

Molecular Dynamics in the Crystals of Long Chain Carboxylic Acid Mixtures: Stearic/Behenic Acid System of Varying Composition

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Introduction

Wide application of the saturated fatty acids ($C_nH_{2n-1}OOH$) with variation in the number n of carbon atoms in the aliphatic chain, in the chemical and pharmaceutical industries requires a good knowledge of their properties and phase behavior, but the study of the crystal forms of pure fatty acids, as well as their binary mixtures still is a challenging task. Due to the high number of crystalline forms of these compounds, the similarity of their structures, the difficulty of obtaining isolated forms, and the difficulty of growing single crystals of suitable quality for single crystal X-ray diffraction, the polymorphism of long-chain carboxylic acids as well as their binary mixtures, is still a matter of discussion. In this work, for the first time, the polymorphism of binary mixtures of saturated fatty acids differing by 4 carbon atoms: stearic, $C_{18}H_{35}OOH$ (SA), and behenic, $C_{22}H_{43}OOH$ (BA), with different molar ratio is explored at the molecular level using DSC measurements complemented by FTIR spectroscopy and X-ray diffraction (XRD). In our previous works, an attempt has been made to apply the Davydov splitting of CH_2 rocking band to the analysis of the polymorphic changes in the SA:BA mixture, however, they did not show any systematic behavior. Here, using the temperature-variable FTIR spectra, new structure-sensitive absorption bands were identified, and it was shown that the structural changes revealed by DSC are accompanied with an increase of conformational disorder of the alkyl chain in the vicinity of the dimer ring. The changes in the binary mixtures molecular structure inferred by an admixture of the shorter homologue and its effect on the lattice instabilities resulting in phase transitions below the melting point are discussed.

Materials & Methods

- **X-ray Diffraction.** XRD profiles of the studied compounds were measured in a 0–10° angular range with Bruker D8 Advance X-ray diffractometer with 2.2 kW Cu anode long fine focus ceramic X-ray tube (Cu-Ka1 radiation, wavelength 1.5406 Å).
- **Differential Scanning Calorimetry.** The heat flow curves were obtained in a 20–110°C temperature range using a Perkin-Elmer Model 8000 differential scanning calorimeter with a cooling/heating rate of 8 degree/min.
- **Variable Temperature FTIR Spectroscopy (VTFTIR).** IR absorption spectra of the samples placed between two KBr windows were measured with Bruker IFS-88 FTIR spectrometer with SPECAC Variable Temperature Cell P/N 21.500 with Eurotherm controller 847 in a 20–130°C temperature range (380–4000 cm^{-1} , 1 cm^{-1} resolution, 64 scans).
- All reagents (SA, BA) were purchased from Sigma-Aldrich (99%) and used without further purification. To obtain a binary mixture, the preset molar amounts of SA and BA were placed in a glass vial, and heated under stirring up to 10 degrees above the BA melting point ~90°C. The mixture was then allowed to cool to room temperature and kept until the analysis. The obtained $SA_x:BA_{(1-x)}$ ($x=0.5; 0.2; 0.4$, and 0.8) solids were characterized with XRD, DSC, and VTFTIR spectroscopy.

Experimental Results

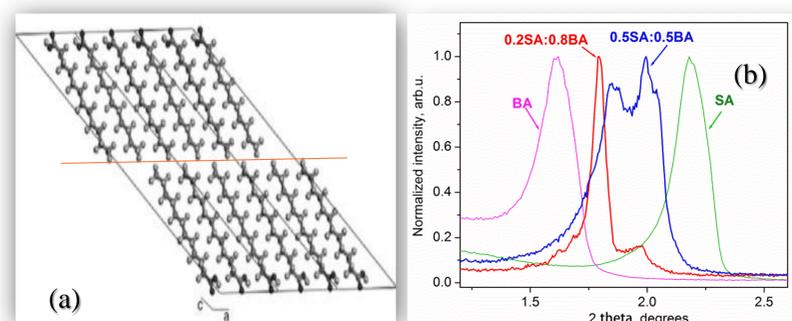


Fig. 1. (a) Schematic of SA dimer lamellar packing in orthorhombic crystal structure. (b) XRD patterns reveal that SA:BA binary mixtures crystallize in a lamellar structure different from that of initial acids.

