Langmuir monolayer miscibility of single-chain partially fluorinated amphiphiles with tetradecanoic acid

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A R T I C L E   I N F O

Article history:
Received 20 March 2009
Accepted 7 May 2009
Available online 19 May 2009

Keywords:
Langmuir monolayer
Partially fluorinated amphiphile
Tetradecanoic acid
Surface pressure
Surface potential
Brewster angle microscopy (BAM)
Fluorescence microscopy (FM)
Atomic force microscopy (AFM)

A B S T R A C T

The surface pressure (π)–molecular area (A) and surface potential (ΔV)–A isotherms have been measured for monolayers of tetradecanoic acid (myristic acid: MA), partially fluorinated amphiphiles [single-chain (perfluoroctyl)pentanol (F8C5OH) and single-chain (perfluoroctyl)pentylphosphocholine (F8C5PC)], and their two-component combinations in order to investigate their miscibility at the air/water interface. The data for these systems were analyzed in terms of an additivity rule and excess Gibbs free energy. An interaction parameter and an interaction energy between the two components were calculated from the Joo equation, which allows description of collapse pressures of miscible monolayers. Two-dimensional phase diagrams for the binary systems were constructed and found to be a positive azeotropic type. These results indicate that the two-component MA/F8C5OH and MA/F8C5PC monolayers are miscible in the monolayer state. To confirm their miscibility and phase behavior upon compression, morphological observations with fluorescence microscopy (FM), Brewster angle microscopy (BAM), and atomic force microscopy (AFM) have been performed. These observations show that the addition of F8C5OH or F8C5PC to MA makes MA ordered domains in the monolayer region fluidize very effectively and that a fern-like network is formed as a 3-D structure by over-compression beyond the monolayer collapse. The present paper systematically clarifies the miscibility between MA and F8C5OH or F8C5PC within the monolayer and indicates that these fluorinated chemicals may have a possibility of biomedical uses and applications.

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1. Introduction

A fluorinated amphiphile is characterized by unique properties such as a stronger surface activity and a formation of micelles and other self-assemblies at lower concentrations in comparison with corresponding hydrogenated analogue [1,2]. Due to its high biological inertness, remarkable ability to solubilize oxygen, and extremely low solubility in water, highly fluorinated compounds have been investigated for various biological applications [3–5]. Many unusual features have been reported in these areas. In particular, stimulating attention have been paid to their potential use as intravascular oxygen transport [6], contrast agent in ultrasound imaging [7], and efficient additive to pulmonary surfactants [8,9]. Perfluoroalkyl chains are considerably different from the normal alkyl chains in their bulkiness, helical conformation, and stiffness [2]. Perfluorocarbon chains are much more hydrophobic than the corresponding hydrocarbon ones and have a pronounced lipophobicity, which is estimated to be about one-third the free energy of transfer of a methylene group from alkane to water [10]. Furthermore, the low polarizability of fluorine atoms results in very weak van der Waals interactions between perfluorocarbon chains. The combination of fluorinated and hydrogenated surfactants generates unusual and interesting phenomena such as miscibility, phase separation, and compartmentalization for micelles, liposomes, and Langmuir monolayers [11–13]. New self-organized films and membranes, discrete objects, and interfaces have been obtained, and novel applications have been explored in the medical area, materials science, and other fields.

Langmuir monolayers at the air/liquid interface, which provide two-dimensional (2-D) structural information, have been intensively adopted as experimental paradigms of a biological membrane for elucidating the interfacial properties and mechanisms of surfactants [14–17]. The monolayer technique has an advantage in simplifying physicochemical behavior compared with the method employed with three-dimensional (3-D) aggregates such as...
micelles, vesicles, and emulsions. In addition, the phase behavior of monolayers at the interface under compression can be visualized at the micro- and nanoscale by optical techniques such as Brewster angle microscopy (BAM) [8,18,19], fluorescence microscopy (FM) [20–22], and atomic force microscopy (AFM) [8,23,24]. Thus, many researchers have used the monolayer techniques to understand the interaction between surfactants, polymers, proteins, peptides, and so on [25–27]. Recently, interesting studies on nucleation process in collapsed monolayers of semifluorinated alkanes have been reported utilizing BAM [28]. When the monolayers of the alkanes were transferred from 2-D to 3-D aggregates upon compression, the different collapse types were observed depending on the magnitude of their fluorination; for example, long ribbon-like, spike-like, and plateau-like structures. Langmuir monolayer conversions to 3-D collapsed aggregates play a key role in several biological processes such as the mechanism of lipid bilayer formation [29] and the hysteresis of compression–expansion cycles in the pulmonary function of lung surfactants [30–32].

