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Miscibility of Semifluorinated Pentadecanol with DPPC at the Air−Water Interface

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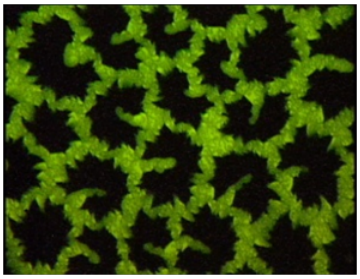
The fundamental research on interactions of partially fluorinated alcohols with dipalmitoyl phosphatidylcholine at the air−water interface is reviewed. We used pentadecanols with different fluorination degrees. Langmuir monolayers of fluorinated compounds are potentially applicable in two-dimensional protein crystallization, microelectronics, and surfactant replacement in the lung. We describe here the monolayer miscibility of the fluorinated alcohols (*F*4*H*11OH, *F*6*H*9OH, and *F*8*H*7OH) with DPPC, which is a major component of native pulmonary surfactants in a mammal. The surface pressure (π)−molecular area (*A*) and surface potential (ΔV)−*A* isotherms for the two-component systems were measured on 0.15 M NaCl at 298.2 K. The phase behavior was visualized with fluorescence microscopy (FM) at the interface and atomic force microscopy (AFM) after transfer on a mica substrate.



Surface pressure-induced melting of ordered (dark) into disordered domains (green).

Keyword: *Fluorinated amphiphiles, DPPC, Monolayer, Surface pressure, Surface potential*

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1. Introduction

A fluorination of amphiphiles gives them unique properties such as combined hydrophobicity and lipophobicity[1)], high gas-dissolving capacity, chemical and biological inertness, low surface tension, and high fluidity[1),2)]. Extensive studies have been done towards the practical application of the fluorinated amphiphiles in the area of medicines, industries, and material sciences[1),3),4)]. The recent research findings along with their application areas are well summarized in the review articles[5-7)].

A pulmonary surfactant (PS) covers the surface of alveoli, thereby regulating the gas exchange and immune system. During respiration, PS reduces the surface tension at the air–alveolar fluid interface to help the work of breathing[8)]. The main component in native PS extracts is dipalmitoylphosphatidylcholine (DPPC) [9-11)]. DPPC contributes mainly to the PS film rigidity but has defects as slow adsorption and poor respreading on the surface.

We have investigated the interaction between fluorinated amphiphiles and phospholipids at the air–water interface[12-15)]. It has been found that the partially fluorinated alcohols improve the PS functions such as control of monolayer fluidity and hysteresis behavior[12)]. However, the relation between the fluorination degree in a molecule and the interaction with lipid monolayers can be disputed. Herein, we review the interplay of partially fluorinated pentadecanol or *H*15OH (*F*4*H*11OH, *F*6*H*9OH, and *F*8*H*7OH) with DPPC in a Langmuir monolayer[7),15),16)].

2. Isotherms of Single Components

The surface pressure (π)–molecular area (A) and surface potential (ΔV)–A isotherms of fluorinated (F+H=15)-OH and DPPC monolayers on 0.15 M NaCl at 298.2 K are shown in Fig. 1. *F*4*H*11OH forms a typical disordered monolayer and its collapse pressure (π^c) is ~44 mN m^{-1}. At the collapsed state, transfer from two-dimensional (2-D) monolayer to three-dimensional (3-D) multilayer begins at the air-water surface. The π–A isotherm for *F*6*H*9OH monolayers has a break at a transition pressure (π^{eq}) of ~8 mN m^{-1}. At this pressure, the monolayer phase changes from disordered to ordered states. On further compression, the monolayer collapses at ~47 mN m^{-1}. *F*8*H*7OH forms a typical ordered monolayer with π^c = ~54 mN m^{-1}. The π–A isotherms of all of thefluorinated (F+H=15)-OH concentrated at ~0.30 nm^2 at the close-packed state. This value agrees well with a cross-sectional area of

