amino acids possessing optical rotation, known to crystallize in two chiral forms, *L*-serine and *D*-serine (space group $P2_12_12_1$), and also as a racemate, *DL*-serine (space group $P2_1/n$) [8]. It is worthy noting, that the pair does not obey the 'Wallach's rule', the density of *L*-serine being noticeably larger, than that of *DL*-serine [8–10]. A remarkable difference in the response of the structures of *L*- and *DL*-serine to variations in *T* and *P* was reported recently – thermal expansion of the *L*- and *DL*-forms as well as the anisotropy of strain on cooling and with increasing pressure are very different [9, 10], besides, *DL*-serine is stable with respect to phase transitions with increasing pressure at least up to 8.6 GPa [11], whereas *L*-serine undergoes phase transitions – at 5.3 GPa

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[11, 12] and at 7.8 GPa [11], which proceed differently in polycrystalline samples and in single crystals (Boldyreva, Sowa, Chernyshev, Drebushchak, Dmitriev and Ahsbahs, to be published).

The aim of the present work was to measure heat capacity of two species of serine, enantiomorphic and racemic, and to search for the difference in their heat capacity. Heat capacity of *L*-serine was measured previously in a temperature range of 11 to 305 K and no phase transitions or even irregularities in function $C_P(T)$ were found [13]. Data on the heat capacity of *DL*-serine, to the best of our knowledge, were unknown. Instead of repeating the experiments with *L*-serine, we chose the opposite counterpart, *D*-serine, to check the difference in their heat capacity as well. Pure *L*- and *D*-forms of any substance with optical rotation are identical in structure. If also identical in composition (purity, isotopic composition of constituent elements, etc.), they have to be identical in thermodynamic properties. Nevertheless, there are sometimes different data for opposite optical counterparts (*L*- and *D*-) in thermodynamic reports (for example, in CRC Thermodynamic Handbook [14]), and we wanted to make an extra test for *L*- and *D*-serine.

Experimental

D-serine of ICN Biomedicals Inc. and *DL*-serine of MERCK-Schuchardt (105.093 g mol^{-1}) were used as purchased. According to X-ray powder diffraction patterns, our *D*-serine is orthorhombic (s.g. $P2_12_12_1$) with a=0.56168(5), b=0.85955(8), c=0.93486(6) nm, and the density of 1.549 g cm^{-3}, what is in a good agreement with the single-crystal data reported for *L*-serine [8, 9]; *DL*-serine is monoclinic (s.g. $P2_1/n$) with a=0.48407(4), b=0.91632(7), c=1.04708(10) nm, β=99.809(4)°, and the density of 1.531 g cm^{-3}, also in a good agreement with the single-crystal data [8–10]. The parameters were refined using software TOPAS after X-ray powder diffraction measurements on diffractometer D8-GADDS (Bruker).

D-serine was found to contain the impurity of racemate, for its X-ray powder diffraction patterns had a very weak peak at 16.54°, assigned to reflection (002) of *DL*-serine. X-ray powder diffraction experiments with binary mixtures of *D* and *DL* samples allowed us to determine that the purchased *D*-serine contains 1.7±0.9% of *DL*-serine.

Low-temperature calorimetric measurements were carried out using vacuum adiabatic calorimetric system working over the temperature range of 4.2–320 K, described elsewhere [15]. Sample mass in the calorimeter of 5.7 cm^3 was 3.9817 g for *DL*-serine and 2.70565 g for *D*-serine. The samples were loaded into the calorimeter, to fill its volume as full as possible. Since the densities of *D*- and *DL*-serine differ by 1.1% only, the large difference in sample mass deserves much attention (‘Results and Discussion’). The calorimeter with the sample was evacuated at ambient temperature and filled with helium at a pressure of 30 mm Hg.