We investigated the miscibility behavior of perfluorocarboxylic acids (FCn, n = 12,14,16,18) with tetradecanoic acid (myristic acid: MA) [33] or dipalmitoylphosphatidylycholine (DPPC) [24] in the monolayer state, which are components in biological membranes. FCn molecules are partially miscible with the lipids depending on compositions and chain lengths, although perfluorocarbons do not commonly mix with normal hydrocarbons in the bulk state. The interfacial behavior of two-component monolayers has been studied for dipalmitoylphosphatidylethanolamine (DPPE) and semifluorinated alkanes without headgroups, where it was found that miscible monolayers and vertically phase-separated bilayers were formed depending on compositions and surface pressures [34]. The driving force in monolayer miscibility is induced by attractive forces between headgroups. Other researchers have extensively examined the surface behavior and miscibility between partially fluorinated compounds and hydrogenated ones [35–38]. In the previous studies, the phase behavior and interaction between partially fluorinated compounds and hydrogenated ones have been systematically reported for two-component monolayers of DPPC, the partially fluorinated n-alcohol (F8C5OH), and alkylphosphocholine (F8C5PC) at the air/water interface [8,39]. In that case, both F8C5OH and F8C5PC are completely miscible with DPPC within a monolayer in spite of the difference in chain length by three methylene groups. In addition, the DPPC/F8C5OH mixtures at a distinct mole fraction showed a triskelion morphology in BAM and FM micrographs differently from the DPPC/F8C5PC system. However, F8C5PC liquidified more than a liquid-condensed (LC) domain of DPPC. The species of headgroups are thought to contribute to the morphological variation. However, the reasons and mechanisms for the outcome have not been made clear yet because of the difference in chain length and number (single or double) of hydrophobic parts between DPPC and the fluorinated compounds. Moreover, there are still few reports on the miscibility behavior and the interaction mode between partially fluorinated amphiphiles and biomembrane components, which provide helpful information to industries, biomedical fields, and environmental sciences. In the present work, our attention is focused on the effect of polar headgroup and hydrophobic parts interactions on the monolayer miscibility. Thus, myristic acid (MA) was chosen as one of the biomembrane components. For example, the myristic acid has a sufficiently high hydrophobicity to become incorporated into the fatty acyl core of the phospholipid bilayer of the plasma membrane of the eukaryotic cell. In this way, myristic acid acts as a lipid anchor in biomembranes. MA has a single chain (C14:0) within a molecule and forms a stable monolayer with temperature-sensitive phase transition at the air/water interface. The MA monolayer behavior has been widely studied using various methods [40–42] and the phase behavior is well known to the researchers employing the monolayer technique. The use of MA as one component allows us to make it easy to interpret the phase variations induced by others. Therefore, to investigate such the interfacial behavior, we selected a binary MA/F8C5OH and MA/F8C5PC systems. F8C5OH and F8C5PC have identical hydrophobic chains. However, the headgroup of F8C5PC is more bulky than its chains. In addition, the three compounds have essentially the same single hydrophobic chain lengths. The aims of this study are to clarify the miscibility of MA with F8C5OH or F8C5PC, the miscibility effect of the fluorinated amphiphiles on the LC domains of MA, and the nucleation mode in their collapsed monolayers. Surface pressure (π)—molecular area (A) and surface potential (ΔV)—A isotherms of the binary monolayers were measured on 0.15 M NaCl (pH 2.0) at 298.2 K. The phase behavior was examined using the additivity rule for the mean A and ΔV as well as an excess Gibbs free energy of mixing. Furthermore, the Langmuir monolayers and Langmuir–Bödgem-Lördige (LB) films were also morphologically investigated using BAM, FM, and AFM.

2. Experimental section

2.1. Materials

(Perfluorooctyl)pentanol (F8C5OH) and (perfluorooctyl)pentylphosphocholine (F8C5PC) were synthesized as reported previously [43]. Tetradecanoic acid (Myristic acid, MA, 99–100%) was purchased from Sigma (St. Louis, MO) and was used without further purification. Octadecyl rhodamine B chloride (R18) was purchased from Molecular Probes, Inc. (Eugene, OR) as a fluorescent probe. n-Hexane (>98.5%) was used from Cica-Merck (Uvasol, Tokyo, Japan) and ethanol (>99.5%) was purchased from nacalai tesque (Kyoto, Japan). The n-hexane/ethanol (9/1, v/v) mixtures were used as a spreading solvent for each sample. Sodium chloride (nacalai tesque) was roasted at 1023 K for 24 h to remove all surface-active organic impurities. Hydrochloric acid (HCl) of ultra fine grade for the preparation of a subphase was purchased from nacalai tesque. The substrate solution was prepared using thrice distilled water (the surface tension = 72.0 mN m⁻¹ at 298.2 K and the electrical resistivity = 18 MΩ cm).

2.2. Methods

2.2.1. Surface pressure—molecular area isotherms

The surface pressure (π) of monolayers was measured using an automated homemade Wilhelmy balance. The surface pressure balance (Mettler Toledo, AG245) had a resolution of 0.01 mN m⁻¹. The pressure-measuring system was equipped with a filter paper (Whatman 541, periphery = 4.0 cm). The trough was made from Teflon-coated brass (area = 720 cm²), and Teflon-made barriers (both hydrophobic and lipophobic) were used in this study. Surface pressure (π)—molecular area (A) isotherms were recorded at 298.2 K within ±0.1 K. Stock solutions (1.0 mM) of MA, F8C5OH, and F8C5PC were prepared in n-hexane/ethanol (9/1, v/v). The spreading solvents were allowed to evaporate for 15 min prior to compression. The monolayer was compressed at a speed of ~0.10 nm² molecule⁻¹ min⁻¹. The standard deviations for molecular surface area and surface pressure were ~0.01 nm² and ~0.1 mN m⁻¹, respectively. The subphase pH of a 0.15 M NaCl solution was adjusted to 2.0 with an adequate amount of HCl.

2.2.2. Surface potential—molecular area isotherms

The surface potential (ΔV) was simultaneously recorded together with the surface pressure while the monolayer was compressed at the air/water interface. It was monitored by using an ionizing 241Am electrode at 1–2 mm above the interface while a
reference electrode was dipped in the subphase. The electrometer (Keithley 6517) was used to measure the surface potential. The standard deviation for the surface potential was 5 mV [8,44–46].