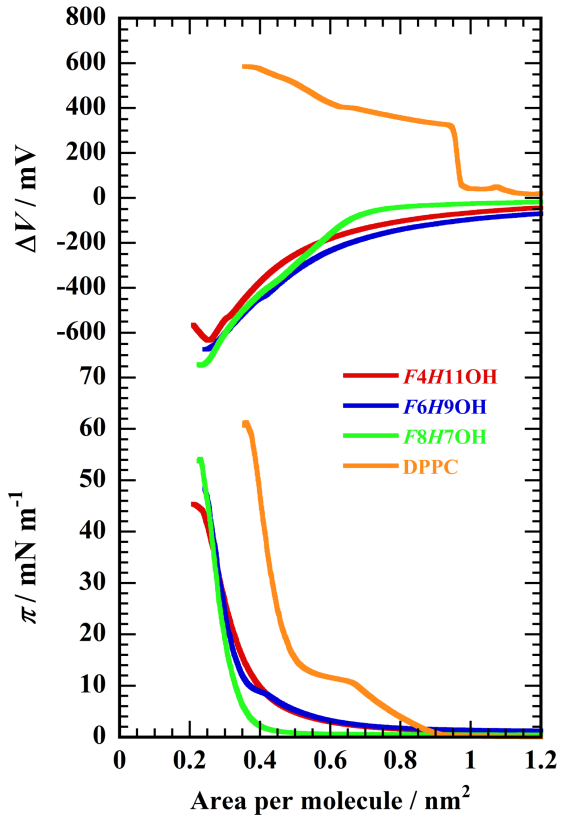

Figure 1. The π–*A* and ΔV–*A* isotherms of the fluorinated (*F*+*H*=15)-OH and DPPC on 0.15 M NaCl at 298.2 K.

fluorocarbon chains (~0.30 nm^2) [1]. As the fluorination degree in *H*15OH increases, the monolayer becomes more ordered and its resistance to lateral pressure is more improved. On the other hand, DPPC monolayers have a liquid-expanded (LE)/liquid-condensed (LC) phase transition at ~11 mN m^{-1}. The π^c value is higher compared to those of the alcohols.

The ΔV–*A* isotherms indicate a completely opposite sign for the fluorinated (*F*+*H*=15)-OH (negative variations) and DPPC (positive variations) monolayers. The absolute value of ΔV values increases upon monolayer compression, which means that the monolayer orientation becomes packed closely. A strong electronegativity of fluorine atoms contributes to the negative ΔV value, which has been well-established in the previous reports[13),17),18)]. The minimum ΔV value of the alcohol monolayers converges at nearly −700 mV. This indicates that a surface density of the terminal group (CF_3−) is very similar at the close-packed state among the alcohols.

3. Isotherms of Binary Monolayers

As seen in Figs. 2-4, the π–*A* isotherms shift to smaller areas with increasing molar fraction of the alcohols ($X_{F4H11OH}$, X_{F6H9OH}, and X_{F8H7OH}). The π^{eq} value, which is indicated by arrows, changes with respect to each mole fraction. In addition, the π^c value also varies against the mole fraction. These changes imply the two-component miscibility within the

