Raman spectroscopic study of a molecular compound formed from a binary mixture of triacylglycerols

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Introduction　　　Triacylglycerols (TAGs) are one of the main forms of energy storage of living organisms. In a biological system, TAGs are present in multicomponent systems consisting of different TAG species. To understand the physical properties, *e.g.* melting point and phase behavior, of the multicomponent systems, many studies have carried out adopting TAG binary mixtures as the model system. In some of these model systems, the formation of "molecular compound" is suggested by thermal analysis and powder X-ray diffraction analysis. In the 1,3-dipalmitoyl-2-oleoyl-*sn*-glycerol (POP) and 1,3-dioleoyl-2-palmitoyl-*sn*-glycerol (OPO) binary mixture, the molecular compound "POP-OPO" is thought to form at an equal concentration ratio of the component TAGs.[1,2] In the present study, the binary mixtures of POP and OPO have been studied with the use of Raman spectroscopy and a singular-value decomposition analysis to elucidate whether the molecular compound is formed.

Materials and methods

POP and OPO (≥99% purity) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Both samples were used without further purification. They were melted at 50°C and mixed to prepare the samples with different molar ratio of POP and OPO. The molar ratio was measured by gas chromatography. Metastable crystals of the samples were prepared by cooling down to 4°C and then incubated at 20°C for 11 days to transform the crystals into more stable forms. Raman spectra were measured after the incubation and the samples were kept at 15°C in a cryostat during the measurement. Raman scattering was exited with the 532-nm line of a Nd:YVO$_4$ laser (Verdi, Coherent, Santa Clara, CA, USA). The back-scattered Raman light from the sample was collected by an objective lens (LUCPlanFLN20x, Olympus, Tokyo) and measured with a spectrometer (Shamrock, Andor, Belfast, UK) and an EMCCD detector (Newton, Andor). The laser power was 3 mW at the sample point. Singular-value decomposition was applied to the data set of the spectra to analyze the number of independent spectral components. The spectrum and the concentration profile of each component were reconstructed under constraints in order to minimize ambiguities. The constraints were as follows: authentic POP and OPO spectra and non-negativity for spectra, and non-negativity, unimodality and closure for concentration profiles.

Results and discussion

The molar ratio of POP and OPO and the Raman spectra of the samples are shown in Fig. 1 and Fig. 2, respectively. The spectral
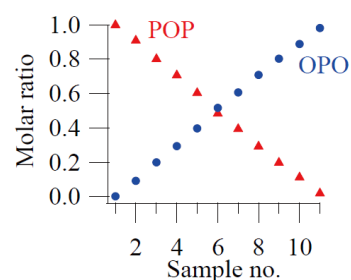

Fig. 1　Molar ratio of POP (▲) and OPO (●) of the samples

data are assembled into a matrix and subjected to singular-value decomposition. It is found that two spectral components are not enough to explain the data set. On the other hand, three components successfully explain the data. Their concentration profiles and spectra are shown in Fig. 3. From these results, it is shown spectrometrically the existence of the third component in the binary system. The formation of the molecular compound is therefore supported. The components 1 and 2 are POP and OPO, respectively, and the component 3 is the POP-OPO molecular compound.

From the concentration profiles (Fig. 3a), it seems likely that the molecular compound (component 3) is formed at a molar ratio of POP:OPO=1:2. This is inconsistent with the previous studies[1,2] which report the compound is the 1:1 complex. It might be because of the difference in the crystallization procedure; the incubation duration is much shorter in the present study than in the previous ones. Shorter incubation time may generate a metastable structure of the molecular compound.
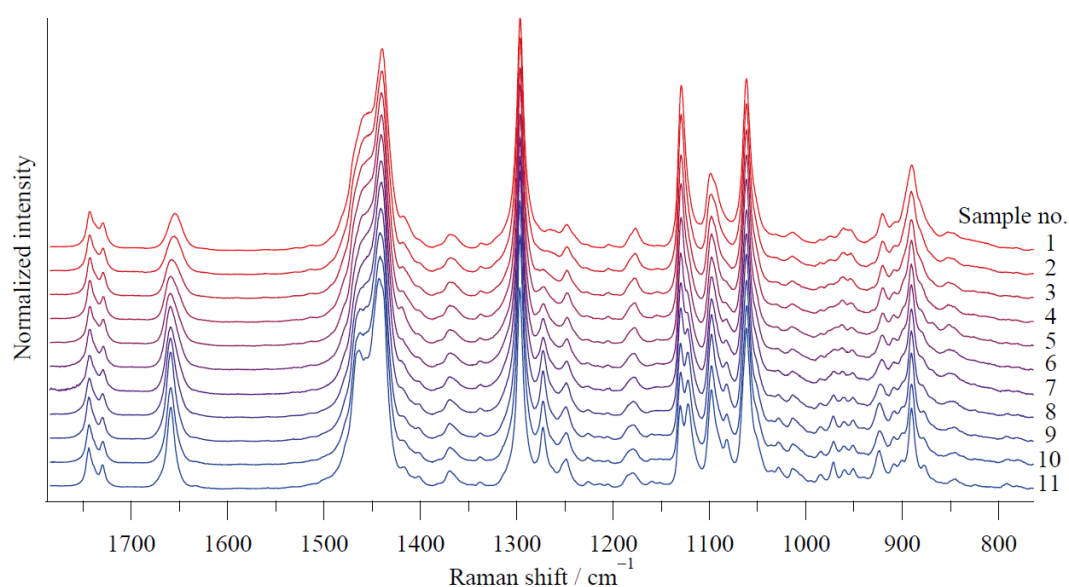

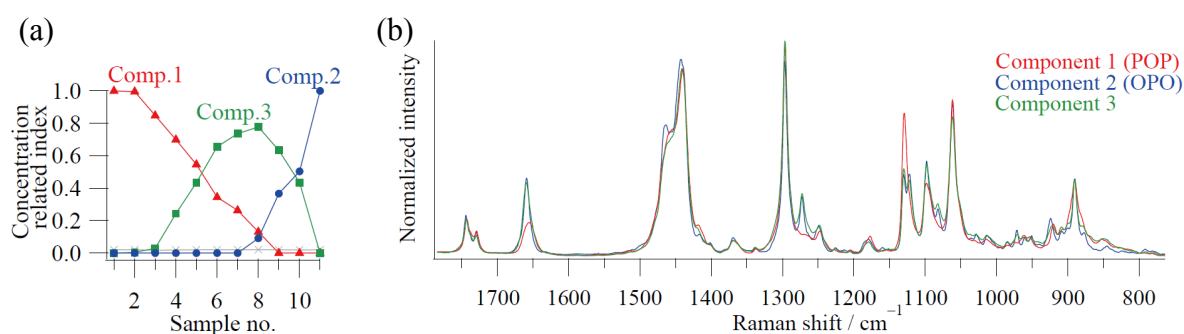Fig. 2   Raman spectra of the samples. Sample numbers are corresponding to those in Fig. 1.

Fig. 3   Results of multivariate-curve resolution. (a), the concentration-related-index profiles of the three components (▲, component 1; ●, component 2; ■, component 3) and the residual (×). (b), the calculated Raman spectra of the components.

References

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