2.2.3. Brewster angle microscopy (BAM)

The monolayer was directly visualized by a Brewster angle microscope (KSV Optrel BAM 300, KSV Instruments Ltd., Finland) coupled to a commercially available film balance system (KSV Minitrough, KSV Instruments Ltd., Finland). The application of a 20 mW He–Ne laser emitting p-polarized light of 632.8 nm wavelength and a 10× objective lens allowed a lateral resolution of ~2 μm. The angle of the incident beam to the air/water interface was fixed to the Brewster angle (53.1°) at 298.2 K. The reflected beam was recorded with a high grade charge coupled device (CCD) camera (EHD kamPro02, EHD Imaging GmbH, Germany), and then the BAM images were digitally saved to the computer hard disk.

2.2.4. Fluorescence microscopy (FM)

The film balance system (KSV Minitrough) was mounted onto the stage of the Olympus microscope BX51WI (Tokyo, Japan) equipped with a 100-W mercury lamp (USH-1030L), an objective lens (LMPPlanFL20×, working distance = 12 mm), and a CCD camera with a camera control unit (IKTU51CU, Toshiba, Japan). The z-directional focus on the monolayer was exactly adjusted using an automation controller (MAC 5000, Ludl Electronic Products Ltd., NY). FM observations and compression isotherm measurements were carried out simultaneously. A spreading solution of the samples was prepared as a mixed solution doped with 1 mol% of a fluorescent probe (Seiko Instruments Co., Chiba, Japan) at room temperature in the system. AFM images were obtained using an SPA 400 instrument (Seiko Instruments Co., Chiba, Japan) at room temperature in the tapping mode, which provided both a topographical image and a phase contrast image. The tapping mode images (256 or 512 points per line) were collected with scan rates of 1 Hz, using silicon tips (Olympus Co., Japan) with a nominal spring constant of 1.8 N m⁻¹ under normal atmosphere [8,47]. The lateral and vertical resolutions were 0.2 and 0.1 nm, respectively. The transferred samples were checked for possible tip-induced deformation by zooming out after a region had been scanned.

3. Results and discussion

3.1. Compression isotherms for pure systems

Under the present subphase condition of pH 2.0, the hydroxyl group of B8C5OH is clearly undissociated and B8C5OH is neutral within a molecule. F8C5PC possesses the PC headgroup, which is in the zwitterionic form in the subphase pH range of 3.5 to 11.5 [48], and is thus charged positively; 98–100% of the phosphate group are expected to be protonated using the pKₐ value of DPPC (pKₐ = 3.8–5.0 [48–50]). In the case of MA molecules (pKₐ = 4.9 [51]), it is found that the carboxyl group is almost undissociated (~8.1% dissociated) even under consideration of the surface pH value (pHₙ) using the Gouy–Chapman approach [52,53]. The following equations were employed above procedure. The monolayer ionization degree (x) is determined by the surface proton concentration [H⁺]ₙ and the surface equilibrium constant K for the acid group dissociation (Kₐ):

\[ \frac{x}{1-x} = \frac{K_a}{[H^+]_n} \]

(1)

The surface proton concentration is calculated by using Boltzmann equation, if the proton concentration in the bulk [H⁺]₀ is known,

\[ [H^+]_n = [H^+]_0 \exp \left( -\frac{z\phi_0}{kT} \right) \]

(2)

where \( \phi_0 \) refers to the electrostatic potential at the interface relative to the adjacent conducting phase (mV), k is the Boltzmann constant, T is the absolute temperature, e is electrostatic unit charge, ε is valency of electrolyte, σ is surface charge density (C m⁻²), ε is the dielectric constant (78.3 at 298.2 K), νₑ is vacuum permittivity (8.854 × 10⁻¹² F m⁻¹), and \( n_0 \) is the number density of charges in the system. On the contrary, pKₐ for monolayer is

\[ \text{pH}_n = \text{pK}_a + \log \left( \frac{1}{1-x} \right) \]

(3)

\[ \text{pH}_n = \text{pK}_a + \log \left( \frac{1}{1-x} \right) - \frac{\phi_0}{2.303kT} \]

(4)

\[ \phi_0 \]

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\[ \phi_0 \]
The $D\bar{V}$ values of F8C5OH and F8C5PC monolayers are always negative and reach minimum values of $700$ and $140$ mV at their collapse pressures, respectively. This negative sign is commonly observed for fluorinated monolayers and is considered to be caused by the strongly electronegative fluorine atoms $[8,21,24,39,44]$. The smaller value of F8C5PC is accounted for the evidence that the spatial bulkiness of the PC headgroup disturbs the enhancement in monolayer orientation of F8C5PC upon compression $[8,39]$. Furthermore, under the present condition, the positive charge of F8C5PC may contribute to the smaller value. In contrast, the $\Delta V$ values of MA monolayers are positive and increase from 0 to $365$ mV upon compression. A positive variation is typical for most surfactants with hydrocarbon chains, although the $\Delta V$ value is, in common, strongly affected by a polar headgroup and a subphase condition $[25,56]$.