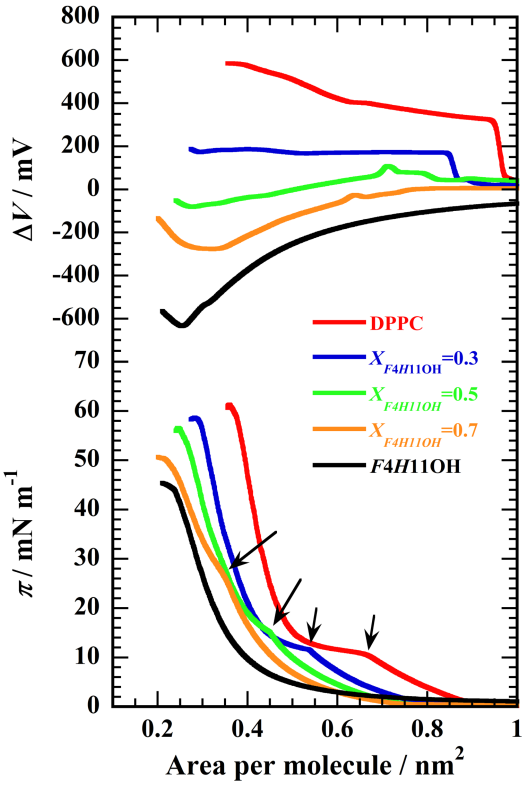

Figure 2. The π–*A* and ΔV–*A* isotherms of the binary DPPC/*F*4*H*11OH system on 0.15 M NaCl at 298.2 K.

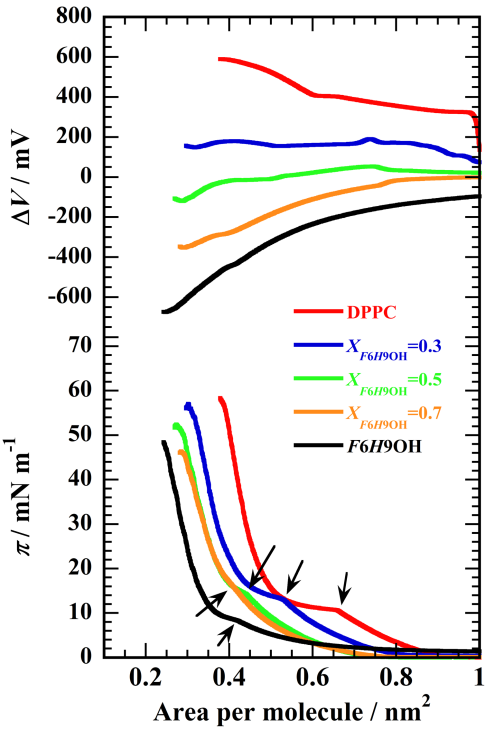

Figure 3. The π–*A* and ΔV–*A* isotherms of the binary DPPC/ *F*6*H*9OH system on 0.15 M NaCl at 298.2 K.

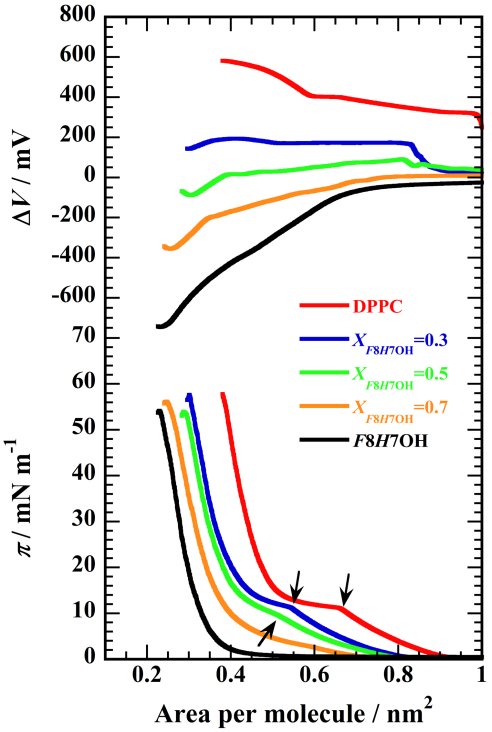

Figure 4. The π–*A* and ΔV–*A* isotherms of the binary DPPC/*F*8*H*7OH system on 0.15 M NaCl at 298.2 K.

monolayer state. The ΔV–*A* isotherms of the whole systems shift from positive to negative values within the isotherms of pure components as the mole fraction increases. The similar variations for hydrocarbon−fluorocarbon systems have been reported previously[14),19),20)].