Results and discussion

Low-temperature heat capacity of *D*-serine was measured at 69 points over the temperature range of 5.5 to 300 K and that of *DL*-serine at 64 points from 5.5 to 304 K. Measured values are listed in Tables 1 and 2 in order of temperature. The standard deviation of the experimental points from the smoothed curve is 0.45% for T<10 K, 0.26% for 10<T<50 K, and 0.04% for T >50 K (*D*-serine) and 0.59% for T<10 K, 0.06% for 10<T<50 K and 0.03% for T>50 K (*DL*-serine). At very low temperatures the heat capacity of both substances can be fitted to the Debye model $C_P=aT^3$ for the extrapolation to zero temperature: 0–5.9 K for *DL*-serine and 0–5.8 K for *D*-serine. The temperature range of the fitting is nearly the same for both substances, but the functional relations $C_P(T)$ differ significantly. These are shown in coordinates C_P/T *vs.* T^2 in Fig. 1. For *DL*-serine, $C_P(T)$ fits quite reasonably to the straight line in a temperature range of 5.5 to 8 K with a=0.694 mJ mol^{-1} K^{-4}. For *D*-serine, the Debye model is applicable only to first two points, with C_P increasing faster than the cubic function of temperature:

$$\frac{d\ln C}{d\ln T}>3 \qquad (1)$$

In general, one should conclude that the Debye model is not quite applicable to the low-temperature heat capacity of *D*-serine. Here, we use it only for the extrapolation of $C_P(T)$ data to zero temperature. Smoothed values of heat capacity and derived thermodynamic functions are in Tables 3 and 4 for *D*- and

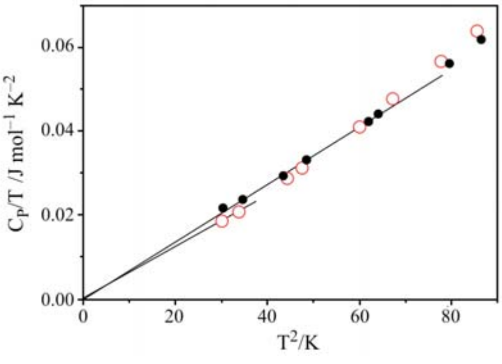

Fig. 1 Low-temperature heat capacity of *D*- (open circles) and *DL*-serine (filled circles). Fitting cubic functions $C_P=aT^3$ for the extrapolation to 0 K are shown by solid lines. Points of *D*-serine cross the solid line of *DL*-serine near 65 K due to the fast growth of C_{PD} with temperature

Table 1 Experimental heat capacities of *D*-serine (formula mass=105.093 g mol^{-1})

Temperature/K	C_P/J mol^{-1} K^{-1}	Temperature/K	C_P/J mol^{-1} K^{-1}	Temperature/K	C_P/J mol^{-1} K^{-1}
5.486	0.1018	30.030	12.90	112.071	66.17
5.814	0.1213	32.590	15.03	119.045	69.28
6.657	0.1917	35.678	17.65	125.985	72.18
6.887	0.2149	38.789	20.27	132.913	75.04
7.739	0.3179	41.861	22.78	139.851	77.76
8.193	0.3917	44.902	25.31	146.810	80.51
8.815	0.5004	48.956	28.58	155.287	83.75
9.245	0.5914	54.010	32.54	165.199	87.43
9.921	0.7444	59.009	36.27	175.045	91.04
10.295	0.8481	63.970	39.79	184.822	94.56
10.976	1.027	68.948	43.17	194.637	98.05
11.349	1.154	73.927	46.24	204.502	101.58
12.409	1.523	78.929	49.24	214.334	105.09
13.592	1.999	81.012	50.58	224.148	108.64
14.859	2.564	82.991	51.74	234.028	112.13
16.106	3.189	83.942	52.17	243.982	115.63
17.370	3.876	84.961	52.80	253.932	119.12
18.644	4.611	86.963	53.93	263.883	122.62
19.906	5.405	88.998	54.99	273.839	126.13
21.652	6.590	89.238	55.10	283.801	129.67
23.730	8.052	94.191	57.69	293.698	133.22
25.842	9.608	99.151	60.21	295.539	133.95
27.958	11.22	105.115	63.00	298.897	135.07

DL-serine, respectively. The functions for *D*-serine were corrected for the impurity of *DL*-serine (1.7%) in the sample.

The functions $C_P(T)$ for *D*- and *DL*-serines are smooth, without sharp or even weak peaks over the whole temperature range of the measurements. There was no evident indication of a phase transition either in *D*-, or in *DL*-serine, but smooth anomalies were found after thorough comparison between them. This agrees with the X-ray diffraction data, at least down to 100 K for *L*-serine [9] and down to 20 K for *DL*-serine [10, 16].

