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Low-temperature phase transformation studies in the stearic acid: C form



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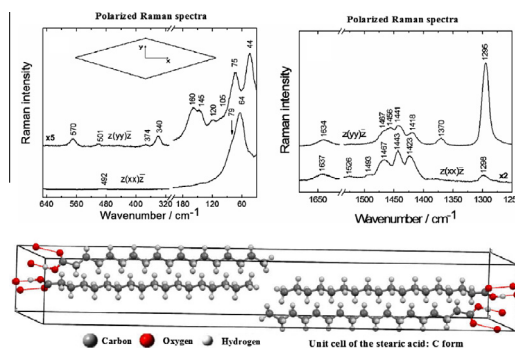
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HIGHLIGHTS

- Temperature dependence polarized Raman spectra in the C form of stearic acid.
- Its structure was refined by Rietveld analysis of XRD data.
- Differential scanning calorimetry measurements.
- The crystal undergone to a phase transition and a conformational change.

GRAPHICAL ABSTRACT

This study reports temperature dependence in the C form of stearic acid. The phase transition undergone by the crystal occurs between 210 and 170 K and a conformational change in the molecule structure continues occurring down to 8 K. The spectral changes in the Raman spectrum, allowed to identify a phase transition undergone by the stearic acid crystal. The X-ray diffraction results showed slight changes in the lattice parameters at ~200 K. Furthermore, an evidence of the phase transformation was provided by the differential scanning calorimetry measurements, which identified an enthalpic anomaly at ~160 K.



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ABSTRACT

This paper reports the temperature-dependent measurements in the C form of stearic acid. Raman scattering, X-ray diffraction, and differential scanning calorimetry measurements were performed at low temperatures. The polarized Raman spectra were measured for temperatures ranging from 8 to 300 K over the spectral range of 30–3000 cm^{-1} . The spectral changes observed in both the lattice vibrational modes and the internal vibrational modes regions of the Raman spectrum, allowed to identify a phase transition undergone by the stearic acid crystal occurring between 210 and 170 K and a change in the structure continues to be observed down to 8 K. The anharmonicity of some vibrational modes and the possible space groups presented by the crystal at low temperatures were also discussed.

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X-ray powder diffraction
Polarized Raman scattering

Low-temperature X-ray diffraction measurements were performed from 290 to 80 K and the results showed slight changes in the lattice parameters at ~200 K. Furthermore, the evidence of the phase transformation was provided by the differential scanning calorimetry measurements, which identified an enthalpic anomaly at about 160 K.

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Introduction

The fatty acids are found abundantly in nature as part of the constituents of several vegetable oils and they are important for providing energy to cells in human body. Since fatty acids have a wide application in the fields of pharmaceuticals, cosmetic and chemistry industries, these acids have received a lot of attention from the scientific community in the last years [1–4].

Several experimental techniques, such as the differential scanning calorimetry (DSC), Fourier transform (FT) Raman spectroscopy and the infrared spectroscopy, have been successfully used in recent years to: (i) characterize the composition of substances found in fatty acids; (ii) search polymorphism and phase transitions in crystals obtained from these substances; (iii) obtain quantitative information about the constituents of the fatty acids [5], among others. Raman spectroscopy is a particularly powerful tool, since the Raman spectrum exhibits well-resolved bands of fundamental vibrational transitions, thus providing important information about the molecular structures and the changes they may experience as a function of temperature and pressure [6–8].

In particular, stearic acid (18:0, octadecanoic acid, SA) is a saturated fatty acid with a molecular structure $\text{CH}_3-(\text{CH}_2)_{16}-\text{COOH}$ and one of the most common saturated fatty acids, which occur as a glycerol ester in both animal and vegetable fats [9]. Due to the rearrangement of the carboxyl and methyl groups into the crystal, many polymorphic phases can be obtained, depending upon the crystallization conditions and the type of the solvent used [10]. Previous studies have reported a complex polymorphism for fatty acids (FA) with long chains and even number of the carbon atoms. The A_1 , A_2 , A_3 , A_{super} -forms crystallize in triclinic symmetry and the B, C, E-forms are found in monoclinic structures. The B and E forms exhibit two poly types being one monoclinic and other orthorhombic (Pbca, with $Z=8$) [11,12]. It is possible to obtain the C form of the SA as by using the crystallization through slow evaporation growth technique in different solvents [10,13–16].