4. Excess Gibbs Free Energy of Mixing

The following equation allows us to evaluate the excess Gibbs free energy of mixing ($\Delta G_{\mathrm{mix}}^{\mathrm{exc}}$) for the binary systems[21)].

$$\Delta G_{\mathrm{mix}}^{\mathrm{exc}} = \int_0^{\pi} (A_{12} - X_1 A_1 - X_2 A_2)\mathrm{d}\pi \quad (1)$$

A_i and X_i are the molecular area and molar fraction of component *i*, respectively, and A_{12} is the mean molecular area in the binary monolayer. The $\Delta G_{\mathrm{mix}}^{\mathrm{exc}}$ value at typical surface pressures is plotted against the respective mole fractions (Fig. 5). The values for the *F*4*H*11OH (Fig.5A) and *F*6*H*9OH (Fig.5B) systems indicate negative variations from ideality ($\Delta G_{\mathrm{mix}}^{\mathrm{exc}} = 0$[22),23)]). The minimum $\Delta G_{\mathrm{mix}}^{\mathrm{exc}}$ value for the *F*6*H*9OH system is nearly two times as negative as that for the *F*4*H*11OH system. This means that attractive interactions between DPPC and *F*6*H*9OH are much larger upon compression. On the other hand, in the *F*8*H*7OH system (Fig. 5C), ideal mixing behavior is observed in the whole X_{F8H7OH} except at X_{F8H7OH} = 0.2 and 0.9. Consequently, the magnitude of attraction with DPPC monolayers is stronger in the order of *F*6*H*9OH > *F*4*H*11OH > *F*8*H*7OH. It is suggested that the interaction of the alcohols with DPPC doesn't change with respect to the fluorination degree, but is affected by the monolayer states of the

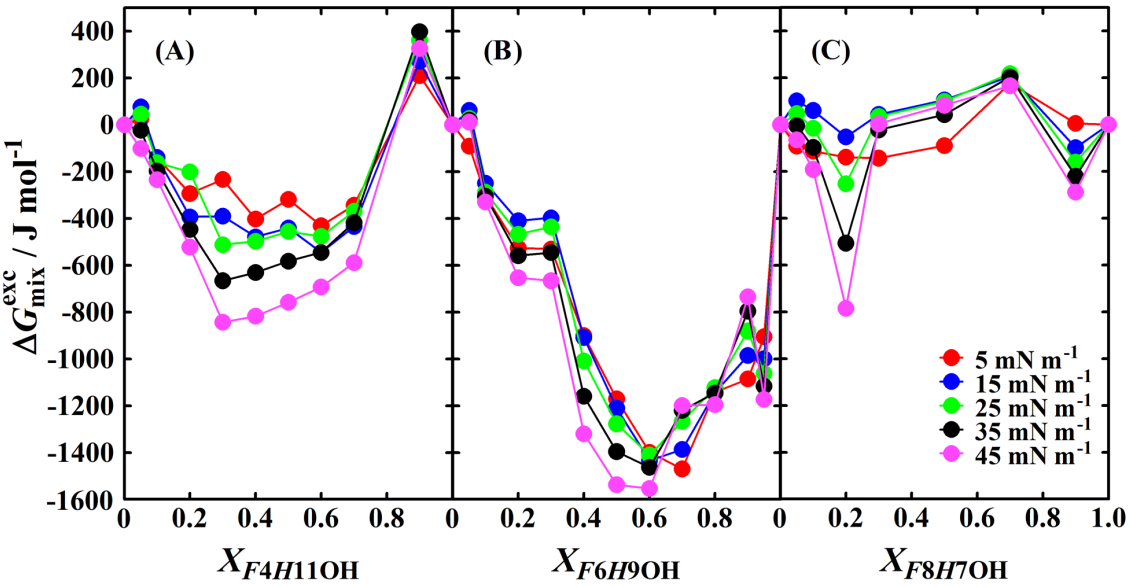

Figure 5. The ΔG^{exc}_{mix}–$X_{F\text{-alcohol}}$ plots of (A) DPPC/*F*4*H*11OH, (B) DPPC/ *F*6*H*9OH, and (C) DPPC/*F*8*H*7OH systems.

alcohols such as disordered and ordered phases. The results provide complementary evidence of the miscibility of three systems within a monolayer state.