Difference in heat capacity among D, L and DL-serines

D- and *L*-serines are to be identical both in structure and in thermodynamic functions. This is the consequence from the principle of symmetry. In comparing our data for *D*-serine with those for *L*-serine in [13], we should consider any difference as the result from the sample quality or inaccuracy of experimental technique. The difference (in per cent) between heat capacities of *L*-serine [13] and *D*-serine (this work) is shown in Fig. 2 (open symbols). The difference is less than 1% above 25 K, and is nearly constant (~0.5%) above 100 K. The difference increases up to 6% at very low temperatures (10 K), and the reason for this is not quite clear.

The difference between heat capacities of *D*- and *DL*-serines (this work) is shown in Fig. 2 (filled circles). This has two peaks, a narrow one near 15 K, and another broad peak with a flat maximum about 70 K. The peak near 15 K is of unknown nature and seems to be similar to the effects found previously in γ-glycine [15] and glycylglycine [17]. The similarity includes the temperature range (13–17 K) and a very fast growth of heat capacity (Eq. (1)). The smooth

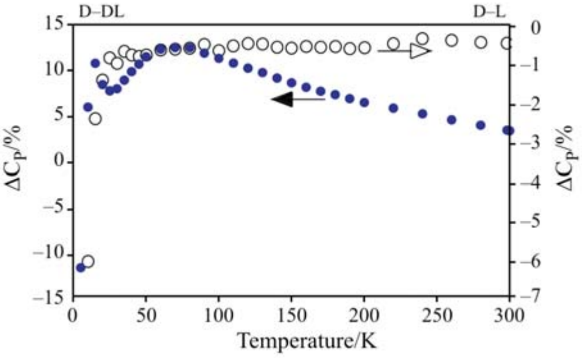

Fig. 2 Differences 1 – between heat capacities of *D*- and *DL*-serine (filled circles, left scale) and 2 – between *D*- and *L*-serine (open circles, right scale). An anomaly near 15 K is seen for *D–DL* as a narrow peak of 11%

Table 2 Experimental heat capacities of *DL*-serine (formula mass=105.093 g mol^{-1})

Temperature/K	C_P/J mol^{-1} K^{-1}	Temperature/K	C_P/J mol^{-1} K^{-1}	Temperature/K	C_P/J mol^{-1} K^{-1}
5.512	0.1197	29.410	11.51	129.053	67.02
5.887	0.1404	32.026	13.45	135.915	69.77
6.592	0.1938	35.182	15.83	142.742	72.47
6.964	0.2312	38.350	18.19	151.121	75.79
7.868	0.3330	41.492	20.45	161.041	79.54
8.000	0.3539	44.583	22.69	170.906	83.18
8.913	0.5019	47.650	24.80	180.746	86.84
9.293	0.5752	51.719	27.61	190.577	90.46
9.972	0.7169	56.782	30.94	200.413	94.06
10.401	0.8157	61.847	34.15	210.261	97.72
11.028	0.9726	66.833	37.19	220.061	101.24
11.492	1.098	71.781	40.04	229.839	104.90
12.651	1.462	76.771	42.76	239.707	108.50
13.918	1.930	81.738	45.41	249.547	112.10
15.203	2.470	86.703	48.02	259.292	115.70
16.523	3.103	87.550	48.51	269.078	119.34
17.978	3.870	92.578	50.97	278.910	123.00
19.589	4.806	97.595	53.39	288.715	126.68
21.229	5.812	102.564	55.68	298.498	130.41
23.118	7.050	108.454	58.32	299.050	130.61
25.223	8.496	115.296	61.29	302.553	132.12
27.311	9.968				

broad ‘peak’ with maximum near 70 K is an unusual finding for crystalline amino acids. Heat capacity of one ‘polymorph’, *D*-serine, is significantly higher than that of another one, *DL*-serine, almost over the whole temperature range of the measurements.

