Foam Films

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Foam Films Obtained with Ionic Liquid

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A foam film generally consists of an aqueous layer with surfaces covered by surfactant.[1–4] The foam film becomes thinner with the drainage of the aqueous layer by capillary pressure. Then the film becomes black because of the diminished reflected light. Such films are categorized into two types: common black films and Newton black films. In general, the former films have a water layer a few tens of nanometers in thickness.[5–7] The latter films contain only water of hydration. Thus, Newton black films are much thinner than common black films.[8–12] Even though black films were discovered more than 300 years ago,[13,14] they have been studied mainly in aqueous systems.[15]

Herein, we report the unprecedented properties of foam films obtained with an ionic liquid. Centimeter-scale foam films of nonionic surfactants were prepared by using 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]) as a solvent, and they were transferred onto submillimeter-sized holes. The films spontaneously became thinner, and finally reversed bilayers solvated with the ionic liquid were left in the holes. The obtained films showed superior thermal stability as compared to that of the aqueous system. In addition, it was possible to subject the films to ultrahigh vacuum conditions. Herein, we tentatively call them Newton black films, although it is not clear whether such films exactly match the definition of Newton black films.[16]

Ionic liquids are different from water in terms of vapor pressure, viscosity, and miscibility with other solvents.[17,18] However, they can dissolve various surfactants, which give molecular assemblies as seen in water. For example, imidazolium-type ionic liquids are good solvents for polyethylene oxide (PEO),[19] and PEO-based surfactants form micelles,[20–22] vesicles,[23] lyotropic liquid-crystalline phases,[24,25] and microemulsions with alkanes[26] when dissolved or dispersed in the ionic liquids. Herein, we used Brij-35, a typical PEO-based surfactant. This molecule has a dodecyl chain linked to 23 ethylene oxide units. A round wire frame with a diameter of 2 cm was immersed in a solution of Brij-35 (50 mM) dissolved in the ionic liquid [EMIM][BF_4]. The frame was carefully lifted into the air and allowed to stand for a few tens of minutes at 25 °C. The foam film formed in the frame gradually became thinner, and then the film started to exhibit bright iridescent colors.

In this process, [EMIM][BF_4] slowly and continuously drains through the wires twisted at the bottom of the frame. Figure 1 a–c shows photographs taken after 5, 30, and 50 min, respectively. The interval of the interference fringes became larger with decreasing thickness and a white region appeared at the top of the film. The thickness of the area marked with a dashed circle in Figure 1 c is in the range of (200 ± 50) nm. Such a film was transferred onto a porous substrate and allowed to stand for one day. Figure 1 d–f illustrates a foam film transferred on a 1000-mesh copper grid that has a regular array of 17.5-μm-wide square holes. The initial film has a core layer of the ionic liquid containing Brij-35. The layer spontaneously thins, and finally a Newton black film solvated with [EMIM][BF_4] forms in the central part of the hole (Figure 1 f). The excess ionic liquid and Brij-35 migrate to the edge of the hole and remain there.

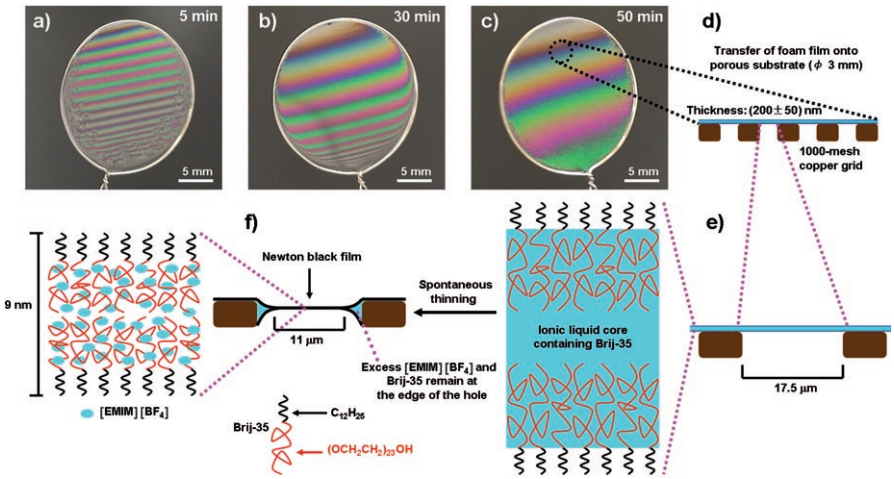

Figure 1. Preparation of Newton black films of Brij-35 by using [EMIM][BF_4]. Photographs were taken a) 5, b) 30, and c) 50 min after lifting the wire frame. The area marked with a circle in (c) was transferred onto a porous substrate (d). e) Film covering a hole in a copper grid. f) The transferred film spontaneously becomes thinner, and finally a Newton black film solvated with [EMIM][BF_4] is formed.