5. 2D Phase Diagrams

Figure 6 exhibits a 2D phase diagram for the binary systems at 298.2 K, which is constructed by plotting the π^{eq} and π^{c} values against the respective mole fractions. The π^{eq} values in the whole systems are kept almost constant at the small mole fractions. With increasing the mole fractions, different behavior is indicated among the three systems: the π^{eq} values increase for DPPC/*F*4*H*11OH, show a convex feature for DPPC/*F*6*H*9OH, and decrease for DPPC/*F*8*H*7OH. It is found that additional effects of the fluorinated alcohols on DPPC monolayers change from fluidization to solidification with respect to the fluorination degree.

In the high surface pressure region, the experimental π^{c} values vary against the mole fractions, which make sure of the binary miscibility. Under the assumption of a regular surface mixture, the coexistence phase boundary between the 2D monolayer phase and 3D bulk phase of the molecules spread on the surface can be theoretically simulated from the Joos equation[24],

$$1 = X_1\exp\{(\pi^{c} - \pi_1^{c})A_1^{c}/kT\}\exp\{\xi(X_2)^2\} + X_2\exp\{(\pi^{c} - \pi_2^{c})A_2^{c}/kT\}\exp\{\xi(X_1)^2\} \quad (2)$$

where π_1^{c} and π_2^{c} are the respective collapse pressures of components 1 and 2, A_1^{c} and A_2^{c} are the corresponding molecular areas at collapse, ξ is the interaction parameter, and kT is the product of the Boltzmann constant and the Kelvin temperature. The blue curve was obtained by adjusting ξ in Eq. (2) to achieve the best fit for the experimental π^{c} values. As a result, the phase diagrams for the DPPC/*F*4*H*11OH (Fig. 6A) and DPPC *F*6*H*9OH (Fig. 6B) systems indicate a positive azeotropic type. The DPPC/*F*8*H*7OH (Fig. 6C) exhibits the diagram assigned to positive ($0 \le X_{F8H7OH} \le 0.3$) and negative ($0.3 \le X_{F8H7OH} \le 1$) azeotropic types. Focused on