### 3.2. Ideal mixing of the binary monolayers

#### 3.2.1. Isotherm behavior

The binary MA/F8C5OH and MA/F8C5PC monolayers have been investigated to clarify the effects of polar headgroups in the fluorinated compounds on their interaction and miscibility within a monolayer. The $\pi$–$A$ and $\Delta V$–$A$ isotherms were measured for various molar fractions of $X_{\text{F8C5OH}}$ or $X_{\text{F8C5PC}}$ at 298.2 K on 0.15 M NaCl (pH 2.0). In the case of the MA/F8C5OH systems (Fig. 2A), all of the $\pi$–$A$ isotherms are located on the similar molecular area at low surface pressures less than $20$ mN m$^{-1}$. The $\pi$–$A$ isotherms display a phase transition pressure that changes from $X_{\text{F8C5OH}} = 0$ to 0.2 and the collapse pressure varies against $X_{\text{F8C5OH}}$ (Figures S1 and 4 (a)). The change in transition and collapse pressure with $X_{\text{F8C5OH}}$ provides the first evidence of the miscibility between the two components in the monolayer state. The value of transition pressures was also confirmed by Brewster angle microscopy (BAM) and fluorescence microscopy (FM) in the later section. In the MA/F8C5PC system (Fig. 2B), the $\pi$–$A$ isotherms clearly have the transition pressure at $0.6$ and the values increase with increasing $X_{\text{F8C5PC}}$. Correspondingly, the collapse pressure changes similarly to the MA/F8C5OH monolayers as shown in Fig. 4. These variations on $\pi$–$A$ isotherms imply that MA is, at least, partially miscible with both F8C5OH and F8C5PC in the monolayer state.

All of the $\Delta V$–$A$ isotherms for F8C5OH and F8C5PC monolayers are always negative and reach minimum values of $-700$ and $-140$ mV at their collapse pressures, respectively. This negative sign is commonly observed for fluorinated monolayers and is considered to be caused by the strongly electronegative fluorine atoms $[8,21,24,39,44]$. The smaller value of F8C5PC is accounted for the evidence that the spatial bulkiness of the PC headgroup disturbs the enhancement in monolayer orientation of F8C5PC upon compression $[8,39]$. Furthermore, under the present condition, the positive charge of F8C5PC may contribute to the smaller value. In contrast, the $\Delta V$ values of MA monolayers are positive and increase from 0 to $365$ mV upon compression. A positive variation is typical for most surfactants with hydrocarbon chains, although the $\Delta V$ value is, in common, strongly affected by a polar headgroup and a subphase condition $[25,56]$. 

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All of the $\Delta V$–$A$ isotherms for the two systems regularly shift to negative $\Delta V$ values with increasing $X_{\text{F8C5OH}}$ or $X_{\text{F8C5PC}}$. The magnitude of variation in $\Delta V$ values against the molar fractions in the MA/F8C5OH system is larger than that in the MA/F8C5PC system. The difference is resulted from the fact that the polar headgroup of F8C5PC is more bulky than that of F8C5OH and then the orientation of F8C5OH cannot be improved upon compression differ-
3.2.2. Excess Gibbs free energy

The miscibility of MA with F8C5OH or F8C5PC can be analyzed in terms of the additivity rule for molecular area (A) and surface potential (\(\Delta V\)) (see Figures S2 and S3) and of the excess Gibbs free energy of mixing \(\Delta G_{\text{exc}}\). The \(\Delta G_{\text{exc}}\) value is evaluated by integration of the \(\pi-A\) isotherms from zero to the selected surface pressure (Eq. (7)) [59],

\[
\Delta G_{\text{exc}} = \int_0^A (A_{12} - X_i A_1 - X_j A_2) d\pi
\]

where \(A_i\) and \(X_i\) are the molecular area and the molar fraction of component \(i\), respectively, and \(A_{12}\) is the mean molecular area in the mixture. In the absence of interactions between components, \(\Delta G_{\text{exc}} = 0\) [57,58]. Negative or positive deviation from ideality indicates more attractive or less attractive interaction, respectively. The variation of \(\Delta G_{\text{exc}}\) for the MA/F8C5OH and MA/F8C5PC monolayers against molar fractions of the fluorinated components at three surface pressures (5, 15, and 25 mN m\(^{-1}\)) is shown in Fig. 3. For the MA/F8C5OH system (Fig. 3(a)), the \(\Delta G_{\text{exc}} - X_{\text{F8C5OH}}\) curves can be divided into two regions; the negative values for \(0 < X_{\text{F8C5OH}} < 0.3\) and the positive values for \(0.3 < X_{\text{F8C5OH}} < 1\). In the former region, MA attractively interacts with F8C5OH in the monolayer state. When a more amount of F8C5OH is added to MA, the interaction becomes weaker. The \(\Delta G_{\text{exc}} - X_{\text{F8C5OH}}\) curves are quite similar in shape to the limit of increasing surface pressure, although the \(\Delta G_{\text{exc}}\) values should become larger in most cases [15,60]. This result indicates that the mutual interaction is kept constant despite a reduction in the intermolecular distance between MA and F8C5OH. In the case of the binary MA/F8C5PC system, the similar behavior is observed in Fig. 3(b). However, compared to the MA/F8C5OH system, the \(\Delta G_{\text{exc}} - X_{\text{F8C5PC}}\) curve at each surface pressure almost exists in the negative region. Furthermore, the amount of \(\Delta G_{\text{exc}}\) increases more negatively with increasing surface pressure. These results demonstrate that the disordered state of F8C5PC is more miscible with MA.