Newton black films were obtained by using various copper grids with hole sizes in the range of 17.5 to 500 μm. Figure 2 a

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and b shows scanning electron microscopy (SEM) images of the films formed on 600- and 100-mesh copper grids. It is apparent that the hexagonal and square holes were uniformly covered with thin Brij-35 films. The films prepared in large holes were occasionally broken when they were placed on a SEM specimen holder. Such a film is shown in Figure 2c. The flexible and uniform film that covered a square hole with 0.4-mm-long sides is clearly visualized in this image.

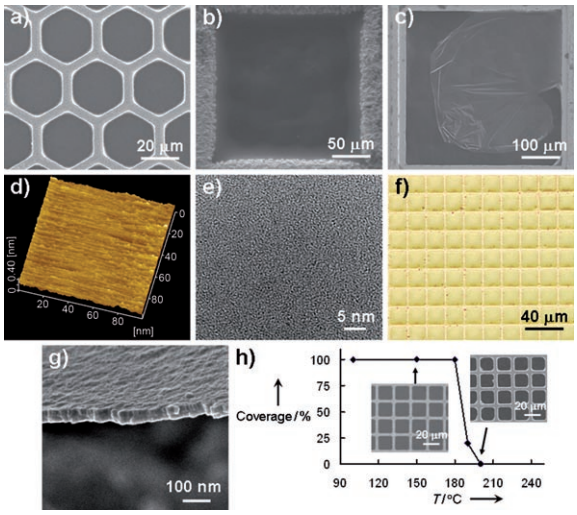

Figure 2. Microscopic images of Brij-35 films and their thermal stability. a–c) SEM images of Brij-35 films formed in hexagonal and square holes of 600-, 100-, and 50-mesh copper grids, respectively. The surface roughness and internal uniformity were characterized by d) AFM and e) TEM. The optical microscopic image (f) and cross-sectional SEM image (g) were obtained after coating an 18-nm-thick platinum layer on one side and on both sides of the films, respectively. h) Temperature dependence of the residual ratio (coverage) of Brij-35 films on 1000-mesh copper grids.

Figure 2d shows an atomic force microscopy (AFM) image of a Brij-35 film. The root-mean-square roughness obtained from a 100-nm square was less than 0.1 nm. This result indicates that the film is quite homogeneous in the observation area. The internal uniformity of this film was confirmed by high-magnification transmission electron microscopy (TEM) measurements (Figure 2e). Notably, Brij-35 films were stable under the irradiation of an electron beam, in which nonconductive organic thin films were often decomposed. The films were also stable under the ultrahigh-vacuum conditions (less than 1×10^{-6} Torr) necessary for TEM observation. The Brij-35 films were invisible in optical microscopy with a detection limit near 10 nm for observing the thickness of organic thin films. Therefore, they were assumed to be thinner than 10 nm. The existence of Brij-35 films was confirmed after coating them with a thick platinum layer (Figure 2f).

Brij-35 films were very flexible if detached from the edge of the copper grid, and the detached films were readily curved by an electron beam when used for cross-sectional SEM observations. However, we succeeded in making observations by coating a thick platinum layer (18 nm) on both sides of the films before they were torn off. Figure 2g shows a cross section for which the observed thickness was (45 ± 2) nm. By subtracting the thickness of the platinum layers, the thickness of the Brij-35 film was estimated to be approximately 9 nm.

When PEO chains align to form a helical conformation in the crystalline state, one ethylene oxide unit gives a length of 0.28 nm in the direction parallel to the helical axis.[27] Therefore, the 23 units should have a length of 6.4 nm. By considering the length of a dodecyl chain (1.5 nm), the total length of Brij-35 is assumed to be 7.9 nm. This value is slightly shorter than the thickness estimated for a Brij-35 film (9 nm). PEO chains solvated with ionic liquid might be in the random coil conformation. The estimated thickness is in good agreement with the diameter of globular micelles in the Brij-35/water binary system (9.0–10.5 nm).[28] The inside of Brij-35 film must be filled with highly entangled PEO moieties, and the surfaces are mainly occupied by the dodecyl chains. In this structure, steric repulsion between two monolayers seems to be present.

