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Thermal study of L-alanine, L-threonine, and taurine crystals related to hydrogen bonding

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Abstract In this study L-alanine, L-threonine, and taurine crystals were characterized through dilatometric technique and thermogravimetric and differential thermal analysis. The dilatometric analysis shows that the thermal expansion of the crystals is correlated with the strengths of local hydrogen bonding in the amino acid structures at room temperature. Thermogravimetric analysis and differential thermal analysis of the L-alanine, taurine, and L-threonine crystals have been performed at high temperatures. No clear correlation between the hydrogen bonding strengths and endothermic peak positions was observed.

Keywords L-Alanine · L-Threonine · Taurine · Thermal analysis · Dilatometry

Introduction

Amino acids are hydrogen-bonded crystals which can crystallize as dipolar species known as zwitterions or dipolar ions. Zwitterions form N–H–O hydrogen bonds between a positively charged segment, ammonium groups $-\text{NH}_3^+$, and a negatively charged segment, $-\text{CO}_2^-$. The

amino acids can involve other important interactions such as van der Waals interaction and electrostatic forces. The interest in hydrogen bonds from a biological point of view has recently increased as a consequence of both the hypotheses concerning the role of the low-barrier hydrogen bonds in enzyme catalysis [1] and the importance of these interactions in theoretical methods for drug design [2]. In amino acids, the basic units of proteins and peptides, the existence of the zwitterions and hydrogen bonds is limited to the solution and solid states, being not observed in gas phase [3].

Experimental investigations of the influence of hydrogen bonds interactions between zwitterions related to the problem of molecular dynamics of ammonium groups ($-\text{NH}_3^+$) in the amino acids L-alanine, taurine, and L-threonine crystals under high-pressure conditions were previously reported [4]. We observed that for L-threonine and taurine the wave number of the bands associated to the torsional vibration of NH_3 increases with pressure increase (a natural behavior), while for L-alanine the wavenumber decreases with pressure increase (a special behavior). These results are explained in terms of differences in both the strengths (evaluated for the average of the length the N–O distances) and the environments of the hydrogen bonding in these specific amino acid structures. This study intends to give a contribution to a unified approach to hydrogen bond theory to amino acid systems through a study of L-alanine, taurine, and L-threonine crystals involving thermomechanical analysis (TMA). The thermal property under the scrutiny is the thermal strain, defined as the product of the coefficient of thermal expansion and the temperature change of the material, $\Delta L/L_0 = \alpha \Delta T$. So, in this study we have performed a TMA of the solid phase of the three amino acid crystals and we have studied utilizing thermogravimetric (TG) and differential thermal analysis

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(DTA) the transition from the zwitterion solid state phase to the non-zwitterion gas phase at high temperatures.

Experimental

Single crystals of L-alanine, taurine, and L-threonine were grown from aqueous solution. Reagents purchased from “Sigma” Chemical Co. purity $\geq 98\%$ were used. The solution was filtered using sintered glass filter of 1- μm pore size. The solution was saturated at room temperature by gradual slow evaporation. Transparent colorless crystals were grown in 30–40 days. To confirm the structure and find the morphology of the crystals, X-ray diffraction patterns of crushed L-alanine, taurine, and L-threonine powder were recorded using a Philips Analytical X-ray diffractometer (Model PW1710) with Cu K α radiation. The 2θ scan angle was varied from 2° to 70° with a step size of 0.020° .

Thermal expansion experiments were performed on a dilatometer DIL 402C from Netzsch at a heating rate of 1°C min^{-1} under vacuum. The relative expanded uncertainty in the measurement was estimated to be 1.1–1.5 %. A software—Proteus Analysis—was used to retrieve, compare and export thermal data to an analysis software. Each sample was heated between the temperature range 40–160 $^\circ\text{C}$. To eliminate the system errors, the dilatometer was calibrated by measuring a standard SiO_2 specimen under identical conditions. TG and DTA measurements were performed using STA409EP–Netzsch at a heating rate of $10^\circ\text{C min}^{-1}$ in N_2 atmosphere.

Results and discussion

It is well known that thermal expansion is due to the anharmonicity of the atomic interactions. Consequently, strongly bonded solids, which have deep, symmetrical potential wells expand at lower rates with temperature than weakly bonded solids with shallow, asymmetrical potential wells [5]. As a consequence, the potential well is not symmetric and it is necessary that the presence of anharmonic parts in the crystal potential energy causes the change. So, thermal expansions are explained by attractive and repulsive forces between atoms in a solid.