3.2.3. Two-dimensional phase diagrams

Two-dimensional phase diagrams for the binary MA/F8C5OH and MA/F8C5PC mixtures were constructed by plotting the transition pressure and collapse pressure values at the various molar fractions. The phase diagrams at 298.2 K are shown in Fig. 4. For both the systems, the transition pressures change positively with an increase in molar fraction of the fluorinated compounds. In addition, the collapse pressures irregularly vary against the molar fractions. The components of the two binary systems are miscible judging from such continuous change of the transition pressures upon composition. The coexistence phase boundary between the monolayer phase and bulk phase can be theoretically simulated from the Joos equation [61].

\[
1 = x_1^6 \exp\left(\frac{\pi_m - \pi_1}{kT} + \exp\left(\frac{\chi_1^2}{\pi}\right)\right)
+ x_2^6 \exp\left(\frac{\pi_m - \pi_2}{kT} + \exp\left(\frac{\chi_2^2}{\pi}\right)\right)
\]

where \(x_1^6\) and \(x_2^6\) denote the respective mole fraction in the two-component monolayers of components 1 and 2, and \(\pi_m\) and \(\pi_1\) are the respective collapse pressure of components 1 and 2, \(\pi_m\) is the collapse pressure of the two-component monolayer at a given composition of \(x_1^6\) and \(x_2^6\), and \(\chi_1^2\) and \(\chi_2^2\) are the corresponding attractive interaction parameter, \(kT\) is the product of the Boltzmann constant and the Kelvin temperature. The solid curve obtained by adjusting the interaction parameter in the above equation (Eq. (8)) coincides with the experimental values. It is noteworthy that the both systems exhibit negative interaction parameters and have two different parameters in the two regions. The negative interaction parameter implies an interaction energy between two kinds of molecules which is higher than the mean energy of interaction among the same molecules. The new finding here is that the MA/F8C5OH system shows two interaction parameters: \(\chi_1^2 = -1.5\) for \(0 < X_{\text{F8C5OH}} < 0.3\) and \(\chi_1^2 = -0.60\) for \(0.3 < X_{\text{F8C5OH}} < 1\). The MA/F8C5PC system also indicates two interaction parameters: \(\chi_1^2 = -1.2\) for \(X_{\text{F8C5PC}} < 0.3\) and \(\chi_1^2 = -0.89\) for \(X_{\text{F8C5PC}} < 1\). At the molar fraction of 0.3, the interaction parameter becomes \(\chi_1^2 = 0\). These signs resemble to the variations of \(\Delta G_{\text{exc}}\) against molar fractions of the fluorinated compounds (Fig. 3). The interaction energies (\(\Delta G_{\text{exc}} = -\Delta (kT)\)) were calculated to be 620 J mol\(^{-1}\) \((\chi_1 = -1.5)\) and 248 J mol\(^{-1}\) \((\chi_1 = -0.60)\) for the MA/F8C5OH system. On the other hand, the MA/F8C5PC system has interaction energies of 496 J mol\(^{-1}\) \((\chi_1 = -1.2)\) and 368 J mol\(^{-1}\) \((\chi_1 = -0.89)\). That is, they are completely miscible, because the interaction energy \(\Delta G_{\text{exc}} < 2RT\) (\(=4958.7\) J mol\(^{-1}\)). The two components are miscible each in both the disordered and ordered states, and the disordered and ordered states.

Fig. 3. Excess Gibbs free energy of mixing (\(\Delta G_{\text{exc}}\)) of (a) MA/F8C5OH and (b) MA/F8C5PC mixtures as a function of \(X_{\text{F8C5OH}}\) and \(X_{\text{F8C5PC}}\) at three different pressures (5, 15, and 25 mN m\(^{-1}\)) on 0.15 M NaCl (pH 2.0) at 298.2 K, respectively. The solid lines represent values calculated from Eq. (7).

Fig. 4. Phase diagrams from the variation of the transition pressure (\(\pi_{\text{exc}}\): open circle) and collapse pressure (\(\pi_{\text{c}}\): solid circle) on 0.15 M NaCl (pH 2.0) at 298.2 K, as a function of composition: (a) MA/F8C5OH and (b) MA/F8C5PC systems. The dashed lines were calculated according to Eq. (8) for \(\chi = 0\). The solid line represents experimental values for collapse pressures. M. indicates a mixed monolayer formed by MA, F8C5OH, and F8C5PC species, whereas Bulk denotes a solid phase of MA, F8C5OH, and F8C5PC ("bulk phase" may be called "solid phase").
This system is likely to be the positive azeotropic type, and the phase diagram is completely constructed.