Absolute values of the difference in heat capacity between *D*- and *DL*-serine *vs*. temperature are plotted in Fig. 3. The difference increases rapidly with temperature from –0.01 J mol^{-1} K^{-1} at 5 K to 6.5 J mol^{-1} K^{-1} near 130 K. These values are much larger, than the difference in heat capacity between polymorphs of glycine [15, 18], or paracetamol [19] that we measured before. It is interesting, that the value of the difference is close to one degree of freedom (R=8.314 J mol^{-1} K^{-1}). The rest 8.3–6.5=1.8 J mol^{-1} K^{-1} is about 2.5% of total heat capacity. This smaller value can result from the difference in crystal structures of *D*- and *DL*-serine (for a comparison, the difference in heat capacity between α- and γ-polymorphs of glycine near 298.15 K is as large as 5%). Similar effects were observed in cation-exchanged forms (Tl and K) of natural zeolite natrolite (mainly Na) [20]. The effect was attributed to the Einstein mode arising from the isolation of a heavy cation (Tl or K) inside the water-cation subsystem of zeolite. Einstein contribution was calculated by the subtraction of C_P of natural sample from that of cation-exchanged one. Here we carried out similar calculations, namely the subtraction of C_P of *DL*-serine from that of *D*-serine. The Einstein contribution with one degree of freedom is

$$C_E(T)=R\frac{x^2}{\exp(x)+\exp(-x)-2},\quad x=\frac{\Theta_E}{T} \tag{2}$$

where Θ_E is the Einstein temperature. Solid line in Fig. 3 was calculated according to Eq. (2) with the value of Θ_E=185 K. The plot is very similar to that of the Einstein contribution for Tl-natrolite: the contribution rapidly increases from the very start and then slowly decreases with temperature after reaching a smooth

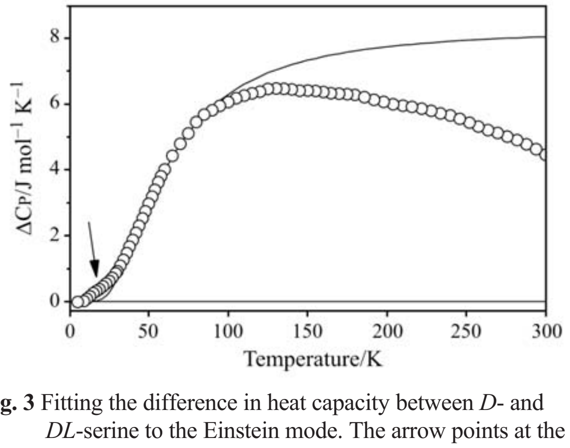

Fig. 3 Fitting the difference in heat capacity between *D*- and *DL*-serine to the Einstein mode. The arrow points at the anomaly in a temperature range of 13–17 K (Fig. 2)

Table 3 Thermodynamic functions of *D*-serine (formula mass=105.093 g mol^{-1})

T/K	C_P/ J mol^{-1} K^{-1}	$H(T)$–$H(0)$/ J mol^{-1}	*S*/ J mol^{-1} K^{-1}
5	0.0769	0.0962	0.0256
10	0.7670	1.761	0.2304
15	2.638	9.801	0.8568
20	5.477	29.74	1.985
25	8.985	65.72	3.576
30	12.90	120.3	5.553
35	17.09	195.2	7.854
40	21.29	291.2	10.41
45	25.42	408.0	13.16
50	29.46	545.2	16.04
60	37.06	878.4	22.10
70	43.90	1284	28.34
80	50.02	1754	34.61
90	55.61	2283	40.83
100	60.67	2864	46.95
110	65.37	3495	52.96
120	69.78	4171	58.84
130	73.97	4890	64.59
140	77.95	5649	70.22
150	81.84	6449	75.72
160	85.62	7286	81.13
170	89.31	8161	86.43
180	92.94	9072	91.64
190	96.51	10019	96.76
200	100.06	11002	101.81
220	107.24	13075	111.68
240	114.35	15291	121.31
260	121.34	17648	130.74
280	128.41	20146	139.99
298.15	134.91	22535	148.25
300	135.58	22785	149.09

maximum, about 1.8 J mol^{-1} K^{-1} less than *R*. We do not know with certainty what is the reason of the Einstein contribution and why it produces only one degree of freedom per molecule of *D*-serine. Anyway, this phenomenon affects the thermodynamic functions of *D*-serine very much as compared to those of *DL*-serine, producing the difference in entropy and enthalpy much greater as compared to the difference resulting from the molecule arrangement in the polymorphs of molecular crystals (glycines, paracetamol). Einstein contribution can be caused by the vibrational mode at 129 cm^{-1}. Unfortunately, we have no information on the low-energy part of the vibrational spectra of *L*-, *D*- and *DL*-forms of serine, their study is in progress.