Some works have reported Raman spectroscopic studies of SA describing the high wavenumber spectral region of the SA at room temperature and ambient pressure [17–21] as well as at high pressure conditions [22]. In these later experiments, several changes in the Raman spectra were observed, thus leading one to infer the crystal undergoes a phase transition. Additionally, the infrared and Raman spectroscopy on the SA (C form) under temperature changes (300–90 K) have been reported [23]. However, a discussion about the changes of the Raman active modes as a function of temperature, as well as the occurrence of any structural phase transformation were not reported. To the best of our knowledge, a detailed analysis of the polarized Raman spectra, as well as the identification of possible phase transformation by using both spectroscopic and X-ray diffraction techniques at low temperatures (from 300 to 8 K) for SA (C form), were not reported up to this date.

The present study aimed to deeply investigate the following issues: (i) the polarized Raman spectra of single crystals from the SA (C-form) for two scattering geometries $[z(yy)z]$ and $[z(xx)z]$ at room temperature; (ii) the stability of the structure and the behavior of Raman active modes, as a function of temperature; (iii) the investigation of low-temperature X-ray powder diffraction (XRPD) measurements, in order to identify an eventual phase

transformation and to verify the behavior of the lattice parameters as a function of temperature; (iv) the investigation of the thermal stability of the SA through differential scanning calorimetry measurements at low temperatures.

Experimental

Stearic acid was purchased from Merck (USA) and the single crystals of this material were recrystallized by slow evaporation in a chloroform saturated solution at controlled temperature ($T=289$ K). Single crystals were obtained in the form of tiny transparent platelets in a lozenge shape, and its polymorphic form was identified by X-ray diffraction measurements. In situ XRPD measurements were carried out on a Philips diffractometer (model PW1170), using the Bragg–Brentano geometry, with an attached Anton-Par TTK450 temperature chamber, in the temperature range 290–80 K. A Cu– $K\alpha$ radiation ($\lambda=1.54056$ Å) was used with the diffractometer operating at 40 kV/30 mA. The diffraction patterns were obtained in the angular range of 3–42° (2θ) with step size of 0.02° (2θ) and counting time of 1 s/step. The results were analyzed by Rietveld refinement using the GSAS program [24].

The Raman spectra were collected using a Jobin Yvon T64000 triple spectrometer in the subtractive mode equipped with an N_2 -cooled charge coupled device (CCD) detector. The spectral resolution was set to 2 cm^{-1} . The Raman spectra were excited with a 514.5 nm line of an Argon ion laser. An Olympus microscope lens with focal length $f=20.5$ mm and numeric aperture $\text{NA}=0.35$ was used to focus the laser beam on the sample surface. In order to reach low temperatures, a helium flux cryostat (THMS 600) system and a temperature controller of about ± 0.1 K were used.

Differential scanning calorimetry (DSC) measurements were recorded using a Netzsch Instrument (DSC 204 F1 – Phoenix) equipped with a liquid nitrogen cooling accessory. About 3 mg of sample was monitored between 130 and 300 K, with a 10 K/min heating rate.

Results and discussion

Raman spectra at room temperature

The characterization of the SA crystals was performed by means of the X-ray powder diffraction technique at room temperature. This investigation showed that the crystal structure belongs to the $P2_1/a$ (C_{2h}^5) space group of the monoclinic symmetry with four molecules per unit cell ($Z=4$). The lattice parameters a , b and c are nearly equal to 9.36(2), 4.95(1) and 50.7(1) Å as well as monoclinic angle $\beta=128.15^\circ$ (1), thus, confirming the occurrences of the C form as previously determined by Malta et al. [25]. The four molecules in the unit cell of the crystal adopt an all-*trans* conformation. The dimers are arranged to exhibit the terminal methyl and terminal carboxyl group monolayers parallel to the (001) plane.

The angles and crystallographic axes of the lozenge single crystals were determined as shown in the inset of Fig. 1(a), where it was used the following axes convention: the x -axis was defined as the axis along the largest dimension of the crystal, whereas the y -axis was defined as perpendicular to the previous axis

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