

Kelvin Problem Solved by Surfactant Micelles

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要旨：Ziherl と Kamien は、コロナ層と核からなるソフト球状ミセルの結晶化では、最初に最密充填格子を組むが、更に濃度を上げるとミセル間の接触面積を最小にしようとし、いわゆる Kelvin 多面体構造を形成することを予言した。比較的長い親水鎖と疎水鎖をもつ球状の非イオン性界面活性剤ミセル水溶液($C_{12}E_8$)の濃度を上げると、この予言に従って六方最密格子(HCP)、体心立方格子(BCC)および新しく発見された Kelvin 多面体である A15 格子を組むことを明らかにした。

1. Introduction

The crystallization of spherical particles is the most fundamental disorder-order transition of the soft matter and has acquired much attention. Recently, Ziherl and Kamien^{1,2} proposed a new principle to explain the stability of packing structures of soft spherical micelles consisting of compact core and brush-like soft corona. According to the principle, the stability of the ordered micellar structures is determined by the balance of a close-packing rule associated with hard-core interactions and positional entropy of particles, and a minimum-area rule associated with the soft tail and internal entropy of the soft coronas. The theory predicts that a series of crystalline phase sequence of FCC (face-centered cubic) - BCC (body-centered cubic) - A15 with increase of volume fraction of soft micelles, where A15 is known to be area minimizing cubic lattice³ since 1994. Thus the A15 is the present solution of Kelvin problem; what regular partition of space into cells of equal volume has the smallest area of cells? A schematic representation for a series of lattices including A15 is shown in Fig. 1. In this study we investigate the structure evolution of nonionic surfactant micelles ($C_{12}E_8$ /water system) in the disorder-order transition, because Clerc³ found a micellar cubic phase with the space group of $Pm\bar{3}n$ and a hexagonally close packed (HCP) lattice phase with $P6_3/mmc$ symmetry in this system. The ordering process of the micelles was followed by a small angle X-ray scattering (SAXS) technique. The stability of ordered phases consisting of surfactant micelles will be discussed in terms of Ziherl and Kamien.

II. Spherical micelle based lattice structures

First we describe the brief phase behavior of the nonionic surfactant ($C_{12}E_8$ /water) micelle system. Scattering profiles in the disordered micelles phase and ordered micelles phases are shown in Fig. 2.

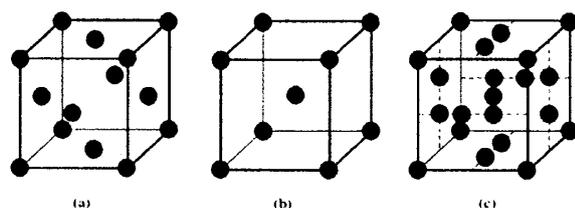


Fig. 1 Schematic representations of (a) FCC lattice, (b) BCC lattice, and (c) A15 lattice.

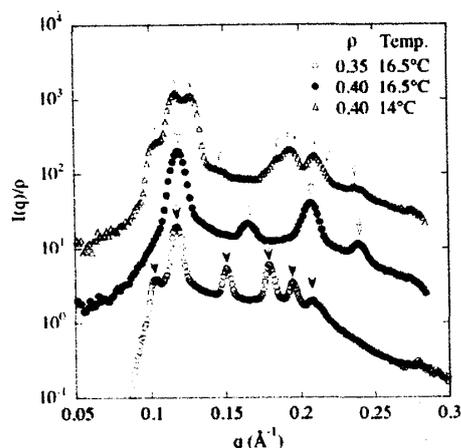


Fig. 2 Evolution of SAXS profiles from HCP to A15 phase.

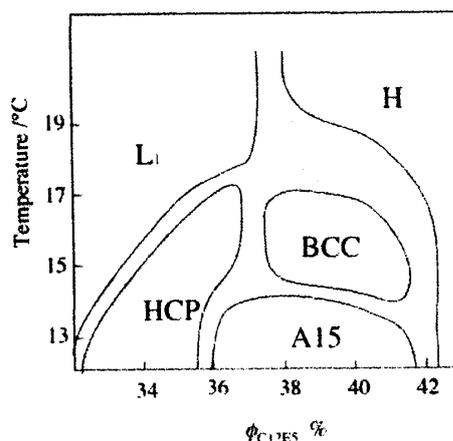


Fig. 3 Phase diagram of $C_{12}E_8$ /water system in the vicinity of HCP, BCC and A15 phases

From the scattering profile of dilute micellar solution, we obtained the following structure parameters, the micelle core radius $R_c=13.2 \text{ \AA}$, the micelle outer shell radius $R_s=35.5 \text{ \AA}$ and the normalized standard deviation $\varepsilon=0.007$. With increasing of the surfactant concentration at 16.5°C the disordered micelles formed a crystal lattice at $\rho=0.35$ as shown in Fig. 2. The peak position data show that this structure is consistent with the HCP lattice of spherical micelles having $P6_3/mmc$ symmetry. The obtained lattice parameters for the HCP phase are $a_{\text{HCP}}=70.2 \text{ \AA}$ and a ratio $R=1.63$, which is very close to the value for ideal HCP lattice of spheres, $R_{\text{ideal}} = \sqrt{8/3} = 1.6330$. The distance between the nearest neighbor micelles $d_n^{\text{HCP}} = a_{\text{HCP}}$ agrees well with the micelle diameter $D_2=2 \times R_2=71 \text{ \AA}$.

Further increasing of the surfactant concentration at 16.5°C , the diffraction pattern transformed to a new pattern at $\rho=0.40$. This new pattern is characterized by the peaks at relative positions $1 : \sqrt{2} : \sqrt{3} : \sqrt{4}$, which consisting of the BCC lattice with space group of $Im\bar{3}m$. When we decreased the temperature from 16.5°C to 14°C at $\rho=0.40$, another kind of SAXS pattern was observed. The observed reflections are compatible with the space group of $Pm\bar{3}n$ which can be attributed to the A15 lattice. Based on these scattering experiments we presented a phase diagram of this system in the vicinity of HCP, BCC and A15 phases in Figure 3. If we take into account that the HCP lattice has almost same free energy as the FCC lattice, this experimental order-order transition sequence, HCP-BCC-A15 agrees with the theoretical predictions. Thus for spherical surfactant micelles, the disordered micelles to HCP transition is governed by the close-packing rule and the HCP-BCC-A15 transition is governed by the minimal-area rule.

References

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