3.3. Morphological observations

3.3.1. Brewster angle microscopy

BAM is an optimal method to visualize the morphologic differences of the condensed (ordered) phase domains without a dye such as a fluorescent probe. In comparison to FM and AFM, however, BAM generally has lower resolution and magnification. Systematic observations with BAM have been performed for the binary systems against molar fractions of the fluorinated compounds and surface pressures. Unfortunately, the resultant BAM images could not provide better understanding of the phase behavior upon compression due to the above-mentioned defects and the narrow range between two phase coexistence states in the binary monolayer systems. Detail phase behavior with surface pressure is presented in the later sections (FM and AFM). Here our attention is focused on the ordered domains at each transition pressure for the binary MA/F8C5OH and MA/F8C5PC monolayers. The BAM images of pure MA, MA/F8C5OH ($X_{F8C5OH} = 0.05, 0.1, and 0.2$), and MA/F8C5PC ($X_{F8C5PC} = 0.05$ and 0.1) monolayers spread on 0.15 M NaCl (pH 2.0) at respective transition pressures are shown in Fig. 5. The BAM image of pure MA monolayers (Fig. 5(a)) shows a characteristic large ordered domain (bright) like a flower and agrees well with that reported previously [62]. When a small amount of F8C5OH is added to MA monolayer, the ordered domains become smaller in size and the branched arms tend to be thicker and shorter as shown in Fig. 5(b)–(d). The condensed domain shape is commonly controlled by line tension of phase boundary and long range dipole interaction. In this system, the flower-like ordered domains shift to the circular domains with increasing $X_{F8C5OH}$. This means that the mixing of F8C5OH improves the line-tension control over the domain shape due to the miscibility between MA and F8C5OH. The similar phase behavior is also observed in the MA/F8C5PC system (Fig. 5(e) and (f)). However, the degree of reducing the size and rounding the shape by the addition of F8C5PC is larger compared with that for the MA/F8C5OH mixtures. This indicates that the mixing of F8C5PC exerts stronger fluidizing effects on the ordered domains. It is demonstrated that the bulkiness in the polar headgroups of fluorinated compounds is important for the fluidization of fatty acid as well as phospholipid monolayers [8].

3.3.2. Fluorescence microscopy

A fluorescent probe is required for in situ FM observations to visualize the monolayer phase behavior. FM provides powerful information on the phase growth and variation with higher resolution and magnification compared with BAM, although the probe may act as an impurity for samples. There is a worry of the possibility that the probe affects the original phase behavior of monolayers. However, the doping of 1 mol% R18 as a fluorescent dye has no influence on the original π–A and ΔV–A isotherms and domain shapes in BAM images. Differences in the dye solubility in between disordered (or LE) and ordered (or LC) phases generate a color contrast. FM images of the binary MA/F8C5OH ($X_{F8C5OH} = 0$ (MA), 0.05, 0.1, and 0.2) monolayers are shown in Fig. 6 at various surface pressures. FM images at the molar fractions are homogeneously bright below the respective transition pressures (data not shown). In the vicinity of the transitions, two different phases can be visualized clearly as seen in each lower row of the images. The percentage (%) in the FM images indicates the ratio of the ordered (LC) domain in the monolayer systems. Detail phase behavior with surface pressure is presented in the later sections (FM and AFM). Here our attention is focused on the ordered domains at each transition pressure for the binary MA/F8C5OH and MA/F8C5PC monolayers. The BAM images of pure MA, MA/F8C5OH ($X_{F8C5OH} = 0.05, 0.1, and 0.2$), and MA/F8C5PC ($X_{F8C5PC} = 0.05$ and 0.1) monolayers spread on 0.15 M NaCl (pH 2.0) at respective transition pressures are shown in Fig. 5. The BAM image of pure MA monolayers (Fig. 5(a)) shows a characteristic large ordered domain (bright) like a flower and agrees well with that reported previously [62]. When a small amount of F8C5OH is added to MA monolayer, the ordered domains become smaller in size and the branched arms tend to be thicker and shorter as shown in Fig. 5(b)–(d). The condensed domain shape is commonly controlled by line tension of phase boundary and long range dipole interaction. In this system, the flower-like ordered domains shift to the circular domains with increasing $X_{F8C5OH}$. This means that the mixing of F8C5OH improves the line-tension control over the domain shape due to the miscibility between MA and F8C5OH. The similar phase behavior is also observed in the MA/F8C5PC system (Fig. 5(e) and (f)). However, the degree of reducing the size and rounding the shape by the addition of F8C5PC is larger compared with that for the MA/F8C5OH mixtures. This indicates that the mixing of F8C5PC exerts stronger fluidizing effects on the ordered domains. It is demonstrated that the bulkiness in the polar headgroups of fluorinated compounds is important for the fluidization of fatty acid as well as phospholipid monolayers [8].

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Fig. 5. Representative BAM images of (a) pure MA at 23 mN m$^{-1}$, (b) MA/F8C5OH ($X_{F8C5OH} = 0.05$) at 25 mN m$^{-1}$, (c) MA/F8C5OH ($X_{F8C5OH} = 0.1$) at 27 mN m$^{-1}$, (d) MA/F8C5OH ($X_{F8C5OH} = 0.2$) at 33 mN m$^{-1}$, (e) MA/F8C5PC ($X_{F8C5PC} = 0.05$) at 24 mN m$^{-1}$, and (f) MA/F8C5PC ($X_{F8C5PC} = 0.1$) monolayers at 28 mN m$^{-1}$ observed on 0.15 M NaCl (pH 2.0) at 298.2 K. The scale bar represents 50 μm.
lar domains are attributed to the domination of line tension in due to the repulsive dipole interactions. The homogeneous circu-
monolayers is observed in the monolayer region. However, the
increase in surface pressure (data not shown).

Typical FM images of the MA/F8C5OH monolayers for $X_{F8C5OH} = 0$ (MA), 0.05, 0.1, and 0.2 on 0.15 M NaCl (pH 2.0) at 298.2 K. Numerical characters in higher-right corner of each micrograph denote surface pressures (mN m$^{-1}$). In the coexistent phases, the percentage (%) in lower-left corner refers to the ordered domains in the micrograph. The monolayer contained 1 mol% fluorescent probe. The scale bar represents 200 \(\mu m\).

