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Preliminary Note

Preparation and surface characteristics of perfluoroalkane Langmuir–Blodgett films

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Abstract

Surface pressure–area curves for the perfluoroalkanes $C_{16}F_{34}$, $C_{20}F_{42}$ and $C_{24}F_{50}$ showed that monolayers were formed on the surface of water. The monolayers of $C_{20}F_{42}$ and $C_{24}F_{50}$ were deposited on various substrates by the Langmuir–Blodgett (LB) technique; LB films on hydrophobized mica show excellent water repellency with contact angles of water of 155° and 153° respectively. It was shown by comparison of the reflection–absorption and transmission IR spectra that difluoromethylene chains in the perfluoroalkane LB films are oriented perpendicular to the substrate.

Keywords: Langmuir–Blodgett; Perfluoroalkane; Monolayer

1. Introduction

Only amphiphilic molecules with a polar head and a hydrophobic tail have been considered to form monolayers at the air–water interface [1–3]. However, Li et al. [4] showed that perfluoroeicosane formed a stable, ordered Langmuir monolayer on water, in which the molecules were vertically aligned and packed in a hexagonal array, although the compound was not amphiphilic. In the perfluoroeicosane monolayer, the interactions within the layer are sufficiently strong to maintain the layer packing when one face of the layer is in contact with water, and the van der Waals' interactions between the monolayer and the water surface are sufficient to stabilize the system as a Langmuir monolayer. Because the surface energies of fluorine-containing compounds are markedly low, coating of a substrate with perfluoroalkane is expected to afford a new fluorinated surface with extremely high water and oil repellency.

In this study, the surface pressure (π) vs. area (A) curves on water for the perfluoroalkanes $C_{16}F_{34}$, $C_{20}F_{42}$ and $C_{24}F_{50}$ were evaluated, which gave Langmuir monolayers. The monolayers of $C_{20}F_{42}$ and $C_{24}F_{50}$ were deposited on various substrates by the Langmuir–Blodgett (LB) technique and the contact angles of water to the coated surfaces were measured. The orientation of the perfluoroalkane molecules in the LB films was evaluated by a comparison of the reflection–absorption (RA) and transmission IR spectra.

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2. Experimental details

The perfluoroalkanes $C_{16}F_{34}$, $C_{24}F_{50}$ (Fluorochem Ltd.) and $C_{20}F_{42}$ (PCR Inc.) were obtained commercially and purified by sublimation before use. Monolayers were obtained in a Kyowa Interface Science Co., Ltd. HBM-AP polytetrafluoroethylene (PTFE)-coated trough, the surface pressures being measured by the Wilhelmy plate method. A perfluorohexane solution of the compound (approximately 0.25 mg ml^{-1}) was spread on purified water (Milli-Q system, Millipore Ltd.) at 5 °C, and the resulting monolayer was compressed at a rate of 56 cm^2 min^{-1} after standing for 3 min. The monolayer was observed under a Nippon Laser and Electronics Lab. NL-EMM670S-01 Brewster angle microscope.

LB films of perfluoroalkanes $C_{20}F_{42}$ and $C_{24}F_{50}$ were prepared on substrates at a transfer rate of 5 mm min^{-1} in the vertical mode at 15 mN m^{-1} and 5 °C. Hydrophobized mica as a substrate was prepared by transferring a dioctadecyldimethylammonium-bromide monolayer at 35 mN m^{-1}, 20 °C and 5 mm min^{-1} in the upstroke mode. The other substrates were commercially obtained and were used after washing with alcohol. Contact angles of water to the LB films (more than 50 layers) were measured with an Erma goniometer G-1. IR spectra were recorded on a Shimadzu FTIR-8000PC for the LB films with a resolution of 2 cm^{-1}. The RA IR spectra were obtained using a reflection attachment RAS-8000 at an incident angle of 75°.

3. Results and discussion

The π–A isotherms of $C_{16}F_{34}$, $C_{20}F_{42}$ and $C_{24}F_{50}$ at 5 °C are shown in Fig. 1. All the perfluoroalkanes form monolayers with collapse pressures of 19.1 mN m^{-1} ($C_{16}F_{34}$), 27.3 mN m^{-1} ($C_{20}F_{42}$) and 21.8 mN m^{-1} ($C_{24}F_{50}$). Conventional linear extrapolation of the high-pressure limbs of the isotherms to zero pressure yields limiting areas of 0.30 nm^2 per molecule for $C_{20}F_{42}$ and $C_{24}F_{50}$, the same as the reported value for $C_{20}F_{42}$ [4]. Although the π–A curve for $C_{16}F_{34}$ is typical and resembles the curves for $C_{20}F_{42}$ and $C_{24}F_{50}$, the limiting area is considerably smaller, 0.10 nm^2 per molecule, which indicates that the molecules sublimate after the solution is spread on water. The fact that the limiting area of $C_{16}F_{34}$ at 20 °C is 0.07 nm^2 per molecule, smaller than the area at 5 °C, supports sublimation. The aggregation processes of the perfluoroalkane monolayers were observed by Brewster angle microscopy, in which the molecules on water formed domains under a low surface pressure, and the domains fused together becoming large with increasing surface pressure. Homogeneously condensed monolayers seemed to form above 15 mN m^{-1}.

