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Bilayer structure of ester-amide-type cationic surfactants in a dilute aqueous solution

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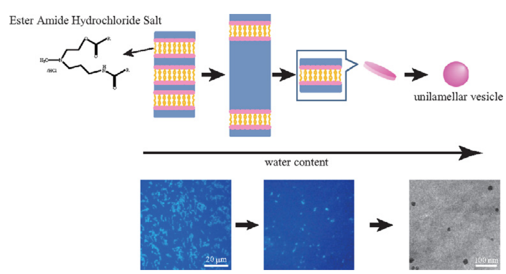
HIGHLIGHTS

- Lamellar structures of ester amide hydrochloride salt solutions are investigated.
- Lamellar repeat distance is swollen up to $d \sim 28$ nm by the dilution.
- Transit ion to unilamellar vesicles is induced below the Krafft temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

The ester-amide-type surfactant (2-[N-[3-alkanoyl(C16-18)aminopropyl]-N-methylamino]ethyl alkano(C16-18)ate, EA) is a dichain cationic amphiphile that has been used as the main base of a fabric softener. We observed the structure of a diluted aqueous solution of EA below the melting temperature (Krafft temperature) using a polarised or fluorescence microscope, small/wide-angle X-ray scattering (SAXS/WAXS), dynamic light scattering (DLS) and cryogenic-temperature transmission electron microscopy (cryo-TEM). From the optical microscope observations, we found that the lamellar domains disappear below the EA concentration (ϕ_{EA}) of ≈3 wt%. Below $\phi_{EA} \sim 1$ wt%, in the cryo-TEM images, we found round dispersions with 35 nm diameters. For the lamellar structure, it was found from the SAXS profiles that the repeat distance of the lamellar gel phase increased up to 28 nm with ϕ_{EA} decreasing to 5 wt%. Furthermore, from the SAXS and DLS analysis, it was also found that unilamellar vesicles, whose diameter is 30–46 nm, are formed below $\phi_{EA} \approx 1$ wt%. All of these experimental results point to the conclusion that the transformations from planar lamellar structures to unilamellar vesicles are induced by dilution of the EA aqueous solution.

1. Introduction

Surfactants are widely used in various fields, such as medical supplies and the industrial materials. While typical examples of surfactant application include washing and emulsification, they are also used as protective materials on the surfaces of solids, lubricants, etc. Dichain cationic surfactants are often used as the main base of fabric softeners because they adsorb onto textiles due to their negative-charged surfaces in water [1]. The adsorbed surfactants are formed in layers on the surface of the textiles; these layers also protect the textiles. Surfactant concentration in the fabric softener is about ~20 wt% depending on the product. The self-assemble structure in the fabric softener is a lamellar gel phase (L_β), and multilamellar vesicles can sometimes form [2,3].

There are some reports where the solution structures composed of dichain cationic surfactants have been investigated [2–11].

