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Mixed Langmuir Monolayers Made from Single-Chain Perfluoroalkylated Amphiphiles

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Received July 1, 2000. In Final Form: September 21, 2000

Surface pressure (π)–area (A), surface potential (ΔV)–area, and dipole moment (μ_{\perp})–area isotherms were obtained for Langmuir monolayers made from (perfluorooctyl) pentylphosphocholine (F8C5PC), (perfluorooctyl) pentanol (F8C5OH), and their combinations. Monolayers were spread on a 0.15 M NaCl subphase. Surface potentials were analyzed using the three-layer model proposed by Demchak and Fort. The contributions of the CF₃ ω -group and the phosphocholine (PC) headgroup to the vertical component of the dipole moment μ_{\perp} were estimated to be -2.5 and 3.3 D, respectively. The miscibility of F8C5PC and F8C5OH in the mixed monolayers was examined by plotting the variation of the molecular area, surface potential, and dipole moment as a function of the F8C5OH molar fraction, using the additivity rule. Negative deviations to the linearity of the molecular area were observed at various surface pressures (5 , 15 , 25 , and 35 mN m⁻¹), showing partial miscibility with attractive interaction between the monolayers' components. Assuming a regular surface mixture, the Joos equation, which was used to describe the collapse pressure of mixed monolayers with miscible components, allowed calculation of the interaction parameter ($\xi = -0.52$) and the interaction energy (210 J/mol) between the two fluorinated amphiphiles.

Introduction

Perfluoroalkylated surfactants are characterized by a strong surface activity and an enhanced propensity to form micelles at very low concentrations as compared to nonfluorinated analogues.¹ A large range of new well-defined and modular fluorinated surfactants was recently synthesized that allowed the preparation and stabilization of various colloidal systems with potential biomedical applications.² These colloidal systems include fluorocarbon-in-water emulsions, reverse water (or hydrocarbon)-in-fluorocarbon emulsions and microemulsions,³ fluorinated vesicles,⁴ and fluorinated microtubules.⁵ Fluorocarbons are efficient oxygen carriers.⁶ A neat fluorocarbon (perfluorooctyl bromide) and a fluorocarbon-in-water emulsion

are currently in advanced clinical trials in Europe and in the U.S. as a liquid ventilation medium and as a temporary blood substitute, respectively.^{7,8} We have shown that a combination of a single-chain perfluoroalkylated amphiphile with a phosphocholine polar head and a perfluoroalkylated alcohol allowed the formation of stable vesicles or of microtubules, depending on the alcohol molar ratio.⁹ It is desirable to better understand the driving forces that determine the formation and evolution of fluorinated self-assemblies. In particular, it is of interest to understand the mechanism of formation of tubules from nonchiral fluorinated surfactants, as chirality was recognized as the driving force of the formation of tubules from hydrogenated lipids.¹⁰

Taking into account the above bulk behavior of fluorinated surfactants when used alone or in mixtures,^{2–5} we undertook to compare their three-dimensional properties with their two-dimensional surface properties. Various kinds of mixed monolayers made from mixtures of hydrogenated surfactants spread at the air/water interface have been studied.^{11–14} Yamamoto et al. have investigated a mixed system made of a phospholipid (dipalmitoylphos-

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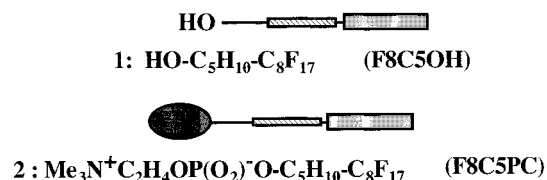
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Chart 1. Chemical Structure of Modular Perfluoroalkylated Amphiphiles Used as Components of Films

phatidylcholine, DPPC) and hydrogenated or perfluoroalkylated fatty acids.¹⁵ These authors reported that perfluorocarboxylic acids and DPPC were partially miscible in the mixed monolayers. Intermolecular interaction was rather strong, suggesting that attractive forces between headgroups contribute more to miscibility than the hydrophobic interactions.¹⁵ Monolayers made from combinations of DPPC or dipalmitoylphosphatidylethanolamine (DPPE) and a semi-fluorinated alkane have also been studied. The results showed that the semi-fluorinated alkane was ejected from the water surface at high pressure and formed a second organized layer on top of a phospholipid-only monolayer.^{16,17}

In the present paper, we have investigated the monolayer behavior of a perfluoroalkylated phosphocholine, C₈F₁₇(CH₂)₅OP(O₂)⁻OCH₂CH₂N(CH₃)₃⁺ (F8C5PC), of a perfluoroalkylated alcohol, C₈F₁₇(CH₂)₅OH (F8C5OH), and of their mixtures. Surface pressure (π)-area (A), surface potential (ΔV)-area, and dipole moment (μ_{\perp})-area isotherms were obtained for the pure compounds and for their combinations. Surface potentials were analyzed using the three-layer model proposed by Demchak and Fort. The phase behavior of the mixed monolayer state was examined in terms of the additivity of the mean molecular surface area, surface potential, and surface dipole moment and through the phase diagram.

