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Dried foam films with a triple bilayer structure induced by ionic liquids†

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Free-standing films with a triple bilayer structure were formed by drying micrometre-scale foam films of zwitterionic surfactants prepared from the aqueous solutions containing a certain concentration range of ionic liquids.

Thin foam films have been known for more than three centuries, and nowadays they have great importance in the chemical industry. In general, foam film is considered as a thin water layer sandwiched by two layers of surfactant molecules.[1,2] When the interstitial water drains or evaporates, the film becomes much thinner than the wavelength of visible light, and then appears to be black due to the diminished reflection intensity.[3–10] Such films are called black films. Two kinds of black films, common black films (CBF) and Newton black films (NBF), are known.[2] The former films have a water layer with a thickness of a few tens of nanometres.[8] On the other hand, the latter films are nothing but the reversed bilayers containing hydration water.[10]

The existence of liquid (or hydration) water had been deemed to be essential for stabilizing black films, since the films usually vanished when the water disappeared from the interstitial space.[11–18] However, very recently, we found that the foam films made of some categories of amphiphilic compounds were very stable in air when the sizes were no more than a few tens of micrometres. The films could exist even under ultrahigh vacuum conditions and at temperatures higher than 100 °C. We coined the term 'dried foam films' for such films.[19] Of course, water is essential for the formation process of dried foam films. One of its major roles is to maintain the structure of a thinning foam film with a high surface tension of water. Another is to remove excess surfactant from the interstitial space. Eventually, all the water and surfactant molecules are eliminated, and then ultrathin, free-standing, reversed bilayer remains.

In the present paper, we examine the influence of ionic liquids[20–22] on the formation process of dried foam films. When a small volume of ionic liquid is added to the aqueous solution of a surfactant, the concentration significantly increases with the evaporation of water. At the end, the non-volatile solvents should remain in the dried foam films. In the course of the study, we found that free-standing films with a triple bilayer structure formed in a wide range of the mixing ratio of ionic liquids against zwitterionic surfactant, dodecylphosphocholine (DPC). This is the first report of dried foam films with multi-bilayer structures.

First, we examined 1-ethyl-3-methylimidazolium chloride (EMICl). A 2000-mesh copper microgrid was immersed in an aqueous solution of DPC (5.6 mM) containing an equimolar amount of EMICl, pulled up perpendicularly, and allowed to stand for one hour in air at a humidity of 40–50%. This copper grid has square pores of 7.5 μm on a side, and each pore captures a small droplet of the DPC–EMICl solution. In the course of evaporation, the droplets become thin foam films, and are then transformed to dried foam films. Fig. 1A shows the scanning electron microscope (SEM) image. The square pores are uniformly covered by thin films, except for a pore at the upper right of the image. Fig. 1B shows the dried foam films prepared in a 1000-mesh copper grid. The pores of 17.5 μm on a side could be covered by the same procedures. We carefully ripped the microgrid with dried foam films, deposited 2-nm thick platinum by using a mild ion-sputter, and then subjected it to cross-sectional SEM observation. As indicated by an arrow in Fig. 1C, we often observed partially separated layers near the edge of the ripped part. The films have a thickness of 13 ± 1 nm (Fig. 1D). Considering the thickness of the platinum layers deposited on both surfaces (4 nm), dried foam films should have a thickness of about 9 nm.