The films were further evaluated by confocal Raman spectroscopy. The spectra showed the characteristic bands of [EMIM][BF_4], which were in good agreement with those reported.[29] This result verifies the presence of the ionic liquid in Brij-35 films. The composite ratio was estimated by X-ray photoelectron spectroscopy (XPS). For the measurements, the film was prepared in a 17.5-μm-wide square hole and the central area (ca. 10 μm) was selectively irradiated with a focused X-ray beam. The resulting spectra showed clear peaks attributable to C, N, O, and F. The atomic ratio of O/N estimated from the corresponding peak areas was 4.2.

By considering the 24 oxygen atoms of a Brij-35 molecule and two nitrogen atoms of an [EMIM][BF_4] molecule, we determined the molar ratio of [EMIM][BF_4]/Brij-35 to be 2.9. It is known that an imidazolium cation has a suitable size to be encircled by eight ethylene oxide units of PEO.[30] The observed molar ratio was consistent with this prediction. The atomic ratio of C/O was 3.7. This value was also in agreement with the ratio (C/O 3.1) expected for the composition $(\text{Brij-35})_{1.0}([\text{EMIM}][BF_4])_{2.9}$. From these data, we concluded that Brij-35 forms Newton black films solvated with a triple molar quantity of [EMIM][BF_4] (Figure 1f).

The thermal stability of Brij-35 films was evaluated from the changes of coverage (residual ratio) with increasing temperature. For the statistical analysis, we investigated more than 600 holes of 1000-mesh copper grids at the given temperature (see Figure 2h). Surprisingly, the coverage was 100% from room temperature up to 180°C, and sharply decreased to 20% when the grid was heated to 190°C. Almost all the films disappeared at 200°C. It is interesting that the films can exist at a temperature much higher than the melting point of Brij-35 (41.3°C). The origin of this thermal stability is not very clear. However, [EMIM][BF_4] must interact with PEO chains and stabilize the two-dimensionally self-assembled structure.[19,30]

The selection of ionic liquid was important. [EMIM][SCN], which has a thiocyanate ion instead of the $[BF_4]^-$ ion of [EMIM][BF_4], was available for the formation of Newton black films. However, the coverage on 1000-mesh grids was no more than 80%. [EMIM][CF_3SO_3] containing a $[CF_3SO_3]^-$ ion tended to form gel when mixed with Brij-35 and was hard

to use as the solvent. On the other hand, [EMIM][BF_4] was suitable for other surfactants. For example, Brij-78 and Brij-700, which have an octadecyl chain linked to 20 and 100 ethylene oxide units, respectively, gave thermally stable Newton black films.

The most important extension was made for an amphiphilic polymer, Pluronic F127, which is a difunctional block copolymer composed of one hydrophobic polypropylene oxide (PPO) part and two hydrophilic PEO parts.[31] SEM images of the films prepared on 75- and 600-mesh copper grids are shown in Figure 3a and b, respectively. The resulting films had very flat and smooth surfaces, the same as Brij-35

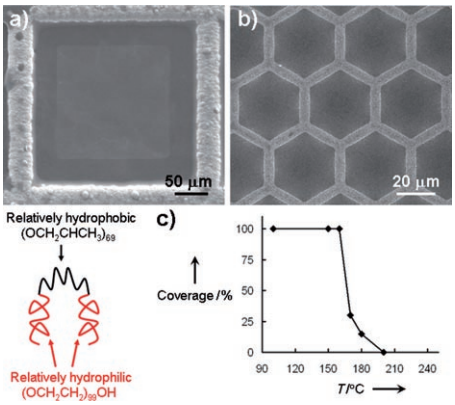

Figure 3. Newton black films of Pluronic F127 obtained with [EMIM]-[BF_4]. a,b) SEM images of the films formed in the holes of 75- and 600-mesh copper grids. c) Temperature dependence of the coverage of Pluronic F127 films on 1000-mesh copper grids, which demonstrates the thermal stability up to 160°C. The concentration of the polymer was 5 mM throughout the experiments.

films. Cross-sectional SEM observations revealed that the films had a thickness of 19 nm. This value was a little smaller than the diameter of the micelles (ca. 24 nm) formed in aqueous solutions of Pluronic F127, which was estimated by the dynamic light scattering technique.[31] The film in Figure 3a has an area of $250 \times 250\ \mu m^2$. The fringes show a little dark color, which indicates that an [EMIM][BF_4]-rich area exists at the edge of the hole. The films formed on 1000-mesh grids could exist at a temperature higher than 150°C (Figure 3c). It is apparent that Pluronic F127 gives submillimeter, thermally stable Newton black films with an ionic liquid.

