Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Numerical modeling of polymorphic transformation of oleic acid via near-infrared spectroscopy and factor analysis

Ling Liu [a], Yuliang Cheng [b], Xiulan Sun [b], Fuwei Pi [b,*]

[a] Wuxi Institute of Technology, Wuxi City, Jiangsu Province 214122, PR China
[b] National Engineering Research Center for Functional Food, School of Food Science and Technology, Jiangnan University, Wuxi City, Jiangsu Province 214122, PR China

ARTICLE INFO

Article history:
Received 30 November 2017
Received in revised form 4 January 2018
Accepted 5 January 2018
Available online xxxx

Keywords:
Near-infrared spectroscopy
Phase transition
Oleic acid
Factor analysis

ABSTRACT

Near-infrared (NIR) spectroscopy as a tool for direct and quantitatively screening the minute polymorphic transitions of bioactive fatty acids was assessed basing on a thermal heating process of oleic acid. Temperature-dependent NIR spectral profiles indicate that dynamical variances of COOH group dominate its γ → α phase transition, while the transition from active α to β phase mainly relates to the conformational transfer of acyl chain. Through operating multivariate curve resolution-alternating least squares with factor analysis, instantaneous contribution of each active polymorph during the transition process was illustrated for displaying the progressive evolutions of functional groups. Calculated contributions reveal that the α phase of oleic acid initially is present at around −18 °C, but sharply grows up around −2.2 °C from the transformation of γ phase and finally disappears at the melting point. On the other hand, the β phase of oleic acid is sole self-generation after melt even it embryonically appears at −2.2 °C. Such mathematical approach based on NIR spectroscopy and factor analysis calculation provides a volatile strategy in quantitatively exploring the transition processes of bioactive fatty acids; meanwhile, it maintains promising possibility for instantaneous quantifying each active polymorph of lipid materials.

1. Introduction

As one of the major biological components, fatty acids play a central role in the construction of cytoplasmic membranes, e.g., mobility, flexibility and material transfer [1–4], and human health [5–7]. Almost all kinds of fatty acids from short-chain to long-chain ones are relevance to physiology, microbiology, biochemistry, and biomedicine [8,9]. Thus, investigations on the properties of fatty acids have been a keen interest of scientists. The active *cis*-unsaturated acyl chains, which are usually linked to the second position of glycerol in phospholipids, which contributes for over 50% of all lipids in plasma membranes [10], easily result in lipid components generating different polymorphs which have distinct physicochemical features and bioactivities due to the special *cis*-olefinic conformations or transitions [11–13]. Therefore, extensive investigation and precise quantification on the polymorphs are very important for good understanding the bio-functions of fatty acids from biochemical and biomedical points of view.

Currently, various characterization methods of polymorphism, for example, X-ray powder diffraction (XPRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Raman spectroscopy, infrared spectroscopy and solid-state nuclear magnetic resonance (NMR) spectroscopy, have been demonstrated to be powerful to explore polymorphic transformation [14–18]. To date, although prominent achievements have been accomplished through employing the above mentioned techniques and/or their combinations, a issue for them is that they are relatively time-consuming and hard to provide dynamical estimation for each active polymorph during transition process. Moreover, for lipid compounds have more than one active phase, for example, polyunsaturated phospholipid with *cis*-olefin group, instantaneous conformations or compositions of polymorphs had been demonstrated to play an important role in modulating the physical properties of cell biomembranes [19,20]. On the other side, evaluation of the active polymorph opens new perspectives for further understanding of the mechanisms dominating their physiological and pathological operations in biological tissue.

Near-infrared (NIR) spectroscopy as one of fast, non-invasive spectroscopic techniques has been extensively employed for solving a variety of quantitative issues at molecular level due to the appropriate molar absorption coefficient in the NIR region and the easy-controlled light path length in bulk phase [21–26]. Moreover, in combination with chemometrics and quantum calculations, such as factor analysis (FA) (e.g. principle component analysis (PCA), evolving factor analysis (EFA)) or multivariate curve resolution, NIR spectroscopy has been shown to be very useful for studying fatty acids and related materials [27–30]. For example, Iwahashi et al. [27] clearly displayed the

* Corresponding author.
E-mail address: pifuwei@jiangnan.edu.cn (F. Pi).

https://doi.org/10.1016/j.saa.2018.01.022
1386-1425/

dissociation process of dimmers of ocatdecenoic acid into its monomeric species and provided the molar absorption coefficient for the OH of the free acid through operating NIR measurements. Basing on the anharmonic density functional theory (DFT), Grabska et al. [28,29] systematically interpreted the NIR spectral figures corresponding to the molecular structures of saturated and unsaturated carboxylic acids from short-chain to medium-chain ones with three, four and six carbons. Such calculations implied that NIR spectroscopy is a powerful tool for monitoring of biological processes of fatty acids, and provide excellent structural markers of different phases. Moreover, through operating EFA algorithm, Yuan et al. [31] confirmed the hydration of complex bovine serum albumin (BSA) at 60 °C and demonstrated the secondly structure of BSA by analyzing the corresponding NIR bands associated with intermolecular beta-sheet structure of BSA. In spite of numerous reports had demonstrated the applicability of NIR spectroscopy in the study of bioactive components and its apparent advantages on timesaving and non-invasive, little work has been done so far to quantitatively monitor the phase transition of lipid materials especially on the evaluations of dynamical polymorphs evolution.