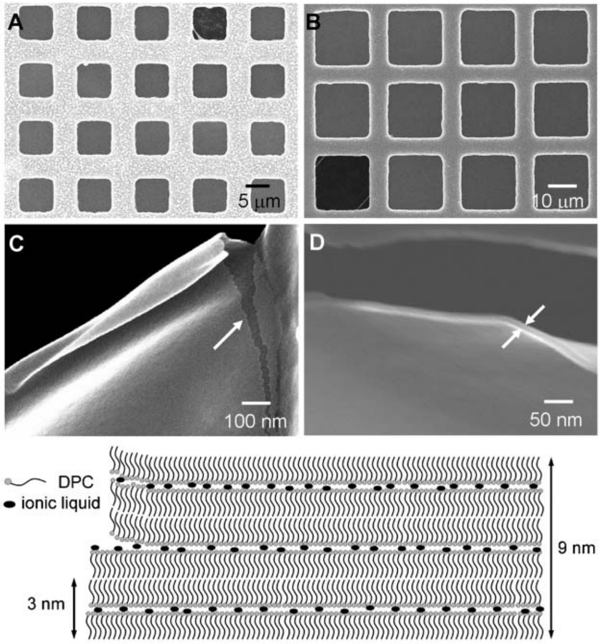

Fig. 1 SEM images of dried foam films prepared from the aqueous solution of DPC and EMICl at a molar ratio of 1/1 and schematic illustration of the triple bilayer structure. (A) and (B) show the dried foam films formed in square pores of 2000-mesh and 1000-mesh copper microgrids. (C) and (D) show the ripped part and the cross-sectional image of the films.

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The dried foam films made of pure DPC had a thickness of 3.0 ± 0.5 nm, as confirmed by high-resolution TEM observation. The films formed from DPC/EMICl (1/1 mol/mol) solution have a thickness three times larger than that of pure DPC films. From the observation of partially separated layers, we presumed that the latter films have a triple bilayer structure. The composition of dried foam films was examined by energy dispersive X-rays (EDX) measurements. For this purpose, we prepared the films in a TEM microgrid with a perforated polymer membrane.[19] This membrane has slightly hydrophobic pores of 2–4 μm which are very suitable for the formation of dried foam films. The molar ratio of EMICl against DPC was 0.11, as estimated from the EDX spectra of chlorine and phosphorus atoms. This indicates that 89% of ionic liquid drained to the edge of the foam film during the thinning process. The conformation of the DPC molecules was examined by FTIR measurements. The spectra with peaks at 2928 and 2858 cm^{-1} strongly indicated that the alkyl chains were highly disordered. We also confirmed that the dried foam films did not have any absorption attributable to the vibration modes of water.[23–25] From these results, we concluded that the film has a triple bilayer structure as illustrated in Fig. 1.

Subsequently, we examined the dried foam films prepared at different EMICl concentrations. The results are summarized in Table 1. When the molar ratio of EMICl against DPC was 0.5 in the mixed solution, films with a thickness of 4 nm were obtained. They had an EMICl content of 0.03 against DPC. The thermal stability decreased about 10 °C from the pure DPC films. At this molar ratio, the films probably have a bilayer structure. When the concentration of EMICl increased, thermal stability gradually decreased. However, the thickness remained at 9 nm until the molar ratio of EMICl/DPC increased to 5. In other words, dried foam films with a triple bilayer structure formed in a wide concentration range of EMICl. The content of EMICl in the films increased to 1.05, which indicated that the major part of the ionic liquid drained during the process of formation of dried foam films.

The internal homogeneity of EMICl-containing films was examined by using a scanning transmission electron microscope (STEM) at an acceleration voltage of 200 kV. Fig. 2A shows a high-resolution image of the film obtained from the solution at the molar ratio of EMICl/DPC = 2. The film was uniform at nanometre scale. In sharp contrast, when the ratio of EMICl was 4, abundant dark spots of 2–4 nm were observed (Fig. 2B). These spots should be caused by the phase separation of EMICl at the interstitial space of the triple bilayer structure. The number of spots increased with the molar ratio of EMICl. This is probably the reason for the lowering of thermal stability.

We also observed that the coverage of dried foam films decreased with the increase of the molar ratio of EMICl. For example, when a perforated polymer membrane was used as the substrate, more than 98% of pores could be covered by the dried foam films. However, the coverage slightly decreased to 95% when the molar ratio of EMICl was 5. At the molar ratio of 6, broken films started appearing. We hardly observed uniform films at the molar ratios of 7 to 10.