Table 4 Thermodynamic functions of *DL*-serine (formula mass=105.093 g mol^{-1})

T/K	C_P/ J mol^{-1} K^{-}	$H(T)$–$H(0)$/ J mol^{-1}	*S*/ J mol^{-1} K^{-1}
5	0.08674	0.1084	0.0289
10	0.7235	1.751	0.2327
15	2.382	9.045	0.8017
20	5.050	27.27	1.832
25	8.336	60.55	3.304
30	11.94	111.2	5.139
35	15.69	180.2	7.261
40	19.38	268.0	9.599
45	22.97	373.9	12.09
50	26.43	497.4	14.69
60	33.00	795.1	20.10
70	39.03	1156	25.65
80	44.49	1574	31.22
90	49.71	2045	36.76
100	54.51	2566	42.25
110	59.00	3134	47.66
120	63.30	3746	52.98
130	67.39	4399	58.21
140	71.41	5093	63.35
150	75.32	5827	68.41
160	79.15	6599	73.39
170	82.89	7410	78.30
180	86.55	8257	83.14
190	90.24	9141	87.92
200	93.93	10062	92.65
220	101.26	12013	101.94
240	108.60	14112	111.07
260	115.96	16358	120.05
280	123.39	18751	128.92
298.15	130.32	21053	136.88
300	131.04	21295	137.69

Relation to the structure

In ‘Experimental’, it was reported that the sample mass of *D*-serine (2.70565 g) placed inside the calorimeter was significantly less than that of *DL*-serine (3.9817 g), despite close densities for the two crystal structures (1.549 and 1.531, respectively). The situation is very similar to that observed for α- and γ-forms of glycine: the sample mass in the calorimeter of 5.7 cm^3 was 5.6988 g for α polymorph and 3.3513 g for γ-polymorph. The difference in the sample mass for glycine polymorphs was due to the difference in the packing of small crystals of a powder. γ-Glycine had the peak in $C_P(T)$ near 15 K due to the fast increase in heat capacity, faster than T^3 of the Debye model [15]. This effect was supposed to be due to the piezoelectric properties of γ-glycine: the crystals of γ-glycine repel from each other due to the dipole electric interaction, whereas the crystals of α-glycine pack in the calorimeter as close as possible. We have no information about piezoelectric properties *L*-serine, but can consider the same phenomenon for the explanation of differences in heat capacity and sample mass in calorimeter, supposing that *D*-serine (sp. gr. $P2_12_12_1$, no inversion center) can be piezoelectric, and *DL*-serine (space group/$P2_1/n$, centrosymmetric) cannot. We plan to perform special experiments to clarify the nature of the difference in heat capacity between *D*- and *DL*-serine and define what is the source of the Einstein mode in *D*-serine.

It was found recently for glycine polymorphs that the phase transitions under variable pressure correlate with anomalies in the heat capacity. Metastable α-glycine has no anomalies both in $C_P(T)$ [15] and in Raman spectra under variable pressure up to 23 GPa [21]. Stable γ-glycine has an anomaly in $C_P(T)$ near 10 K [15] and an extended phase transition starting from 2 GPa, detected by Raman spectra [22] and X-ray diffraction under variable pressure [23–27]. Unstable β-glycine has the second-order phase transition at 252 K, manifesting itself as a peak in $C_P(T)$ [18], and a reversible phase transition at 0.76 GPa, detected by Raman spectroscopy [28] and X-ray diffraction [27]. In continuing the analogy between the effects of temperature and pressure in glycine polymorphs, we would expect that *L*-serine has to possess an anomaly in the heat capacity at very low pressures, as compared to *DL*-serine. The present study has confirmed this hypothesis. Further comparative studies of the effect of low temperature and high pressure on *L*- and *DL*-amino acids will show, if the existence of anomalies in heat capacity at very low temperatures really correlate with the occurrence of phase transitions under increasing pressure.

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