Among the different kinds of forces that are present in amino acid crystals our analyses of thermal expansion will focus in hydrogen bond interactions. In zwitterionic compounds, the hydrogen bonds can be qualitatively defined as asymmetrical potential wells and dominate the thermal expansion phenomenon. In fact, numerous studies were devoted to analyze the effect of the hydrogen bond on the anharmonicity of the potential functions of vibrations affected by hydrogen bonding [6].

The thermal strain along mutually perpendicular x -, y -, and z - axes in L-alanine, taurine and L-threonine crystals are displayed in Figs. 1, 2, and 3, respectively.

The linear expansion coefficient (α_i), described as the slope of thermal strain [$\alpha_i = (1/L_0) (\partial L/\partial T)$], and the structural data of these crystals are given in Table 1. The coefficient of thermal expansion of taurine and L-threonine crystals is almost constant in the investigated range of temperature. However, the coefficient of thermal expansion of L-alanine crystal is not an invariant property over the temperature range, except for the y -axis.

It was assumed that data like average distance of hydrogen bonds as well as number and orientation of these bonds is essential to understand the thermal expansion. In

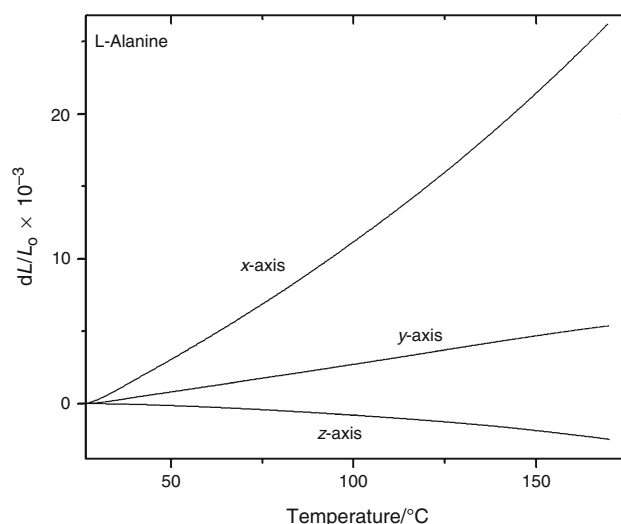


Fig. 1 Thermal strain along mutually perpendicular x -, y -, and z -axes for L-alanine crystals

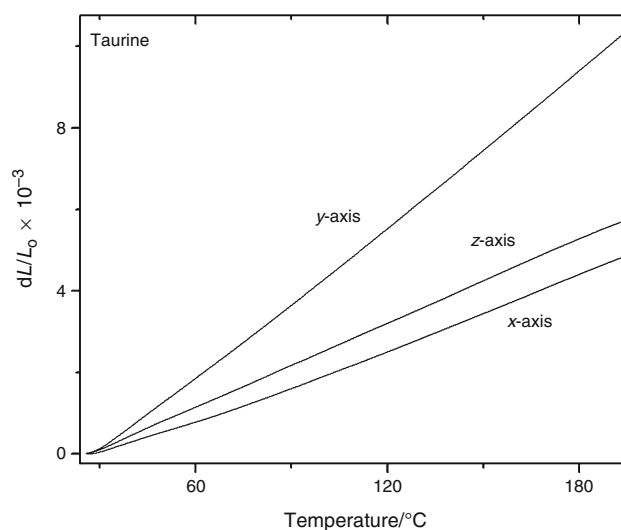


Fig. 2 Thermal strain along mutually perpendicular x -, y -, and z -axes for taurine crystal

our point of view, reduction of the average of hydrogen bond strength and increase of the number of these bonds should contribute negatively to thermal expansion. In Figs. 1, 2, and 3, we present the thermal strain along three axes for L-alanine, taurine, and L-threonine over a large temperature interval has characteristic values. The L-threonine bulk expansion coefficient is lower as compared with the L-alanine and taurine. This reduction can be attributed