Table 1 Thickness, thermal stability and composition of dried foam films formed from DPC/EMICl solutions

	Dried foam films						
EMICl/DPC[a]	0	0.5	1	2	3	4	5
Thickness (nm)	3	4	9	9	9	9	9
Thermal stability (°C)	150	140	120	110	100	80	80
EMICl content[b]	0	0.03	0.11	0.14	0.31	0.62	1.05

[a] Molar ratio of EMICl against DPC in the solutions used for the formation of dried foam films. [b] Molar ratio of EMICl against DPC in dried foam films.

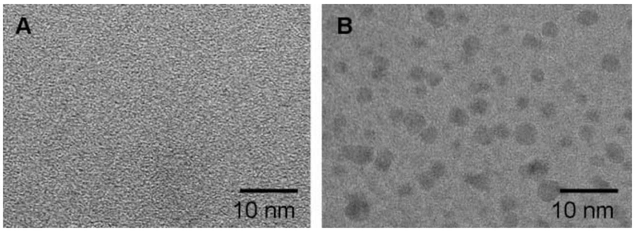
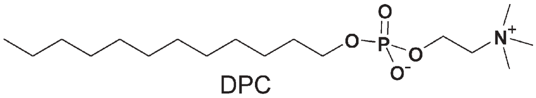
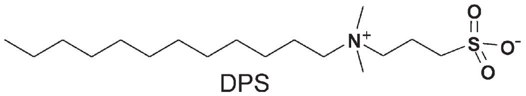


Fig. 2 STEM images of dried foam films prepared from the mixed solutions of DPC and EMICl. The molar ratios of EMICl against DPC are 2 in (A) and 4 in (B).

The dried foam films with a triple bilayer structure were obtainable by using a similar ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate ($\mathrm{EMIBF_4}$). On the other hand, when the counter anion was bromide (EMIBr) or hexafluorophosphate ($\mathrm{EMIPF_6}$), it was difficult to prepare uniform films with a triple bilayer structure. Anions and anionic molecules electrostatically interact with the trimethylammonium group of DPC. The latter bromide and hexafluorophosphate ions might have too strong an interaction with the hydrophilic moiety of this surfactant to give a triple bilayer structure.



DPC



DPS

Next, we examined another zwitterionic surfactant with a negative charge at the end of the structure, 3-dodecyldimethylammoniopropanesulfonate (DPS). The dried foam films made of this surfactant disappeared at 50 °C, while those of DPC can exist up to 150 °C. The thermal instability seems to be due to the low structurability of the hydrophilic moiety. When the films were made from the 1 : 1 mixture of DPS and $\mathrm{EMIBF_4}$, the thermal stability increased by 20 °C.

On the other hand, $\mathrm{EMIPF_6}$ showed a further increase of thermal stability. The dried foam films obtained at the molar ratio of $\mathrm{EMIPF_6}$/DPS = 0.5 were stable up to 100 °C, and the films made from the 1 : 1 mixture were stable up to 130 °C (Fig. 3). SEM observation revealed that the thickness of these films increased with the concentration of $\mathrm{EMIPF_6}$. For example, the former films had a thickness of 5 nm, and the thickness of the latter films was 12 nm, as shown in Fig. 4. In the case of DPS films, the addition of ionic liquids seems to induce continuous stratification, which relates to the thermal stabilization of dried foam films.

