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STABILIZATION AND FACILITATED DEPOSITION OF SURFACE MONOLAYERS OF FLUOROCARBON AMPHIPHILES THROUGH POLYION COMPLEX FORMATION[1)]

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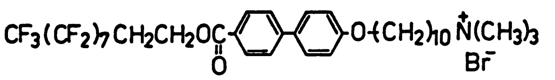
Bilayer-forming ammonium amphiphiles with one, two, or three fluorocarbon chains formed surface monolayers on water, which were stabilized by polyions in the subphase and deposited on polycarbonate films as polyion complexes by the Langmuir-Blodgett technique.

We have demonstrated that synthetic amphiphiles with one, two, or three fluorocarbon chains form spontaneously stable bilayer membranes in water.2-4) Transparent cast films were readily obtained from these aqueous bilayer dispersions,5) and those of fluorocarbon bilayers exhibited high degrees of molecular orientation and selective permeation of O_2 over N_2.6) The fluorocarbon component was concentrated near the film surface in multi-bilayer films of hydrocarbon and fluorocarbon amphiphiles.7)

The formation of surface monolayers was reported thirty years ago for a perfluoroalkyl carboxylic acid and a perfluoroalkyl alcohol by Arrington and Patterson,8) and for a perfluoroalkylammonium iodide by Ellison and Zisman (on mineral oil).9) Elbert and others10) discussed the surface pressure-area characteristics and the phase separation behavior of surface monolayers of several double-chain (fluorocarbon), ammonium amphiphiles. Deposition of monolayers of some perfluoroalkyl carboxylic acids on subphases containing Al^{3+} was reported very recently by Miyata and Nakahama.11) On the other hand, Mitsuya and Taniguchi12) mentioned that vacuum deposition on glass of more than one molecular layers of perfluoroalkyl carboxylic acids was not possible. In our related experiments, only a single layer of the Ba salt of a perfluoroalkyl carboxylic acid ($C_8F_{17}CH_2CH_2COOH$) could be deposited on a multilayer of stearic acid, while ten layers (the Z type) of a double-chain fluorocarbon amphiphile (**2**) were deposited.13)

The present communication describes stabilization and facilitated deposition by polyion complex formation of surface monolayers of single-chain, double-chain, and triple-chain fluorocarbon amphiphiles (**1**, **2**, and **3**). The preparations and aggregation characteristics of these amphiphiles,2-4) and the formation of polyion complexes from hydrocarbon bilayer membranes and oppositely-charged polymers in water14) and at the air-water interface15) have been reported elsewhere.

The measurement of the surface pressure (π)-area (A) curves and the deposition of surface monolayers were conducted by using a home-made, microprocessor-



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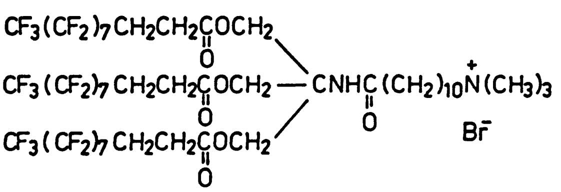

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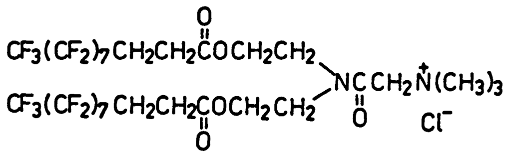

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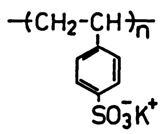

PSS⁻K⁺

controlled film balance. Figure 1 displays π-A curves for the three amphiphiles on purified water ("Milli-Q" system, Millipore Ltd.), and on aqueous potassium poly(styrenesulfonate)(PSS^-K^+, 2×10^{-5} unitM; 1 M = 1 $mol \cdot dm^{-3}$). The amphiphiles were dissolved in ethanol-benzene (1:9 vol/vol) and spread at 20 °C. On pure water, amphiphiles 1 and 2 formed stable monolayers with collapse pressures at ca. 60 $mN \cdot m^{-1}$. Extrapolation of the linear portion of the condensed phase to the zero pressure gave molecular areas of 0.31 nm^2 for 1 and 0.60 nm^2 for 2. These values are consistent with close packing of the fluorocarbon chain normal to the water surface, since the molecular cross section of the fluorocarbon chain is 0.29 nm^2.[8)] In contrast, amphiphile 3 did not produce a condensed monolayer. The π-A curves were noticeably affected by the presence of PSS^-K^+ in the subphase. The condensed phases were produced at lower surface pressures.