Experimental Section

(Perfluorooctyl) pentylphosphocholine (F8C5PC) and (perfluorooctyl) pentanol (F8C5OH) (Chart 1) were synthesized as reported previously.¹⁸ F8C5PC was purified by column chromatography, followed by repeated recrystallizations from chloroform/acetonitrile (9:1). F8C5OH was recrystallized repeatedly from chloroform. The purity of these amphiphiles was checked by ¹H NMR (Bruker AC 200 and JEOL GSX-270) and ³¹P (Bruker AC 200) measurement, high-performance liquid chromatography (HPLC), and elemental analysis. The pure compounds or their mixtures were spread from an *n*-hexane/ethanol mixture (9/1) at the air/aqueous solution interface. *n*-Hexane and ethanol came from Merck (Uvasol) and Nacalai Tesque, respectively.

The 0.15 M sodium chloride (Nacalai Tesque) substrate solution was prepared using thrice-distilled water (surface tension, 72.7 mN m⁻¹ at 293.2 K; resistivity, 18 MΩ). Sodium chloride was roasted at 973 K for 24 h to remove any surface active organic impurities.

The surface pressure of the monolayer, π , was measured using an automated Langmuir film balance, which was the same as that used in the previous studies.¹⁹ The surface pressure balance (Chan RG, Langmuir float type) has a resolution of 0.01 mN m⁻¹. The trough was made from brass coated with Teflon (area of 750 cm²). The monolayer was compressed at the speed of 2.00×10^{-1}

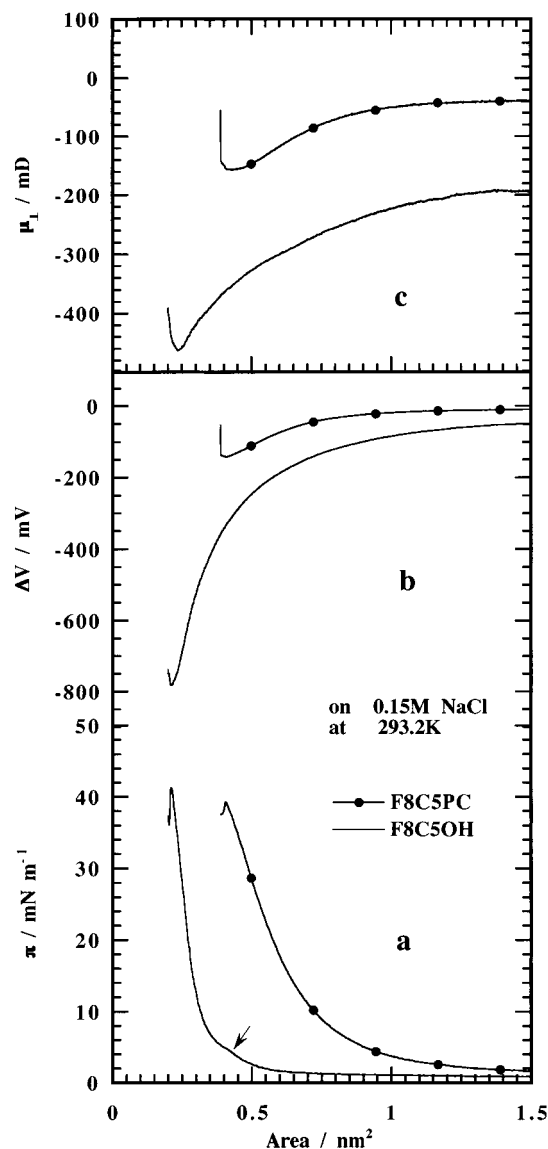


Figure 1. Surface pressure (π)-area (A) isotherms (a), surface potential (ΔV)- A isotherms (b), and surface dipole moment (μ_{\perp})- A isotherms (c) of F8C5PC and F8C5OH on 0.15 M NaCl at 293.2 K.