Recently, we reported that water-free reversed bilayers were obtained by drying foam films of some amphiphilic compounds.[32] However, the films were limited in size from submicrometers to micrometers. To prepare much larger films, we examined the addition of ionic liquids to aqueous solutions of surfactants. However, such an approach resulted in the stratification of the surfactant films.[33] In the present study, we demonstrated that submillimeter films that are very stable in a vacuum are obtainable by means of a nonvolatile ionic liquid. In addition, these are the first examples of thermally stable black films containing solvent. [EMIM][BF_4] has a viscosity 38 times higher than that of water.[34] Such a nature enabled us to readily transfer foam films of large area onto porous substrates, with 100% coverage of the holes.

In previous reports, the formation of Newton black films required a considerable concentration of electrolyte, such as NaCl or KCl. These electrolytes have been explained to screen the electrostatic repulsions among the hydrophilic heads of nonionic surfactants.[1,12] In our system, [EMIM]-[BF_4] seems to play a role similar to the electrolytes in the conventional Newton black films. Exerowa and co-workers reported that amphiphilic triblock copolymers similar to Pluronic F127 gave only common black films, even from aqueous solutions containing a high concentration of electrolytes.[6,7] This finding was attributed to the considerable steric repulsion of a brush-to-brush contact of PEO chains. In the present study, Newton black films of a triblock copolymer were readily obtained by using [EMIM][BF_4]. The strong interaction between PEO and the imidazolium cation[19,30] may generate an attractive force to make two polymer layers close together. The incomplete draining of [EMIM][BF_4] in the films implies the high affinity of PEO chains and [EMIM][BF_4]. Finally, it should be stressed that conventional foam films have been studied mainly from the viewpoint of physicochemical properties under controlled humidity.[1–4,8–12] In sharp contrast, we provide herein a novel materials processing system based on the transfer of free-standing liquid films, in which a centimeter-scale film is converted into submillimeter films with nanometer thickness. Such processing will be useful for the fabrication of nanoseparation membranes and organic optical devices.

Experimental Section

The foam films were prepared on a frame made of stainless-steel wire with a width of 0.35 mm. The thinning process was monitored by a digital video camera (Sony HDR-SR1); photographic images were taken with the same camera. The thickness slowly decreased with the draining of the surfactant solution through the wires twisted at the bottom of the frame. The foam film usually vanished after black film spread at the top. The foam film suddenly disappeared; in other words, it had no specific lifetime. A movie of the thinning process is available in the Supporting Information. The foam film transferred on a copper grid was allowed to stand for one day in air for further thinning to Newton black films.

Materials and experimental details of the microscopic observations are described in the Supporting Information.

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[1] D. Exerowa, P. M. Kruglyakov, *Foam and Foam Films: Theory, Experiment, Application*, Elsevier, Amsterdam, **1998**.
[2] D. Platikanov, D. Exerowa in *Fundamentals of Interface and Colloid Science*, *Vol. 5* (Ed.: J. Lyklema), Elsevier, Amsterdam, **2005**.
[3] V. Bergeron, *J. Phys. Condens. Matter* **1999**, *11*, R215–R238.
[4] C. Stubenrauch, R. Klitzing, *J. Phys. Condens. Matter* **2003**, *15*, R1197–R1232.