Deposition of these surface monolayers was examined by using a porous polycarbonate film (Nuclepore Membrane, Nomura Micro Science Co., Ltd., pore size = 0.03 μm). The monolayers on pure water could not be deposited at 20 °C under surface pressures of 30 $mN \cdot m^{-1}$ for 1 and 35 $mN \cdot m^{-1}$ for 2 and 3. In contrast, the monolayers on aqueous PSS^-K^+ were readily transferred in the downward and upward strokes. The transfer ratio could not be determined, since polycarbonate substrates were further supported by Teflon plates. However, the formation of the Y-type multilayers[16)] was assured, because decreases in the surface area were the same in the downward and upward strokes. The deposition could be repeated at least 80 times.

The composition of the LB films was determined by X-ray photoelectron spectroscopy (XPS; instrument, ESCA 750 Shimadzu Co., Ltd.). XPS spectra for a LB film of 2 with aqueous PSS^-K^+ subphase are shown in Fig. 2. The observed peaks include those of C_{1s}, N_{1s}, O_{1s} (not shown), F_{1s}, and S_{2p}. The S_{2p} peak is derived from PSS^-. Peaks due to K_{2p} and Cl_{2p} are not detected. The elemental ratio, N/S, is determined to be 2.0 from the area ratio of the N_{1s} and S_{2p} peaks after correction for the relative photoelectron signal intensity. These XPS data clearly show that the LB film is composed of a 1:1 polyion complex of double-chain amphiphile 2 and PSS^-. The formation of a 1:1 complex was observed also for single-chain amphiphile 1 (N/S = 2.0), whereas the N/S ratio was 1.7 - 1.8 for triple-chain amphiphile 3. Apparently, the bulky triple-chain caused incorporation of the polymer more than expected from the 1:1 ion pair formation.

Figure 3 gives depth prophiles of the fraction of the fluorinated carbon (CF_3 and CF_2) in the total C_{1s} intensity and of the ratio of fluorine and nitrogen intensities (F/N) for the 1:1 LB film of 2/PSS^-. The broken lines correspond to the respective calculated values for the 1:1 complex. At the take-off angle (θ) of

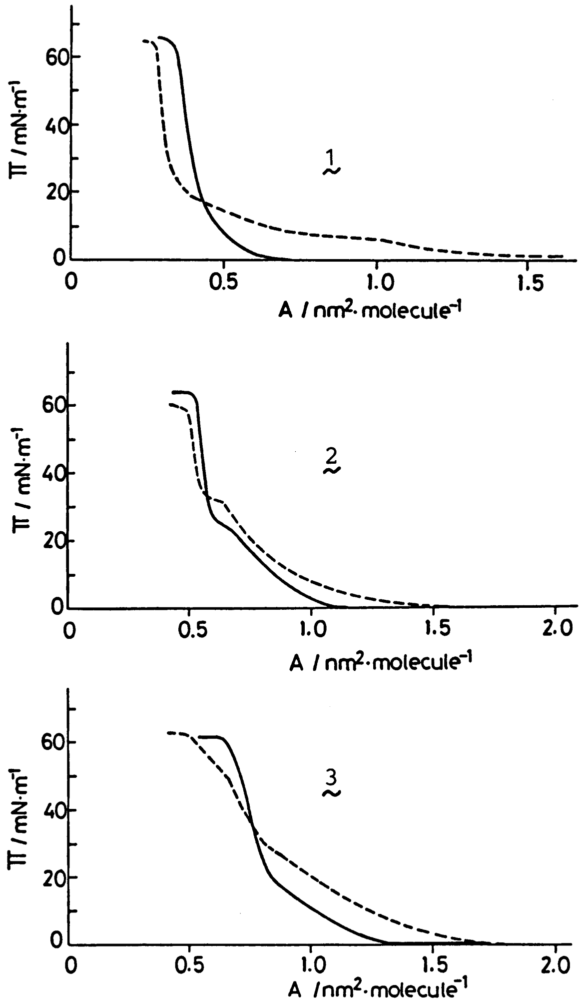

Fig. 1. Surface pressure-area isotherms of fluorocarbon amphiphiles at 20 °C on pure water(broken curve) and on aqueous PSS$^-$K$^+$(solid curve).
PSS$^-$K$^+$: molecular weight, 2.8 x 10^6; concentration, 2 x 10^{-5} unitM.