nm² molecule⁻¹ min⁻¹. No influence of the compression rate (at 6.60×10^{-2} , 1.00×10^{-1} , and 2.00×10^{-1} nm² molecule⁻¹ min⁻¹) was detected within the limits of the experimental error. Surface potential was simultaneously recorded while the monolayer was compressed. It was monitored using an ionizing ²⁴¹Am electrode at 1–2 mm above the interface, while a reference electrode was dipped in the subphase. The standard deviation for area measurements was approximately 1.00×10^{-2} nm², and that for surface potential measurements was 10 mV. Other experimental conditions were the same as described in the previous papers.¹⁹

Results and Discussion

Surface Pressure (π)-Area (A), Surface Potential (ΔV)-Area, and Dipole Moment (μ_{\perp})-Area Isotherms. The π - A , ΔV - A , and μ_{\perp} - A isotherms of monolayers made from pure F8C5PC and F8C5OH spread on

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Table 1. Surface Potential Data^a

compound	A_0 (nm ²)	ΔV (mV)
stearic acid	0.20 ± 0.01	$+300 \pm 10$
F8C5PC	0.74 ± 0.02	-140 ± 10
F8C5OH	0.32 ± 0.02	-440 ± 10

^a Surface potential data obtained on all compounds investigated to date. A_0 is the area per molecule obtained by extrapolating the high-pressure portion of the π - A isotherms to zero pressure. ΔV is the surface potential at maximum compression. In all cases, the subphase was 0.15 M NaCl at 293.2 K.

a 0.15 M NaCl subsolution (at 293.2 K) are shown in Figure 1a–c. The vertical component of the surface dipole moment, μ_{\perp} , was calculated from the Helmholtz equation:

$$\Delta V = \mu_{\perp} / \epsilon_0 \epsilon A \quad (1)$$

where ϵ_0 is the permittivity of a vacuum and ϵ is the mean permittivity of the monolayer (which is assumed to be 1).

F8C5OH was stable up to 41 mN m⁻¹ with a transition between a liquid-expanded (LE) phase and a liquid-condensed (LC) phase at 4.5 mN m⁻¹ (0.43 nm²), as indicated by an arrow (Figure 1a). The extrapolated area in the condensed state was 0.33 nm², and the collapse area was 0.21 nm². These values indicate that the fluorinated chains are in close contact at high pressure. The F8C5PC isotherm was more expanded, indicating that the monolayer was in a LE phase. It collapsed at 39 mN m⁻¹ (0.42 nm²). The extrapolated area was 0.75 nm².

The surface potentials (ΔV) of F8C5PC and F8C5OH were found to be always negative (Figure 1b, Table 1). The F8C5OH monolayer showed a large variation of ΔV under compression. ΔV became increasingly negative and reached a value of around -800 mV (starting from -50 mV, an absolute difference of around 730 mV) at the collapse area (0.21 nm²). The F8C5PC monolayer displayed a much smaller variation of ΔV (from around 0 to -140 mV) at the collapse area (0.42 nm²). It has been shown that the surface potentials of monolayers of a series of ω -monohalogenated fatty acids and alcohols and progressively fluorinated fatty acids were negative because of the strong electronegativity of fluorine atoms, whereas they were positive for the unsubstituted acids or alcohols.^{20–22} It was also found that ΔV did not vary with the number of carbon atoms in the fluorinated chain.²² ΔV values involve the resultant of the dipole moments carried by the polar head (PC or OH), the C–F bond (the CF₃ ω -group), and the subphase. In non-fluorinated analogues for which the surface potential is positive,^{20–22} as the subphase and the hydrophobic tails are identical for the two compounds the difference observed in the values of ΔV for F8C5PC and F8C5OH clearly evidences the influence of the polar head. The small change to negative potential (F8C5PC) reflects the orientation change of the PC head of F8C5PC during compression, and a change in ΔV may also result from a change in PC hydration. Also, the value of μ_{\perp} for PC must reflect the water structure. The PC head area is much larger than the OH head area, which results in a loose packing of F8C5PC chains. A larger change to more negative potential observed in the case of F8C5OH can be explained by the higher organization of the monolayer as compared to that of F8C5PC, because of increased mutual polarization.

The variations of the vertical component of the surface dipole moment, μ_{\perp} , of F8C5OH and F8C5PC monolayers

under compression are shown in Figure 1c. The value of μ_{\perp} strongly depends on the polar headgroup's nature. Upon compression, μ_{\perp} (F8C5OH) decreased from about -200 to -460 mD, whereas μ_{\perp} (F8C5PC) decreased only from -50 to -150 mD. Under compression from 0.35 nm² to 0.20 nm², the μ_{\perp} - A isotherm of F8C5OH did not reach a limiting value as was usually observed^{22,23} but passed reproducibly through a minimum (-0.46 D) at 0.235 nm². This suggests that a conformational change occurred in the monolayer, although the nature of this conformational change cannot be specified. A similar decrease of μ_{\perp} from 0.250 D at 0.222 nm² to 0.240 D at 0.200 nm² was observed for eicosanol monolayers.¹² A nonmonotonic variation of μ_{\perp} was also reported for octadecyl nitrile²³ and for *n*-heptanol and 16-bromohexanol monolayers.²⁴

In the case of F8C5PC, it cannot be ascertained that the variation of μ_{\perp} is nonmonotonic because of the small magnitude of the ΔV variation and because the change occurred near the collapse of the monolayer.