Table 1. Most structure-sensitive IR absorption bands of the carboxylic groups in SA and BA dimers

Type of vibration	Frequency, cm^{-1}	Intensity
OH stretching	~3000	Broad and strong
Overtone and combinations	2700–2500	Medium–weak
C=O stretching asymmetric	1740–1660	Broad and very strong
C=O stretching symmetric	1687–1625	Weak
C–OH bending in plane	1440–1395	Medium
C–O stretching	1315–1280	Strong
O–H bending out of plane	960–875	Medium
O–C=O	690–630	Strong

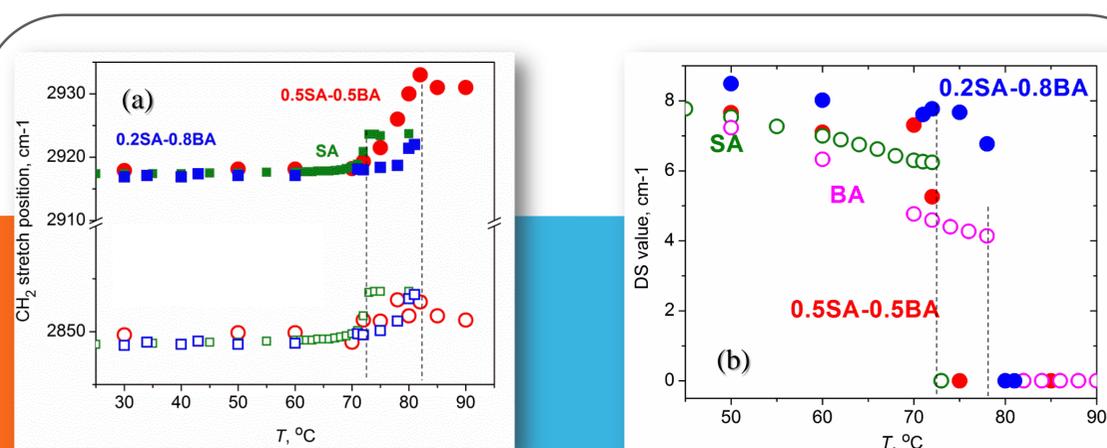


Fig. 3. Temperature dependence of spectral parameters for CH_2 (a) stretching and (b) rocking vibrations.

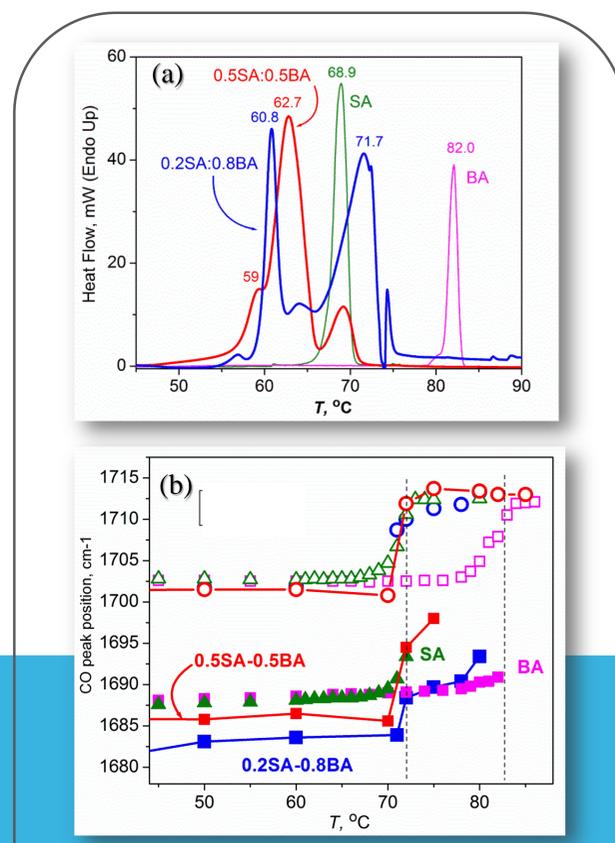


Fig. 4. Correlation between (a) DSC curves and (b) temperature dependence of C=O stretching mode.

Conclusions

- For the first time, the $SA_x:BA_{1-x}$ ($x=0.5; 0.2; 0.4$, and 0.8) binary mixtures of stearic and behenic fatty acids were studied using XRD, DSC and VTFTIR spectroscopy.
- XRD patterns reveal that $SA_x:BA_{1-x}$ binary mixtures of different composition x crystallize in a lamellar structure different from that of initial acids. A significant difference in methylene chains packing in $SA_x:BA_{1-x}$ solids was found to depend on the molar ratio.
- With FTIR spectroscopy it is shown that the $SA_x:BA_{1-x}$ mixtures adopt the C crystal form with all-trans conformation of the alkyl chains. Therefore, FTIR is the proper technique to distinguish the different crystal forms and therefore it complements the information extracted from X-ray powder diffraction data.
- DSC study show that the investigated mixtures exhibit a series of solid-solid phase transitions below the melting point, contrary to a single melting transition observed for the initial acids. Two phase transitions in $SA_x:BA_{1-x}$ binary mixtures correspond to different high-temperature crystal forms; the melting temperature of the mixtures significantly decreases compared to the initial acids being close to that of the shorter acid.
- With FT-IR spectroscopy it is shown that $SA_x:BA_{1-x}$ binary mixtures phase behavior is far more complex than previously admitted. It is caused by conformational changes in the hydrogen-bonded dimer rings followed by sequential melting of shorter and longer methylene chains and a change in the crystalline structure.