The monolayers of $C_{20}F_{42}$ and $C_{24}F_{50}$ were deposited on glass, quartz, KRS-5 plate, mica and hydrophobized mica surfaces by the LB technique. The IR spectra for the $C_{20}F_{42}$ LB film on a KRS-5 plate are shown in Fig. 2. The deposition was confirmed by the IR spectra, in which the absorption due to the CF_2 symmetric and antisymmetric stretching bands (1151 and 1210 cm^{-1}) increases with the deposition cycle [5]. The orientation of the perfluoroalkane molecules on the substrates was evaluated by the RA and transmission IR spectra. As shown in Fig. 3, the absorption due to the CF_2 groups is weaker in the RA spectrum than in the transmission spectrum. This demonstrates that the difluoromethylene chains are oriented perpendicular to the substrate [6,7].

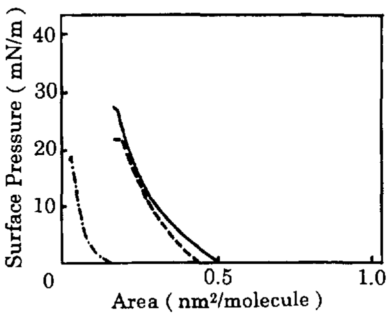

Fig. 1. Surface pressure–area isotherms of perfluoroalkanes at 5 °C: ———, $C_{20}F_{42}$; - - -, $C_{24}F_{50}$; – · –, $C_{16}F_{34}$.

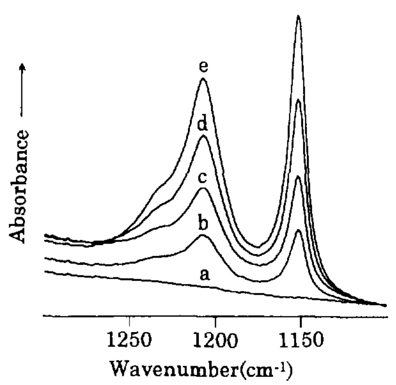

Fig. 2. Transmission IR spectra for a $C_{20}F_{42}$ LB film on a KRS-5 plate: curve a, bare; curve b, 5 layers; curve c, 10 layers; curve d, 15 layers; curve e, 20 layers.

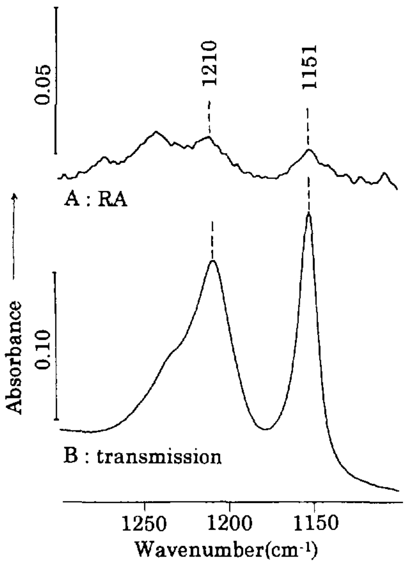

Fig. 3. FTIR spectra for a $C_{20}F_{42}$ LB film (50 layers). (A) Reflection–absorption spectrum for an LB film deposited on an Al plate. (B) Transmission spectrum for an LB film deposited on a KRS-5 plate.

The LB films on hydrophobized mica have excellent water repellency with contact angles of water of 155° ($C_{20}F_{42}$) and 153° ($C_{24}F_{50}$), which are much larger than the values for PTFE (110°) and fluorinated graphite (147°). This arises from the large CF_3 content at the LB film surface due to the perfluoroalkane arrangement, because the surface energy of the CF_3 group is lower than that of the CF_2 group [8]. The contact angles of water to $C_{20}F_{42}$ LB films on glass (149°), quartz (132°), KRS-5 plate (144°) and mica (120°) are somewhat small; this may be attributed to the surface properties of the substrates, such as the hydrophilicity and unevenness, which cause imperfections in the LB films resulting in a decrease in the CF_3 content at the film surfaces.

4. Conclusions

Linear perfluoroalkanes of appropriate chain length form monolayers on water as well as conventional amphiphiles. The perfluoroalkane monolayers can be deposited on various substrates by the LB technique; the perfluoroalkane molecules are oriented perpendicular to the substrate and the coated surfaces have excellent water repellency.

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