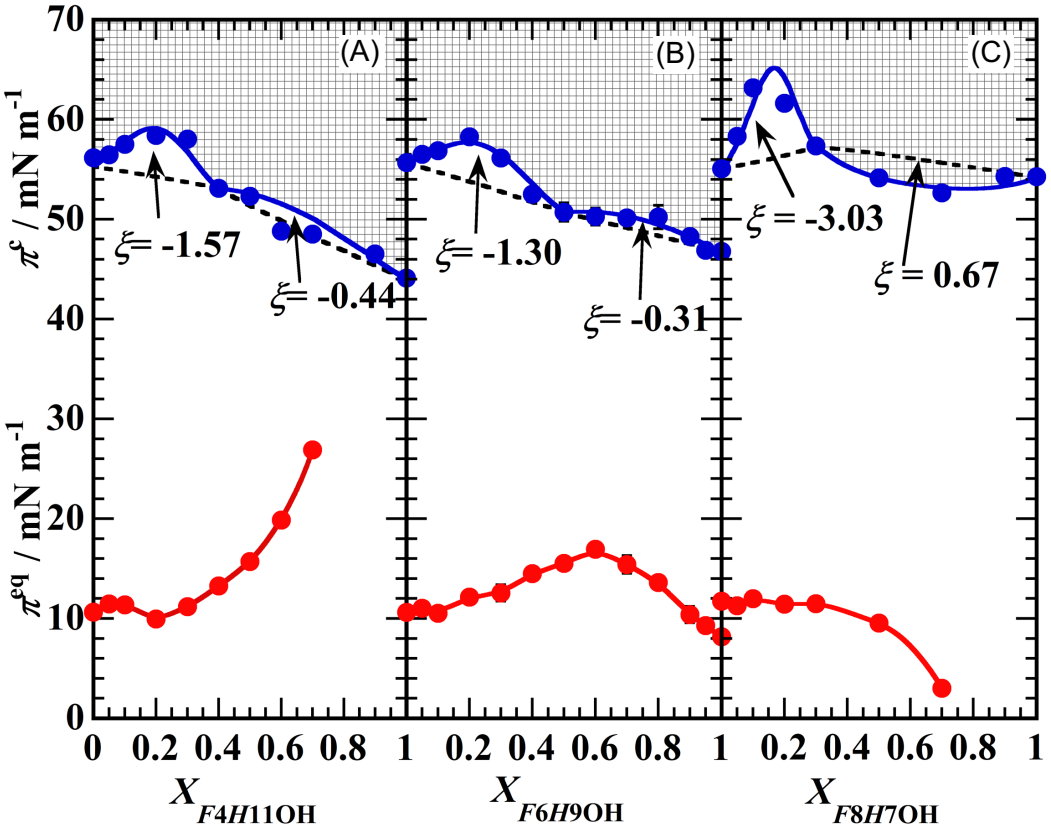

Figure 6. The 2D phase diagrams of (A) DPPC/*F*4*H*11OH, (B) DPPC/*F*6*H*9OH, and (C) DPPC/*F*8*H*7OH systems. The dashed lines were calculated according to Eq. (2) for $\xi = 0$. The solid line at high surface pressures was obtained by curve fitting of experimental π^c to Eq. (2). The shaded area above the solid lines indicates a bulk phase.

the small mole fractions, heterogeneous interactions become stronger at high surface pressures as the fluorination degree in the alcohols increases. These results suggest that the mode of interplays between DPPC and the fluorinated alcohols is completely different at low and high surface pressures. This is considered to because of the fact that van der Waals attraction between fluorocarbons is weaker than that between hydrocarbons.

6. Fluorescence Microscopy

The binary DPPC/*F*4*H*11OH monolayer is visualized with fluorescence microscopy (FM) in situ at the air–water interface (Fig. 7). In the picture, a small amount of a fluorescent probe (1 mol% NBD-PC) was dipped into the monolayer. Thus, green and black colors in the image correspond to disordered and ordered phases, respectively[25]. It is commonly accepted that a domain formation is controlled by balance of a line tension at the boundary between disordered and ordered domains and a long-range dipole-dipole interaction between ordered domains[25-31]. The image of single DPPC monolayers indicate a coexistence of LE (green) and LC (black) phases above the π^{eq} of ~11 mN m^{-1} (data not shown[15),16),32]). When a small amount of *F*4*H*11OH is added into DPPC monolayers ($X_{F4H11OH}$ = 0.1), the ordered

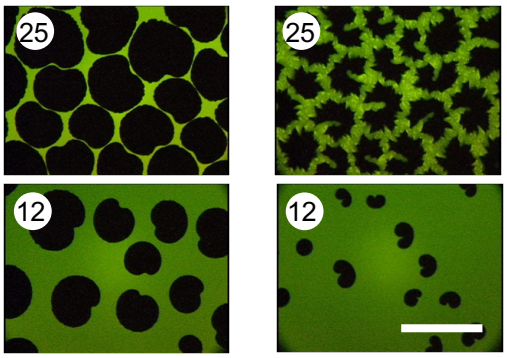

Figure 7. FM images of the binary DPPC/*F*4*H*11OH monolayers on 0.15M NaCl at 298.2 K. Numerical values in the upper left means surface pressures (in mN m^{-1}). The scale bar in the lower right represents 100 μm.

domain become larger in size and the domain shape changes to a nearly circular or bean-like form. This means that the *F*4*H*11OH addition enhances contribution of the line tension at the phase boundary. However, the further addition induces the size reduction of ordered domains and modification of the shape at $X_{F4H11OH}$ = 0.3. At 25 mN m^{-1}, the edge of the ordered domains changes into disordered phase. In other words, the ordered domain begins to dissolve into the disordered phase upon lateral compression. Surprisingly, this fluidizing effect of *F*4*H*11OH on DPPC monolayers is induced by surface pressures increase like a melting of hydrogen oxides under pressures. This is considered to be attributed to the strong dipole moment at the junction between fluorocarbon and hydrocarbon of the alcohols, which is recognized as a driving force of self-assembly at the interface[33].