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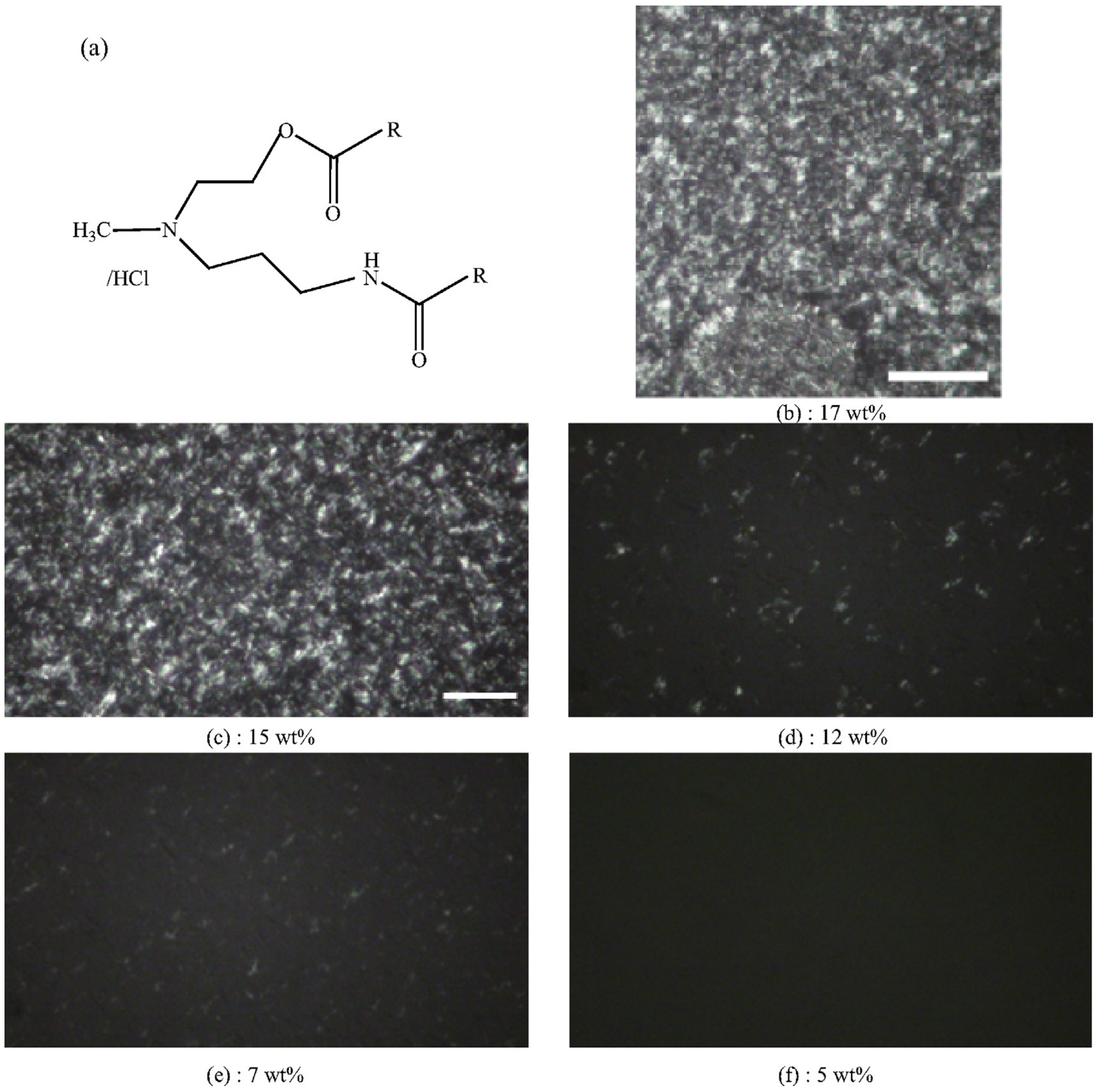

Fig. 1. (a) Structural formula of ester-amide-type cationic surfactant (EA) where *R* is alkyl (C16-18). (b) Polarised microscope image of EA solution whose EA concentration ϕ_{EA} is 17 wt%. (c)–(f) The polarised microscope images of the dilute EA solutions at each EA concentration. Birefringence due to the planar lamellar structures decreases with the EA concentration decreasing. (Scale bar is 100 μm.)

Zemb et al. [4] and Dubois and Zemb [5] have reported the phase behaviour of DDAB (didodececyldimethylammonium bromide) or DHDA (dihexadecyldimethylammonium acetate) aqueous solutions over a wide concentration range. They have showed that the lamellar phase is highly swollen up to ~1.4 wt% and that a critical behaviour near the lamellar-lamellar phase separation region exists. Caboi and Monduzzi [6] have also reported this phase separation of the DDAB system. They found that the two coexisting lamellar phases correspond to vesicles and planar lamellae in the lower and higher concentrations, respectively, and that the vesicles in the lower concentration transformed into the planar lamellae with increasing temperature at a fixed concentration. Haas et al. [7] have investigated the phase structures of dichain cationic surfactants with symmetric or asymmetric alkyl chains and showed that planar bilayers are transformed into multilamellar vesicles by decreasing the surfactant concentration. Tucker et al. [8–11] reported the phase behaviour of DHDAB (dihexadecyldimethylammonium bromide)/water and DHDAB/polyoxyethylene type surfactant (C_iE_j)/water systems. They performed a curve analysis of the small-angle neutron scattering profiles and explained the phase behaviour by using the obtained structural parameters that characterise lamellar or vesicular phases.

On the other hand, the ester-amide-type surfactant 2-[N-[3-alkanoyl(C16-18)amino propyl]-N-methylamino]ethyl alkano(C16-18)ate, hydrochloride (EA) is also a dichain cationic amphiphile and has been used as the main base for fabric softeners (Fig. 1(a)). An aqueous solution of EA is believed to have high product stability because of its characteristic feature of planar lamellar structures that form at higher concentrations by using polyoxyethylene-type nonionic surfactant as the co-surfactant. Fig. 1(b) shows a polarised microscope image of the EA aqueous solution. It is clear that any Maltese crosses, which show the existence of vesicles, cannot be found. However, until now, structures of EA solutions at dilute concentrations have not been clarified. These are important for understanding the function of EA as a fabric softener in a laundry setting.

In this research, we observed the structure of an EA dilute solution by using polarised or fluorescence microscopy, small/wide-angle X-ray scattering (SAXS/WAXS), dynamic light scattering (DLS) and cryogenic-temperature transmission electron microscopy (cryo-TEM). We found that upon decreasing the EA concentration, the repeat distance of the lamellar gel phase increased up to 28 nm. Below the EA concentration of 3 wt%, the planar