Contribution of ω -Group (CF₃) and Polar Headgroups to Dipole Moment. The surface potential of monolayers was often analyzed using the three-layer model proposed by Demchak and Fort,²³ as suggested by Davies and Rideal.²⁵ This model postulates independent contributions of the subphase (layer 1), polar headgroup (layer 2), and hydrophobic chain (layer 3). Independent dipole moments and effective local dielectric constants are attributed to each of the three layers. Other models, such as the Helmholtz model and the Vogel and Möbius model,^{26,30} are also available. These different models were reviewed in ref 27. The conclusion was that despite its limitations the Demchak and Fort model provides a good agreement between the values of dipole moments estimated from the monolayer surface potentials for various aliphatic compounds and those determined from measurements on bulk material.

We have thus compared the experimental values of the vertical components μ_{\perp} in the close-packed state with the values of $\mu_{\perp\text{calc}}$ calculated from the equation based on the three-layer model:

$$\mu_{\perp\text{calc}} = (\mu_1/\epsilon_1) + (\mu_2/\epsilon_2) + (\mu_3/\epsilon_3) \quad (2)$$

where μ_1/ϵ_1 , μ_2/ϵ_2 , and μ_3/ϵ_3 are the contributions of the subphase, polar headgroup, and tail group, respectively.

We wanted to determine the contribution of the CF₃ terminal group and that of the phosphocholine (PC) group. The latter has been determined in the case of dipalmitoylphosphatidylcholine.^{27,29,30} However, the conformation of the PC group is likely to be different in the case of the single-chain F8C5PC investigated here.

The initial set of values proposed by Demchak and Fort ($\mu_1/\epsilon_1 = 0.040$ D, $\epsilon_2 = 7.6$, $\epsilon_3 = 5.3$)²³ was determined for monolayers made from terphenyl derivatives and octadecyl nitrile. Another set of values was determined in papers by Taylor and Oliveira ($\mu_1/\epsilon_1 = -0.065$ D, $\epsilon_2 = 6.4$, $\epsilon_3 = 2.8$) for monolayers of ω -halogenated fatty acids and amines.^{27,28} We have used a set of values introduced in a recent study²⁴ ($\mu_1/\epsilon_1 = 0.025$ D, $\epsilon_2 = 7.6$, $\epsilon_3 = 4.2$) because

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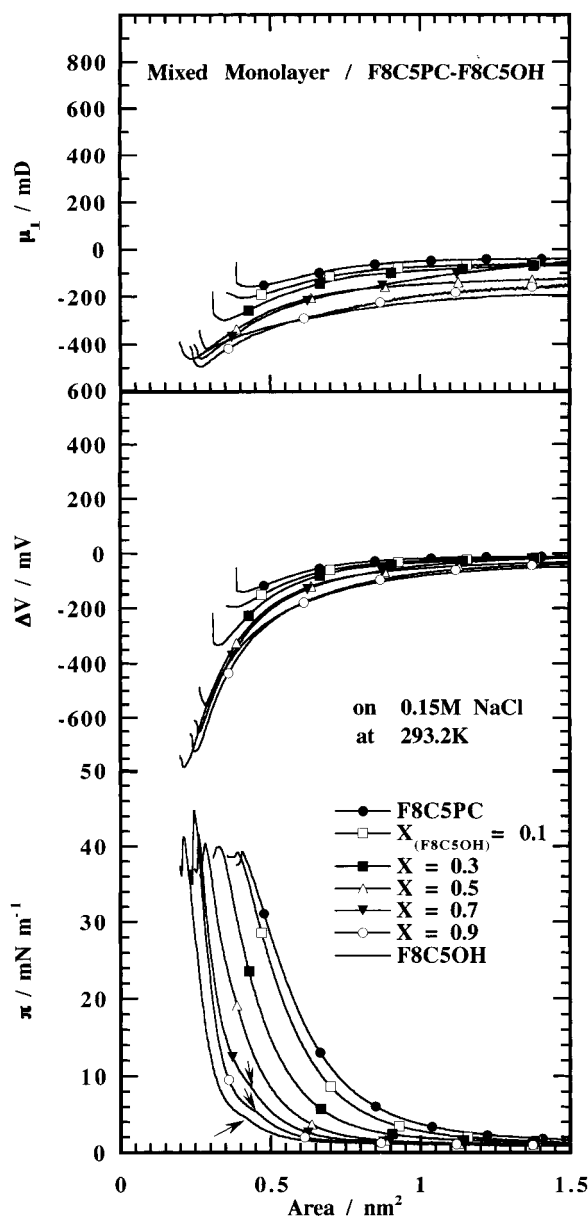