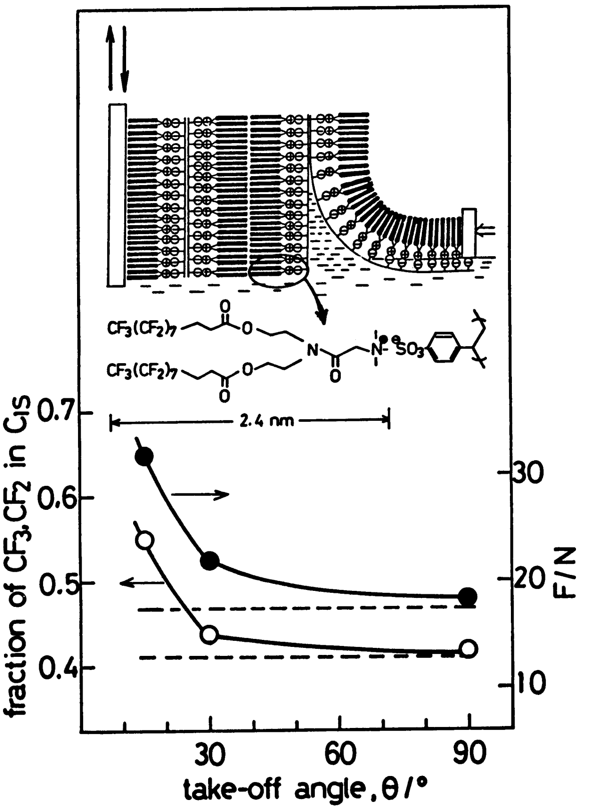

Fig. 3. Depth profile of the fraction of $\underline{C}F_3$,$\underline{C}F_2$ in the total C_{1s} (○) and F/N (●) for 2/PSS$^-$ LB film(10 layers). Broken lines are calculated values. Insert: schematic illustration of the dipping process.

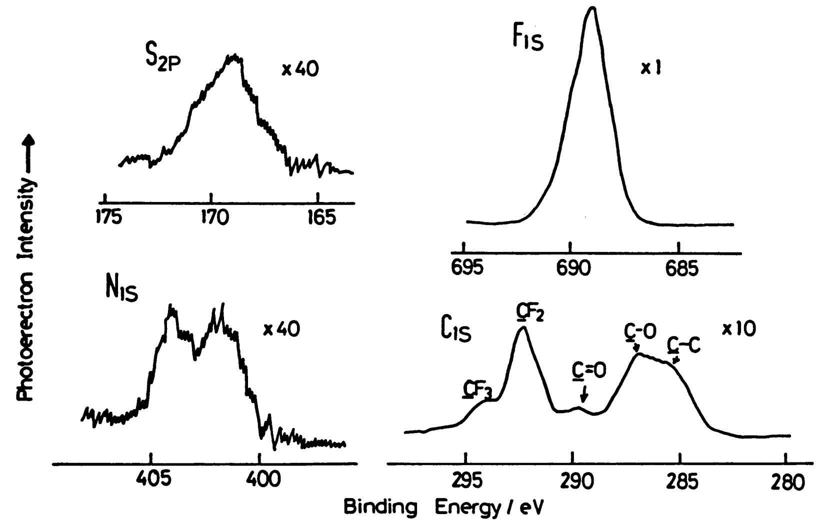

Fig. 2. X-Ray photoelectron spectra of 2/PSS$^-$ LB film (10 layers).
Take-off angle of photoelectron is 90°.

90° that corresponds to the probing depth of 3 - 6 nm,[17)] the observed elemental ratios agree with the calculated values. The ratios increase with decreasing take-off angles. The N/S ratio is 2 irrespective of θ. These data indicate (1) that the head group portion of the amphiphile (as represented by nitrogen) is located very closely to the polymer charge (represented by sulfur), and (2) that the fluorocarbon chains are located at the very surface and detected preferentially when the probing depth ($\leqslant$1.5 nm at θ = 15°) is shorter than the molecular length of the amphiphile (2.4 nm as estimated from the CPK molecular model of **2**, see insert).

The contact angles of this LB film against water and methylene iodide were 117° and 100° ,respectively, at 20 °C (instrument, FACE contact angle meter, Kyowakagaku Co., Ltd.). The surface free energy (γ_s) determined by the method of Owens and Wendt[18)] was 8.9 erg$\cdot$cm^{-2} (1 erg = 1 x 10^{-7} J). This value is very close to that of a 11-(perfluorodecyl)-undecanoic acid monolayer on Pt (γ_s = 8.5 erg$\cdot$cm^{-2}),[18,19)] which is, to date, the most unwettable solid surface. Therefore, the fluorocarbon chain of **2** is densely packed at the surface of the LB film.

In conclusion, bilayer-forming ammonium amphiphiles with one, two, or three fluorocarbon chains can produce stable surface monolayers which are further stabilized by formation of polyion complexes with an anionic polymer in the subphase. The monolayer-polymer complexes are readily transferred onto solid supports. The present technique appears very useful for preparing fluorocarbon LB films, since surface monolayers of fluorocarbon compounds are not readily deposited.

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