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The kinetic study for fat crystallization process in O/W emulsion

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Introduction

Crystallization of oil phase in oil-in-water (O/W) emulsion is an important process for coagulation of the emulsions at chilled states, demulsifying process of whipping creams, freezing of ice creams, etc.

Many studies have recently been performed on clarification of the fat crystallization process in the O/W emulsion, whose complexity may be revealed in the rate and extent of crystallization of fats, polymorphism, effects of emusifiers on the crystallization, influences of emulsion droplet sizes, effects of rate of cooling and subsequent temperature history on the physical properties of fats, etc [1, 2].

Revealing the crystallization mechanisms in this system, we studied a model O/W emulsion system of even-carbon number alkan such as n-hexadecane(C_{16}) as oil phase by time-resolved X-ray diffraction.

Materials and methods

Materials: Even-carbon number alkan, from C_{12} to C_{22}, and Tween 20 (polyoxysorbitan monolaurate) were used as oil phase and emulsifier, respectively. Sucrose oligoesters (SOEs), polyglycerol polyesters (PGEs) and diacylglycerols, whose concentrations were 1 wt% and 0.2 wt% for oil phase, were added in oil phase as additives for promoting crystallization of oil phase.

Methods: SAXS-WAXS-DSC simultaneous measurement was performed at BL-15A and BL-9C. Data for X-ray diffraction were detected in every 10 sec. DSC was operated on the cooling and following heating between 25 °C and –10 °C with ±2 °C/min.

Results and Discussion

We, here, mainly report the results of the system of n-hexadecane in oil phase. As for the other alkans, the same kinds of results of n-hexadecane were observed.

O/W emulsion without additives:

When the DSC exothermic and endothermic peaks, which corresponded to the crystallization and melting of n-hexadecane, appeared at 2.0 °C and 19.4 °C, respectively, the XRD peaks, at 2.09, 0.46, 0.45, 0.40, 0.38, 0.36 nm, also appeared and disappeared. This suggest that all of the diffraction peaks correspond the crystallization and melting of n-hexadecane.

O/W emulsion with additives:

In the cooling process, when the first exothermic DSC peak appeared at 7.7 °C, the 2.2, 0.42, 0.38 nm diffraction peaks, which did not appeared in the non-additive system, appeared. In the following, the diffraction peaks which corresponded those of n-hexadecane mentioned the previous paragraph appeared when the second DSC peak appeared at 5.5 °C. When the third DSC peak appeared at -4.3 °C, the diffraction peak at 0.42 nm suddenly shifted to 0.41 nm. In the heating process, 0.41 nm suddenly shifted to 0.42 nm corresponding to the DSC endothermic peak at 4.3 °C. The diffraction peaks at 2.2 and 0.42 nm disappeared corresponding to the DSC endothermic peak at 16.6 °C. Finally, when the DSC endothermic peak appeared at 19.4 °C, the rest diffraction peaks which were corresponded to those of n-hexadecane disappeared.

Since those peaks at 2.2, 0.42, 0.38 nm appeared neither in the mixed bulk system nor in the non-additive O/W emulsion system, we thought as follows; (1) these peaks indicated the existence of a complex crystal whose period of lamellar and lateral packings are 2.2 nm, and 0.42 and 0.38 nm, respectively, (2) this complex existed on the surface between water and oil droplet, (3) the melting and crystallization temperature of this complex were 16.6 and 7.7 °C, respectively. The lowest DSC peak corresponded to the transformation of this complex at 4.3 °C in heating and -4.3 °C in cooling process, (4) as for crystallization of n-hexadecane, at first, the complex structure forms, and, secondly, the crystallization of the n-hexadecane occurs; namely, the complex works a kind of template for crystallization of the oil phase.

After additional SAXS-WAXS-DSC simultaneous experiment for O/W emultion using odd-number alkan, pentadecane(C15), heptadecane(C17), nonadecane(C19), as oil phase, it was revealed that the “complex” was the crystal of orthorhombic form for even-number alkan; the same WAXS diffraction peaks, 0.42 and 0.38 nm, and shift from 0.42 to 0.41 nm appeared in odd-number alkan O/W emulsions. While even-number alkan normally forms triclinic polymorph in bulk system, odd-number alkan forms orthorhombic one.

In conclusion, at first, a special orthorhombic crystal for even-number alkan was crystallized along the oil-water interface consist of emulsifier and additives, and, secondly, this crystal worked as a kind of template for crystallizing the next normal triclinic polymorph of oil phase.

References

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