

Time resolved simultaneous SAXS/DSC study on oil crystallization in O/W monodispersed emulsion

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Introduction

Oil crystallization in oil-in-water (O/W) emulsions has been studied extensively in terms of the emulsion stability. However, past researches were carried out with emulsion samples having a wide distribution of particle size. So, the information from these researches was that averaged over various sizes of emulsions, and hence was ambiguous. Here, we have used monodispersed emulsions, which have a narrow distribution of particle size so that we could discuss the behavior of oil crystallization in O/W emulsions in relation to their sizes. Here, we will report on the behavior of oil crystallization in well-defined-sized emulsions observed by time resolved simultaneous SAXS/DSC (Difference Scanning Calorimetry) measurement.

Experimental

O/W emulsion samples were made by micro-channel emulsification method [1] at National Food Research Institute. Samples consisted of n-hexadecane (oil phase), distilled water (continuous phase), and Tween20 (emulsifier). Emulsion sizes were 40 and 10 μm in diameter. We also made samples, in which oleophilic surfactant, DAS-750, was added to the oil phase as an additive, because it was reported that adding DAS-750 accelerates crystallization of n-hexadecane [2]. The simultaneous SAXS/DSC measurements were carried out at BL-15A, at a cooling rate of 2 degrees/min from room temperature. X-ray beam size was about $1 \times 1 \text{mm}^2$.

Results and discussion

Fig.1 shows DSC profiles and temperature dependence of integrated intensity of the SAXS peak from n-hexadecane lamellar structure ($\approx 20\text{\AA}$), in the case of 40 μm emulsions. In Fig.1, the integrated intensity increases with two steps, and DSC profiles have corresponding two peaks. So, it is obvious that crystallization of n-hexadecane in emulsion system includes two different behaviors. Crystallization at a higher temperature takes place at 14°C , which is exactly equal to the crystallization temperature of n-hexadecane in bulk system. So, it is considered that crystallization at a higher temperature is analogous to that in bulk system. On the other hand, crystallization at a lower temperature is specific to emulsion system. And adding DAS-750 raises the temperature of this crystallization.

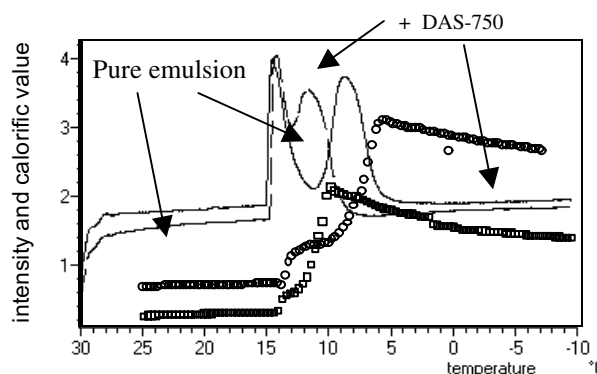


Fig.1 DSC profiles and temperature dependence of the integrated intensity of SAXS n-hexadecane peak (40 μm emulsion).

In previous experiments [2] carried out with much smaller-sized emulsions (0.9 μm), only crystallization specific to emulsion system was observed. However, we have found that bulk-like crystallization also takes place in larger-sized (40 and 10 μm) emulsions. In the experiment with 10 μm emulsions, integrated intensity of the peak hardly increase at 13°C , at which lower-temperature crystallization takes place (not shown). But it isn't reasonable to interpret that the rate of the bulk-like crystallization depends on emulsion size. So, we would interpret that the integrated intensity of n-hexadecane peak in Fig.1 reflects the product of the number and the volume of emulsions in which n-hexadecane is crystallized, rather than genuine crystallization rate. In some emulsions, bulk-like crystallization takes place, whereas in other emulsions, crystallization specific to emulsion system does. Because crystallization takes place within the volume of individual emulsions, when macroscopically observed, it seems that crystallization rate is lower in the case of smaller-sized (10 μm) emulsions.

SAXS profiles showed another peak at a smaller angle ($\approx 22\text{\AA}$) when DAS-750 was added (not shown). This peak was observed also in the previous report [2], but in this experiment, it disappeared on the way of cooling process. It seems this behavior of the smaller angle peak is also specific to large-sized monodispersed emulsion samples.

References

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