[5] H. D. Yaros, J. Newman, C. J. Radke, *J. Colloid Interface Sci.* **2003**, *262*, 442 – 455.
[6] D. Exerowa, R. Sedev, R. Ivanova, T. Kolarov, T. F. Tadros, *Colloids Surf. A* **1997**, *123–124*, 277 – 282.
[7] R. Sedev, R. Ivanova, T. Kolarov, D. Exerowa, *J. Dispersion Sci. Technol.* **1997**, *18*, 751 – 767.
[8] O. Bélorgey, J. J. Benattar, *Phys. Rev. Lett.* **1991**, *66*, 313 – 316.
[9] M. Nedyalkov, R. Krustev, A. Stankova, D. Platikanov, *Langmuir* **1992**, *8*, 3142 – 3144.
[10] N. Krasteva, R. Krustev, H. J. Müller, D. Vollhardt, H. Möhwald, *J. Phys. Chem. B* **2001**, *105*, 1185 – 1190.
[11] J. J. Benattar, M. Nedyalkov, F. K. Lee, O. K. C. Tsui, *Angew. Chem.* **2006**, *118*, 4292 – 4294; *Angew. Chem. Int. Ed.* **2006**, *45*, 4186 – 4188.
[12] R. M. Muruganathan, H. J. Müller, H. Möhwald, R. Krastev, *Langmuir* **2005**, *21*, 12222 – 12228.
[13] R. Hooke, *Communications to the Royal Society*, March **1672**, p. 28.
[14] I. Newton, *Opticks Book II*, *Part I*, Smith and Walford, London, **1704**.
[15] There are some reports on oil-based foam or black films: a) V. Bergeron, J. E. Hanssen, F. N. Shoghl, *Colloids Surf. A* **1997**, *123–124*, 609 – 622; b) K. Khristov, S. D. Taylor, J. Czarnecki, J. Masliyah, *Colloids Surf. A* **2000**, *174*, 183 – 196.
[16] L. T. Minassian-Saraga, B. Vincent, M. Adler, A. Barraud, N. V. Churaev, D. F. Eaton, H. Kuhn, M. Misono, D. Platikanov, J. Ralston, A. Silberberg, J. N. Zemel, *Thin Solid Films* **1996**, *277*, 7 – 78.
[17] M. J. Earle, J. M. S. S. Esperança, M. A. Gilea, J. N. C. Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon, J. A. Widegren, *Nature* **2006**, *439*, 831 – 834.
[18] J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667 – 3692.
[19] A. Triolo, O. Russina, U. Keiderling, J. Kohlbrecher, *J. Phys. Chem. B* **2006**, *110*, 1513 – 1515.
[20] J. L. Anderson, V. Pino, E. C. Hagberg, V. V. Sheares, D. W. Armstrong, *Chem. Commun.* **2003**, 2444 – 2445.
[21] K. A. Fletcher, S. Pandey, *Langmuir* **2004**, *20*, 33 – 36.
[22] C. Patrascu, F. Gauffre, F. Nallet, R. Bordes, J. Oberdisse, N. de Lauth-Viguerie, C. Mingotaud, *ChemPhysChem* **2006**, *7*, 99 – 101.
[23] Y. He, Z. Li, P. Simone, T. P. Lodge, *J. Am. Chem. Soc.* **2006**, *128*, 2745 – 2750.
[24] M. U. Araos, G. G. Warr, *J. Phys. Chem. B* **2005**, *109*, 14275 – 14277.
[25] L. Wang, X. Chen, Y. Chai, J. Hao, Z. Sui, W. Zhuang, Z. Sun, *Chem. Commun.* **2004**, 2840 – 2841.
[26] R. Atkin, G. G. Warr, *J. Phys. Chem. B* **2007**, *111*, 9309 – 9316.
[27] Y. Takahashi, H. Tadokoro, *Macromolecules* **1973**, *6*, 672 – 675.
[28] M. Tomšič, M. Bešter-Rogač, A. Jamnik, W. Kunz, D. Touraud, A. Bergmann, O. Glatter, *J. Phys. Chem. B* **2004**, *108*, 7021 – 7032.
[29] Y. Umebayashi, T. Fujimori, T. Sukizaki, M. Asada, K. Fujii, R. Kanzaki, S. Ishiguro, *J. Phys. Chem. A* **2005**, *109*, 8976 – 8982.
[30] L. T. Costa, M. C. C. Ribeiro, *J. Chem. Phys.* **2006**, *124*, 184902.
[31] C. Wu, T. Liu, B. Chu, D. K. Schneider, V. Graziano, *Macromolecules* **1997**, *30*, 4574 – 4583.
[32] J. Jin, J. Huang, I. Ichinose, *Angew. Chem.* **2005**, *117*, 4608 – 4611; *Angew. Chem. Int. Ed.* **2005**, *44*, 4532 – 4535.
[33] W. Bu, J. Jin, I. Ichinose, *Chem. Commun.* **2007**, 1325 – 1327.
[34] R. Hagiwara, Y. Ito, *J. Fluorine Chem.* **2000**, *105*, 221 – 227.