The phase behavior in the binary DPPC/*F*6*H*9OH system at X_{F6H9OH} = 0.1 (Fig. 8) is very similar to the DPPC/*F*4*H*11OH system. At X_{F6H9OH} = 0.2, with increasing surface pressures from 12 to 25 mN m^{-1}, the surface pressure-induced fluidization is observed.

As opposed to the *F*4*H*11OH and *F*6*H*9OH systems, the addition of *F*8*H*7OH makes the ordered domain round in shape at X_{F8H7OH} = 0.1 (Fig. 9). The size of ordered domains become smaller at X_{F8H7OH} = 0.2. It is noticed that the domain shape transforms from the

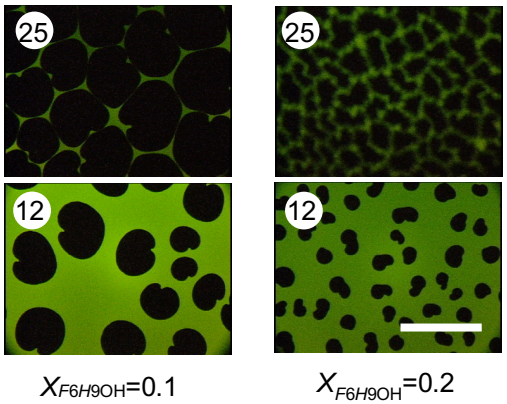

Figure 8. FM images of the binary DPPC/*F*6*H*9OH monolayers on 0.15M NaCl at 298.2 K. Numerical values in the upper left means surface pressures (in mN m^{-1}). The scale bar in the lower right represents 100 μm.

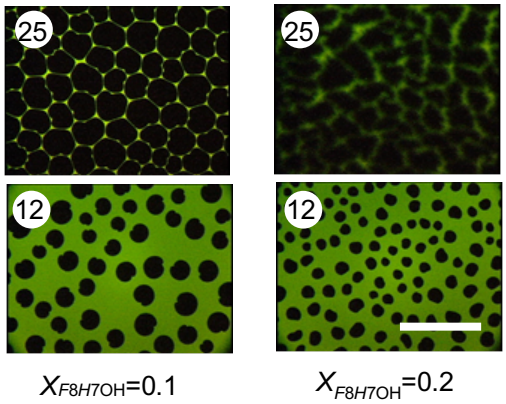

Figure 9. FM images of the binary DPPC/*F*8*H*7OH monolayers on 0.15M NaCl at 298.2 K. Numerical values in the upper left means surface pressures (in mN m^{-1}). The scale bar in the lower right represents 100 μm.

round form to the rough-edged form with an increment in surface pressures from 12 to 25 mN m^{-1}. In addition, the ordered domain fuses with each other and the contrast of the image becomes unclear. It is found that the surface pressure-induced fluidization occurs similarly to the other systems. This unique effect is brought about by incorporation of the amphiphiles with fluorocarbon chains shorter than 8. This is because there exist many papers on the fluidizing effect induced by monolayer compositions containing the compounds with longer fluorocarbon chains [18),34-36)]. The present systems support the above consideration by the fact that the addition of fluorinated alcohols exerts not only the surface pressure-induced effect but also the surface composition-induced effect on DPPC monolayers.