The incorporation of the partially fluorinated amphiphiles treated here also generates a drastic effect on the ordered domains of DPPC monolayers [8]. The fluorinated amphiphiles achieve fluidization of the DPPC monolayers. F8C5PC has the potential of fluidizing the DPPC ordered domains more effectively than F8C5OH. These trends are also observed in the present systems, too. However, especially in the DPPC/F8C5OH system, the shape of the DPPC ordered domains considerably changes by the addition of F8C5OH ($X_{F8C5OH} = 0.1$). That is, the domains transform into a triskelion-shaped domain like a whirlpool with an anticlockwise branch. Then, the further F8C5OH addition to DPPC varies the domain shape from the triskelion to circular features. On the contrary, the domain shape does not change at smaller molar fractions in the present systems. Considering that the elongation of ordered domains is strongly influenced by the long range dipole interaction, the partially fluorinated chains interact with double hydrocarbon chains (DPPC) rather than single ones (MA) within the smaller molar fraction range. If the composition of the DPPC/F8C5OH (or F8C5PC) systems is recalculated as the molar fraction per single chain; e.g., $X_{F8C5OH} = 0.1$ (per molecule) corresponds to $X_{F8C5OH} = 0.05$ (per single chain), a quite smaller addition of the fluorinated amphiphiles results in variation of the LC domain shape of DPPC.

Shown in Fig. 8 are the FM images of the MA/F8C5OH and MA/F8C5PC systems above the collapse pressures. When the monolayers of both systems ($X_{F8C5OH} = 0.1$ and $X_{F8C5PC} > 0.2$) are compressed beyond the respective collapse pressures, a large organization like a fern leaf abruptly emerges and grows up in size, which is observed in BAM and FM images. Considering that the large organization does not contain the FM prove and is visualized as a dark contrast, it is a rigid 3-D aggregate (or collapsed material) induced by over-compression of monolayers. Pure components of MA, F8C5OH, and F8C5PC do not undergo such 3-D aggregates formation under the over-compression. In the case of the MA/F8C5OH system (Fig. 8(A)), the large organization
corrodes monolayer regions of disordered/ordered states (the FM image of $X_{\text{F8C5OH}} = 0.2$). The collapsed organization becomes smaller in size with increasing $X_{\text{F8C5OH}}$ to 0.3 and its shape resembles that of the LC domain of pure MA monolayers apart from their size. The behavior suggests that the collapsed aggregate might be made mainly of MA. As for the MA/F8C5PC system (Fig. 8(B)), on the other hand, the collapsed aggregates are smaller in size and possess less complex branches in comparison to those for the MA/F8C5OH system. This is resulted from a difference in condition surrounding MA between the F8C5OH and F8C5PC monolayers, which resembles a difference in crystal form induced by solvent effect. In addition, the degree and trend of

**Fig. 7.** Typical FM images of the MA/F8C5PC monolayers for $X_{\text{F8C5PC}} = 0$ (MA), 0.05, 0.1, and 0.2 on 0.15 M NaCl (pH 2.0) at 298.2 K. Numerical characters in higher-right corner of each micrograph denote surface pressures (nN m$^{-1}$). In the coexistent phases, the percentage (%) in lower-left corner refers to the ordered domains in the micrograph. The monolayer contained 1 mol% fluorescent probe. The scale bar represents 200 μm.

**Fig. 8.** Typical FM images of the (A) MA/F8C5OH and (B) MA/F8C5PC monolayers for $X_{\text{F8C5OH}}$ (or $X_{\text{F8C5PC}}$) = 0.2 and 0.3 above the collapse pressure on 0.15 M NaCl (pH 2.0) at 298.2 K. The monolayer contained 1 mol% fluorescent probe. Numerical characters in higher-right corner of each micrograph denote approximate surface pressures (nN m$^{-1}$) beyond the monolayer collapse. The scale bar represents 200 μm.
collapsed-domain dispersions correspond to those of ordered-domain dispersions for the monolayer state (Figs. 6 and 7). Similarly to Fig. 8(A), an increase in $X_{\text{F8C5PC}}$ leads to reduction in size of the collapsed aggregates (Fig. 8(B)). It is worth noting that some collapsed aggregates have a vanishing contrast, which is indicated by white arrows in the FM image of $X_{\text{F8C5PC}} = 0.3$. This means that the aggregates with a vanishing contrast are formed below the monolayers. With increasing $X_{\text{F8C5PC}}$ from 0.2 to 0.3, the translucent aggregates increase in number or amount. Some mechanisms on forming direction (toward the air or into the subphase) of collapsed aggregates have been proposed. It is suggested that the collapse process depends on surface pressure [63], compression rate [64], and subphase condition (i.e., ions and pH) [65]. However, these factors have been determined for pure components. In the present study, we are focusing on the binary systems, and thus the FM images in Fig. 8 are observed under the almost same conditions except for the sample compositions. Considering no formation of collapsed aggregates for pure components, it is supposed that the fluorinated chain generate an important driving force of the formation. In addition, the phenomenon of forming the aggregates into subphase (Fig. 8(B)) indicates that the affinity between headgroups (−COOH and -PC) becomes larger than that between hydrophobic chains with an increase in $X_{\text{F8C5PC}}$. In particular, the steric interaction between headgroups (COOH/PC for MA/F8C5PC and COOH/OH for MA/F8C5OH) is found to contribute to the formation (vanishing contrast) into subphase.