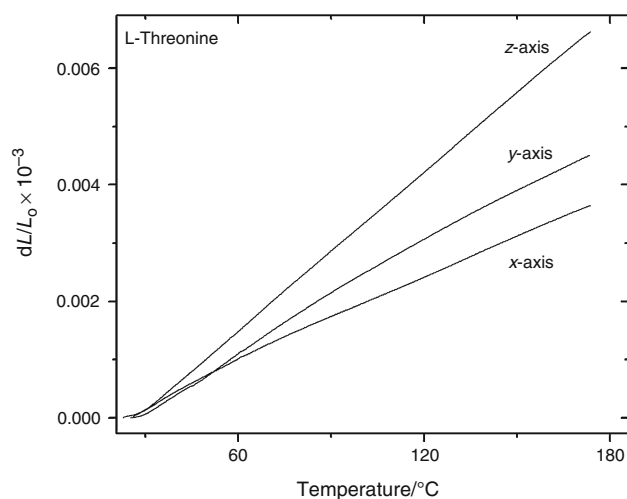


Fig. 3 Thermal strain along mutually perpendicular *x*-, *y*-, and *z*-axes for L-threonine crystal

to the strong O–H–O hydrogen bonds (2.660 Å) that occurs in the L-threonine structure at room temperature [7]. Also, strong intermolecular O–H–O bonds are observed in crystal structures of the β -diketo enols and some dibasic acids [1]. In L-alanine and taurine there is no O–H...O bond, being only observed a more weak N–H–O hydrogen bond form. Beyond this, the L-alanine N–H–O bond average distance is relatively short compared with taurine crystals (Table 1), the average distance being 2.83 Å in L-alanine [8] and 2.90 Å in taurine [9]. The higher bulk expansion coefficient in taurine can be attributed to the flexible and weak intermolecular N–H...O bonding.

Another fact is that the thermal expansions of the three crystallographic axes of L-threonine and taurine are positive, as occur with most of the materials. However, for L-alanine, whilst the expansion of the *x*- and the *y*-axes and the volume thermal expansion coefficient are positive for all temperatures, the thermal expansion of the *z* axis is very small and negative in the same range of temperature. The smallness of this value is influenced by the short N–H–O bond (2.812 Å) that lies in the *z*-axis direction [8]. The effect of this short bond was also observed by Raman spectroscopy in the torsional modes of NH_3^+ bands [4, 10]. In particular, it was possible to observe a relationship between the average distance of hydrogen bonds in the three crystals and the behavior of the wavenumber of torsional vibrations of NH_3^+ under pressure conditions.

Table 1 Crystal data, average hydrogen-bond dimensions, linear expansion coefficients, bulk expansion coefficients, and endothermic peaks of L-alanine, L-threonine, and taurine crystals

Crystal	L-Alanine [8]	L-Threonine [7]	Taurine [9]
Molecular formula	$(\text{NH}_3^+)\text{CH}_3\text{CH}(\text{CO}_2^-)$	$(\text{NH}_3^+)\text{CHCHOH}(\text{CO}_2^-)$	$(\text{NH}_3^+)\text{CH}_2\text{CH}_2(\text{SO}_3^-)$
Crystal data	$\text{P2}_1\text{2}_1\text{2}_1$ $a = 6.0310 \text{ \AA}$ $b = 12,3510 \text{ \AA}$ $c = 5.7820 \text{ \AA}$ $Z = 4$	$\text{P2}_1\text{2}_1\text{2}_1$ $a = 13.611 \text{ \AA}$ $b = 7.738 \text{ \AA}$ $c = 5.144 \text{ \AA}$ $Z = 4$	$\text{P2}_1/\text{a}$ $a = 7,9250 \text{ \AA}$ $b = 11,6400 \text{ \AA}$ $c = 5,2780 \text{ \AA}$ $\beta = 94,0900^\circ$ $Z = 4$
Hydrogen bond			
N–H–O	Three contacts with 2.83 Å (average) in NO distances.	Three contacts with 2.86 Å (average) in NO distances.	Four contacts with 2.90 Å (average) in NO distances.
O–H–O	–	One contact with 2.660 Å in OO distances.	–
Linear expansion coefficient	$\alpha_x = 9.36629 \times 10^{-5} \text{ }^\circ\text{C}^{-1} + 9.08647 \times 10^{-7} \text{ }^\circ\text{C}^{-2} T$ $\alpha_y = 3.85 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ $\alpha_z = -1.686 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$	$\alpha_x = 3.08917 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ $\alpha_y = 2.38309 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ $\alpha_z = 4.54049 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$	$\alpha_x = 2.98578 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ $\alpha_y = 6.26243 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ $\alpha_z = 3.43823 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$
Bulk expansion coefficient	$\alpha_v = 11.53029 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ $+0.0908647 \times 10^{-5} \text{ }^\circ\text{C}^{-2} T$ (<i>T</i> temperature)	$\alpha_v = 10.01275 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$	$\alpha_v = 12.68644 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$
Endothermic peaks	$\sim 300 \text{ }^\circ\text{C}$	$\sim 280 \text{ }^\circ\text{C}$	$\sim 340 \text{ }^\circ\text{C}$

Analysis of our results indicates that in the temperature range investigated, the thermal expansions of all crystals analyzed are markedly non-isotropic. The thermal expansion for these amino acids are considered “colossal” by the definition given by Goodwin et al. ($\alpha_{\text{bulk}} > 100 \times 10^{-6} \text{ K}^{-1}$) [11].