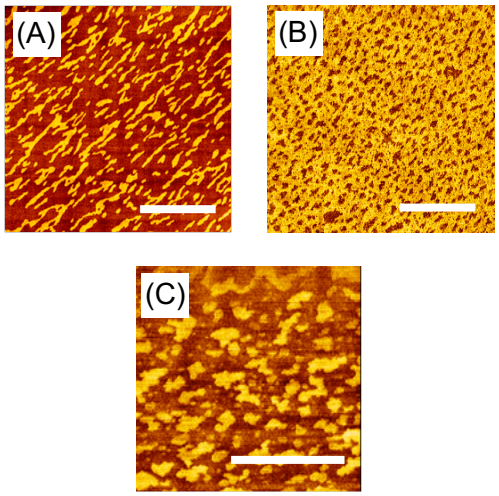

Figure 10. AFM images of the binary (A) DPPC/*F*4*H*11OH ($X_{F4H11OH}$ = 0.5), (B) DPPC/*F*6*H*9OH (X_{F6H9OH} = 0.3), and (C) DPPC/*F*8*H*7OH (X_{F8H7OH} = 0.3) systems at 35 mN m^{-1}. on 0.15M NaCl at 298.2 K. The scale bar in the lower right represents 500 nm.

7. Atomic Force Microscopy

The phase behavior of the binary systems in the larger mole fractions of the alcohols is not possible to be caught by in situ microscopic methods such as FM and Brewster angle microscopy due to its limitation of resolution and magnification. Therefore, the surface topographic image of Langmuir-Blodgett (LB) films transferred from the interface onto a mica has been measured with atomic force microscopy (AFM). The AFM topography in the DPPC/*F*4*H*11OH system at $X_{F4H11OH}$ = 0.5 shows many string-like fragments (bright contrast) composed almost of DPPC (Fig. 10A). The assignment of each contrast was done by considering molecular lengths and changing $X_{F4H11OH}$. Considering the FM pictures, the fragment is generated by the fluidization of *F*4*H*11OH. In the DPPC/*F*6*H*9OH system at X_{F6H9OH} = 0.3 (Fig. 10B), the bright network corresponding mainly to DPPC monolayers is observed as opposed to the DPPC/*F*4*H*11OH system. This implies that the fluidizing effect of *F*6*H*9OH comes to attenuate. The LB film of the DPPC/*F*8*H*7OH system at X_{F8H7OH} = 0.3 indicates bright fragments composed almost completely of DPPC (Fig. 10C). It is noticed that this phenomenon is the fragmentation not fluidization on the basis of the 2D phase diagram (Fig. 6C). That is, the relatively weak van der Waals interactions or cohesive forces of the perfluorooctyl moiety are contributed to fragmentation of the mixed DPPC/*F*8*H*7OH domains by shortness of the molecular distance between DPPC and *F*8*H*7OH upon lateral compression.

8. Conclusions and Perspectives

The surface interaction between DPPC and partially fluorinated pentadecanols (*F*4*H*11OH, *F*6*H*9OH, and *F*8*H*7OH) has been elucidated employing the monolayer technique at the air-water interface. Despite the difference in fluorination degree of the alcohols, the whole binary systems here are miscible with in a monolayer state. Structurally, the fluorination degree is higher, the hydrophobicity is assumed to be stronger. Along this, incorporation of the alcohols to DPPC produces different functions against the monolayer such as fluidization and solidification. Furthermore, the miscibility behavior at low and high surface pressures is significantly different. The microscopic images can catch the dissolution phenomena of ordered domains into the surrounding disordered domains, which is induced by an increment in surface pressures. This is deeply related to the strong dipole moment at the junction of $-CF_2CH_2-$ in the partially fluorinated alcohols. The surface pressure (π)-induced dispersing or fluidizing effect is specific to partially fluorinated amphiphiles which have a fluorocarbon shorter than perfluorooctyl chains. Generally perfluorinated and highly fluorinated amphiphiles demonstrate greater ability to accumulate in the human body and the environment. Hence, partially fluorinated compounds with *F*4–*F*8 chains may find potential application in medical and pharmaceutical fields as well as in industrial and materials science.

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