Recently, mathematical and phenomenological studies on monolayer collapse, which is the spontaneous transition from 2-D to 3-D phases, have been performed [65–68]. In particular, pure components except for isomeric molecular species containing enantiomer and diastereoisomer have been extensively examined to obtain a thorough understanding of the collapse mechanism. Over-compression above the monolayer collapse pressure produces a remarkably rich variety of 3-D structures such as vesicle [69], giant folds [64], fiber-like networks [70], and so on. In the present study, the both mixtures of MA/F8C5OH and MA/F8C5PC generate fern-like networks as 3-D structures. The fern-like networks resemble fiber-like networks, which is formed on single monolayers of 2-azido-4-fluoro-3-hydroxystearates (EAFHSs) [70] in their growth and shape, although the present systems contain two components. Considering no appearance of 3-D collapsed structures for pure components investigated, the formation of the structures as observed in Fig. 8 collaterally supports the binary miscibility of MA with F8C5OH and with F8C5PC in the monolayer state.

3.3.3. Atomic force microscopy

AFM observations of Langmuir–Blodgett (LB) films transferred onto mica have been performed to confirm the miscibility of the present systems on the nanometer level. The films transferred at selected surface pressures were examined in the tapping mode, providing simultaneously topography and phase contrast images [8,47]. Notice that there are few differences in chain lengths between MA and F8C5OH or F8C5PC, which induces the defect in detection limit and resolution under the AFM measurements. In the disordered states below the respective transition pressures (see Fig. 4), AFM topographies and phase contrasts for the two binary systems were homogeneous images within height difference of 0.2 nm. Therefore, an experimental attention was focused on the disordered/ordered coexistence regions between transition pressure and collapse one. Fig. 9 shows typical AFM height images for the MA/F8C5OH and MA/F8C5PC systems at 30 or 35 mN m$^{-1}$. For the MA/F8C5OH system, the AFM image at $X_{\text{F8C5OH}} = 0.1$ (Fig. 9(a)) exhibits a larger and higher island than the surroundings. The island is the ordered domain made mainly of MA as observed in the BAM and FM images. However, a lot of lower defects with height difference of 0.3 ± 0.1 nm exist in the islands (see the cross-sectional image). It means that F8C5OH disperses the ordered domains into the disordered phases in the shape of a worm-eaten spot. When more amounts of F8C5OH are added (Fig. 9(b)), the islands become smaller in size and are dispersed in the same manner; the height difference within the islands is 0.4 ± 0.1 nm. As shown in Fig. 9(c), on the other hand, the AFM image for the MA/F8C5PC system ($X_{\text{F8C5PC}} = 0.1$) indicates the similar behavior to that for the MA/F8C5OH mixture. However, it is noted that the island is more finely dispersed by the F8C5PC addition compared with the case of F8C5OH (Fig. 9(a)). The height difference in the island (0.5 ± 0.1 nm) is slightly larger than that in Fig. 9(a). This is attributed to the looser molecular orientation of F8C5PC induced by its bulky headgroup. From the point of view of fluidizing lipids, it is possible to say that the fluorinated amphiphiles structurally require the spatially bulky moiety such as phosphocholine (or phosphatidylcholine) headgroup. The AFM observations demonstrated that the mode of miscibility of MA with F8C5OH and with F8C5PC is strongly dominated by the fluidizing or dispersing effect of the fluorinated compounds on the ordered domain of MA monolayers.

![Figure 9](image-url)
4. Conclusions

It was proved that MA is miscible with F8C5OH or F8C5PC in the disordered as well as in the ordered monolayer state on 0.15 M NaCl (pH 2.0) subphase. Both of the MA/F8C5OH and MA/F8C5PC systems were classified into a positive azetrotype type. Assuming a regular surface mixture, an interaction parameter (ξ) and interaction energy were calculated using the Joos equation. The binary systems separately have two interaction parameters which change at X_{F8C5OH} (or X_{F8C5PC}) = 0.3: the MA/F8C5OH (or F8C5PC) systems have ξ = −1.5 (−1.2) for 0 ≤ X ≤ 0.3 and ξ = −0.6 (−0.89) for 0.3 ≤ X ≤ 1, respectively. The parameters reveal the presence of relatively stronger interactions between MA and F8C5PC under compression. Morphological observations with BAM, FM, and AFM collaboratively support the two-component miscibility. A new finding in this study is that the both binary mixtures investigated here generate fern-like networks as 3-D structures in the monolayer collapse state. The difference in shape of the collapsed structures between the two systems may be responsible for a difference in crystal form which is often induced by solvent effect. Furthermore, these observations suggest that the miscibility behavior is strongly dominated by the fluidizing effect of the fluorinated compounds on the ordered domain of MA monolayers. In particular, F8C5PC exerts the stronger fluidizing effect, indicating a significance of bulkiness of polar headgroups in fluorinated compounds for the lipid fluidization. Focused on the shape of ordered domains, however, the present systems did not show the large variation in shape differently from the previous DPPC systems, where the domain shape transformed to triskelion at the specific molar fraction. Above all, these results indicate that F8C5OH and F8C5PC liquefied MA and DPPC monolayers in different extent, which is useful to develop their innovative applications to the biomedical field such as selective drug delivery and lung surfactant additive.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research 20500441 from the Japan Society for the Promotion of Science (JSPS). This work was also supported by a Grant-in-Aid for Young Scientists 20810041 from JSPS (H.N.).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2009.05.022.

References