The temperature dependences of the thermal strain show no anomalies in the temperature range studied. Thus, we are led to conclude that none of the three amino acids structures undergoes any phase transition in this temperature range.

Thermogravimetric and differential thermal analysis curves recorded for L-alanine, taurine and L-threonine crystals are shown in Figs. 4 and 5.

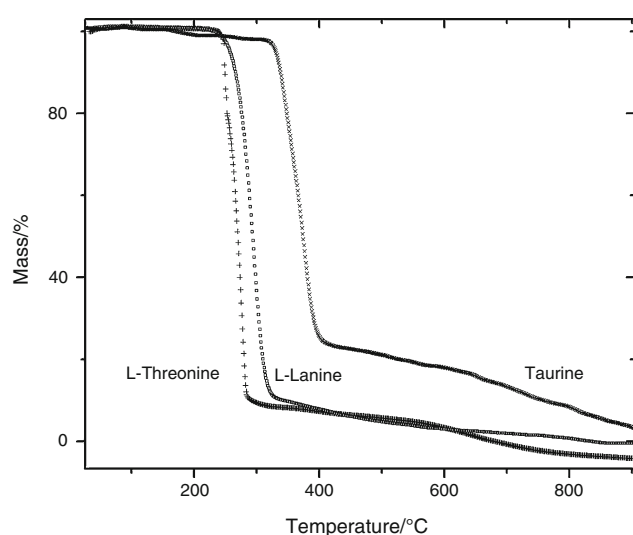


Fig. 4 Thermogravimetric curves for L-alanine, taurine, and L-threonine crystals from 30 to 900 °C

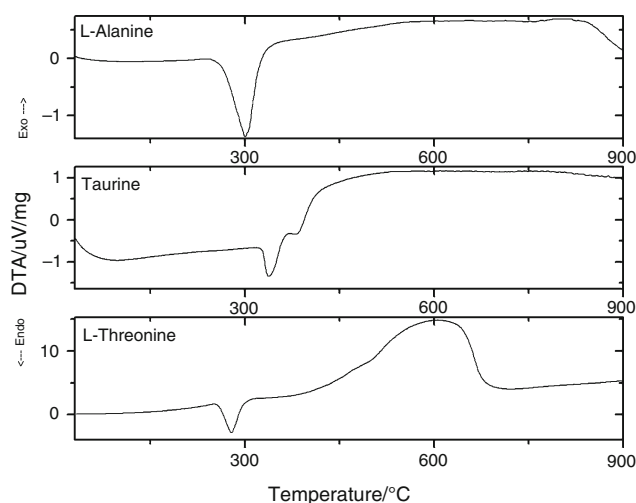


Fig. 5 Differential thermal analysis curves for L-alanine, taurine, and L-threonine crystals from 30 to 900 °C

Thermogravimetric analysis shows the softening of the crystals accompanied by a loss of material and associated to an endothermic peak in DTA curves that characterizes a typical decomposition process. Such peaks are observed for all three materials, being observed as follows: at 300 °C for L-alanine, at 280 °C for L-threonine and at ~340 °C for taurine. Here, the zwitterions solid phase decomposition occurs and can not more be interpreted in terms of differences in strengths of the hydrogen bonding in crystals at room temperature. The most stable crystal is the taurine (Table 1) that presents weaker N–H–O hydrogen bonds at room temperature. In this study it was not possible to find a correlation between the endothermic decomposition and the strengths of the hydrogen bonds at room temperature, meaning that other factors beyond hydrogen bonds are responsible for the decomposition of the three materials.

Conclusions

The study performed with dilatometric and thermogravimetric techniques as well as differential thermal analysis in L-alanine, L-threonine, and taurine crystals allowed us to conclude that the thermal expansion is correlated with the strengths of local hydrogen bonding in these amino acid structures at room temperature, being the L-threonine crystal dominated by strong O–H–O hydrogen bonds (2.660 Å). However, no correlation was observed between the endothermic decomposition peak and the strengths or number of hydrogen bonds at room temperature as observed previously from X-ray diffraction experiments.

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