Aim of the current work is to investigate the analytical potential of NIR spectroscopy as quantitative tool for showing the dynamical evolutions of active polymorphs during phase transition of lipid component. Studies were carried out basing on a heating process of one representative fatty acid, oleic acid (*cis*-9-octadecenoic acid), from −30 to 30 °C. The molecular structure of oleic acid was plotted in Fig.1 as inset. Oleic acid is the most abundant *cis*-monounsaturated fatty acid in nature, which has three main polymorphic phases with temperature, α (mp 13.3 °C), β (mp 16.2 °C), and γ [32,33]. Furthermore, for the special conformation of *cis*-olefin group, the γ phase of oleic acid consisting of parallel molecular chains was proven to change into α phase at −2.2 °C through a local conformational disordering in the methyl-sided acyl chain [34,35]; while the β phase of oleic acid maintains an unique interdigitated structure, $-CH_3$ end overlapped with –COOH dimer ring, present after 16 °C [33,36]. Such distinct variances on molecular structures make it as an ideal candidate for carrying out polymorphic studies on active lipid component. Herein, evolutions for different active polymorphs of oleic acid shall be numerically illustrated and interpreted through operating FA analysis on NIR spectroscopy in this work.

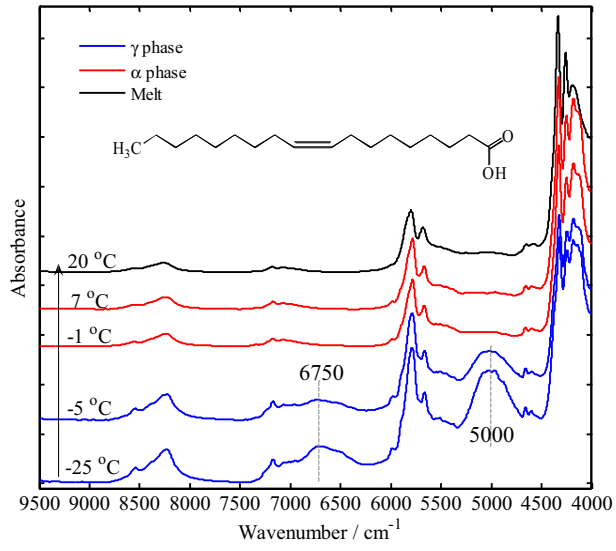

Fig. 1. Temperature-dependent NIR spectra of oleic acid at selected temperatures as representatives of the γ, α and melting states in the region of 9500–4000 cm^{-1}. Inset is the chemical structure of oleic acid molecule.

2. Materials and Methods

2.1. Materials

The specimen of oleic acid (purity >99.9%) was supplied by Research Institute of Biological Materials (Kyoto, Japan), and was used without further treatment.

2.2. Fourier Transform Near-infrared Measurements

NIR spectra of oleic acid were collected on PerkinElmer Spectrum One NTS FT-NIR spectrometer (PerkinElmer Inc.) equipped with a DTGS detector. Transmission mode of NIR spectra were recorded at a 2 cm^{-1} resolution with co-adding 64 scans for an acceptable S/N ratio.

For obtaining the γ phase of oleic acid, liquid sample was first filled into a quartz rectangle cell with 2 mm thickness. Then, the cell was mounted on the cold finger of a cryostat set in the spectrometer and was cooled down to −30 °C by pumping liquid nitrogen. After the specimen maintaining at −30 °C for one hour, it was heated at a rate of 2 °C/min to a predetermined temperature for NIR measurements. An equilibrium time of 20 min was carried out to ensure the temperatures are same between the specimen and the temperature sensor of thermometer for each step. Sample temperature was controlled by a digital thermometer (Instec HCS302, Instec, Inc., Colorado) with an accuracy of ±0.1 °C.

2.3. Near-infrared Spectral Processing

Obtained NIR spectra suffer from light scattering effect observed as baseline shift and title for the varying crystalline sizes in the solid state. To preserve the original features and enhance effective visual inspection, a Rubberband baseline correction and Savitzky-Golay smoothing with 21 points of window width and second order polynomial were performed in OPUS (Version 7.2, Bruker Optics Inc.) software package. All of the mathematical analyses in the present study were executed based on the noise-reduced and baseline corrected data set. MATLAB codes of SVD, EFA, and alternating least-square (ALS) optimization algorithms (Eigenvector Research, Inc.) were operated in Matlab 7.0.4 software package (The MathWorks Inc., Natick, MA).

3. Statistical Methodology

3.1. Singular Value Decomposition (SVD)

For any data matrix $X(m \times n)(m \geq n)$, one can obtain its eigenvalues and eigenvectors for estimating chemical ranks through operating SVD technique. The SVD calculation decomposes the matrix into three matrices as $X = USV^t$, where U, which usually is called "scores", is the column orthogonal matrix; $S$is a diagonal matrix with its diagonal elements are the square roots of the corresponding eigenvalues; while V, which is called "loadings", is a row orthogonal matrix, where its column vectors are orthogonal to one another [37].

3.2. Evolving Factor Analysis (EFA)

EFA calculations usually are performed in two directions: forward (in the same direction of the experiment) and backward (in the reverse direction of the experiment). Contribution of a new compound present in EFA is indicated as the upsurging of a new singular value in the forward direction. Reversely, the upsurging of a new singular value in the backward direction means the disappearance of a component. Fundamental idea of forward calculation behind EFA is nothing else but careful to follow the change of the rank of the data matrix X with progressing elution by rank analysis of the submatrices X_i formed by the first 1, 2, ···, m spectra of X. It is straightforward to obtain the backward calculation through repeating the EFA calculation from the reverse end,

Please cite this article as: L. Liu, et al., Numerical modeling of polymorphic transformation of oleic acid via near-infrared spectroscopy and factor analysis, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy (2018), https://doi.org/10.1016/j.saa.2018.01.022