The stratification of thin foam films has been observed since the beginning of the last century.[26,27] In the reports, the films often gave consecutive stepwise thinning under constant capillary pressure, when the surfactant concentration was much higher than the critical micelle concentration (CMC). The surface

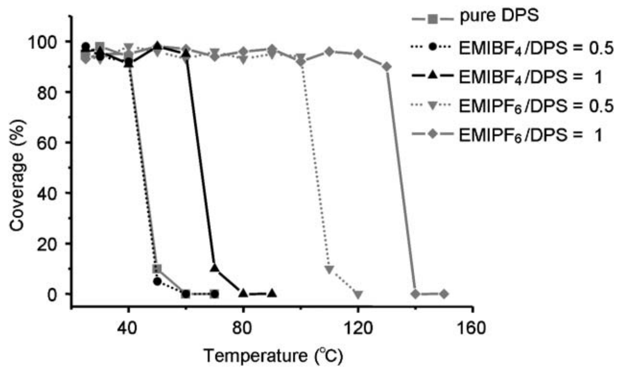


Fig. 3 Temperature dependence of the coverage of pure DPS films, DPS/EMIBF$_4$ films and DPS/EMIPF$_6$ films.

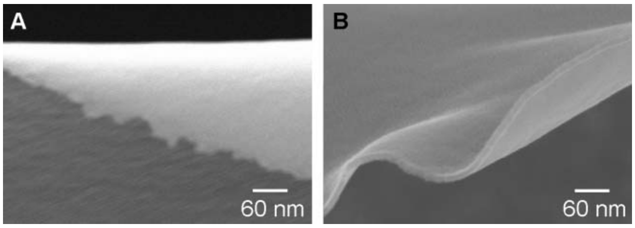


Fig. 4 Cross-sectional SEM images of dried foam films prepared from the mixed solutions of DPS and EMIPF$_6$. The molar ratios of EMIPF$_6$ against DPS are 0.5 in (A) and 1 in (B).

elasticity and the structuring of surfactant were suggested as the important factors for the stratification.[26–32] The ordered surfactant layers inside the foam films flow out towards the periphery during the drainage of water. Therefore, they are generally considered as non-equilibrium state. Eventually, the multilayer films turn to more stable Newton black films. In fact, DPC/EMICl films at the ratio of 0.5 gave a bilayer structure. However, this was not the case when the molar ratio of the ionic liquid was 1 to 5. The generally metastable stratified films were stabilized by the ionic liquid and fixed as they were.

The effects of ionic liquids are thought to be as follows. First, they are non-volatile solvents, so that the concentration increases during the process of formation of dried foam films. Most of the ionic liquids move to the edge of the film. That is to say, the periphery of the film becomes a rich part of ionic liquids. In contrast, a small amount of ionic liquids remains in the interstitial space of foam films, as confirmed by EDX measurements. The consecutive changes in the composition of ionic liquids in dried foam films indicate that the incorporation is caused by the difference in the chemical potentials between the edge and central parts. Ionic liquids at the edge of the film might give a capillary pressure to the central part. This pressure needs to be compensated by the tension caused by the structuring of surfactant molecules. In the cases of DPC and some ionic liquids, a triple bilayer structure was obtained in a wide range of the mixing ratio, instead of the usual bilayer structure. In such cases, ordered aggregates such as bilayer vesicles might be induced by the ionic liquids at the interstitial layer of foam film and they are immobilized as double bilayers between two surface monolayers. Actually, the solubility of DPC in the ionic liquids is not very high. In general, the low solubility facilitates the formation of molecular assemblies.

In conclusion, uniform free-standing films with a multiple bilayer structure were obtained from the aqueous solution of zwitterionic surfactants containing ionic liquids. In the past, dried foam films were defined as free-standing reversed bilayers, since we could not observe any molecules (including water) at the interstitial space of two surface monolayers.[19] In contrast, in the present paper, we could extend the concept of dried foam films to stratified surfactant films. These films are close to but different from the metastable and transient stratified films observed in surfactant/water systems. We have demonstrated that the films were very stable under ultrahigh vacuum conditions. The thermal stability could be controlled by the selection of surfactants and by the molar ratio of ionic liquids. Especially, triple bilayer structure was widely observed in our system. This is also the first report of ionic liquids being used for the preparation of foam films as well as dried foam films. The non-volatile property enables us to combine the free-standing surfactant films prepared by a wet process and the deposition techniques under ultrahigh vacuum conditions. Such an investigation is now in progress in our group.

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