Figure 2. Surface pressure (π)-area (A) isotherms, surface potential (ΔV)- A isotherms, and surface dipole moment (μ_{\perp})- A isotherms of F8C5PC and F8C5OH mixed monolayers on 0.15 M NaCl at 293.2 K.

they provide a good agreement between calculated values and experimental values of dipole moments measured for monolayers spread on a saline phase. Values have been proposed for μ_2 for the different conformations of the OH group:²⁴ μ_2 (OH-gauche) = 1.00 D, μ_2 (OH-trans) = -0.63 D, and μ_2 (OH-free) = 0.18 D. We have used the μ_2 (OH-gauche) value as many studies support the gauche conformation for condensed alkyl alcohol monolayers.^{23,24}

Using the experimentally determined μ_{\perp} values and assuming the values $\mu_1/\epsilon_1 = 0.025$ D, $\epsilon_2 = 7.6$, and $\mu_2 = 1.00$ D, we were able to calculate $\mu_3/\epsilon_3 = -0.597$; that is, $\mu_3 = -2.51$ D from eq 3.

$$\mu_{\perp}(\text{F8C5OH}) = (\mu_1/\epsilon_1) + (\mu_2^{\text{OH}}/\epsilon_2) + (\mu_3^{\text{F8C5}}/\epsilon_3) = -0.44 \text{ D} \quad (3)$$

This value is larger than those reported for ω -halogenated alcohol (-0.68 D)²² and tri-fluoropalmitic acid²⁸ monolayers. However, it is closer to the value of the dipole

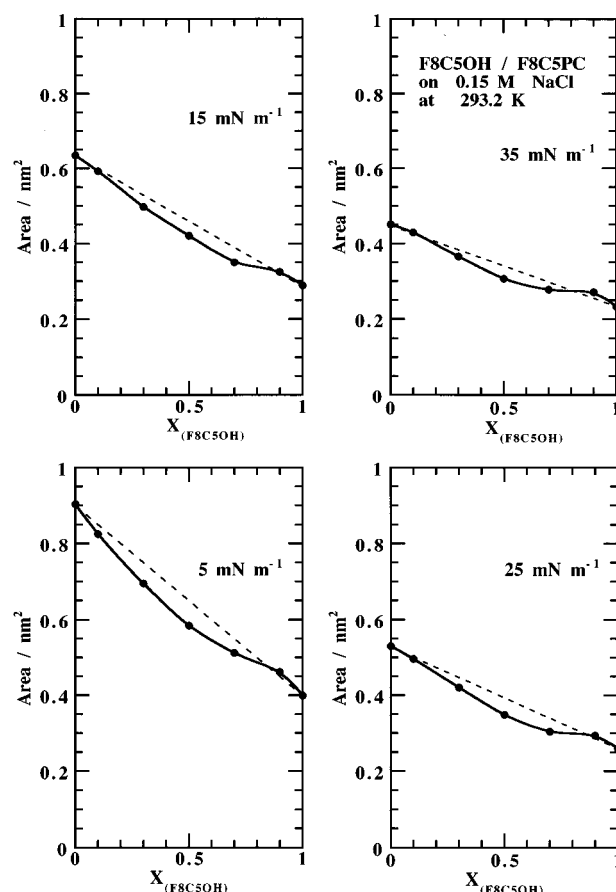


Figure 3. Mean molecular area (A) of the mixed F8C5PC and F8C5OH system as a function of the composition of F8C5OH at four different pressures. The dashed lines were calculated by assuming the additivity rule, and the solid circles represent experimental values.

moment measurements based on the dielectric constant for compounds in the gaseous state (1.9 D).

This value ($\mu_3^{\text{F8C5}}/\epsilon_3$) was reported in eq 4,

$$\mu_{\perp}(\text{F8C5PC}) = (\mu_1/\epsilon_1) + (\mu_2^{\text{PC}}/\epsilon_2) + (\mu_2^{\text{F8C5}}/\epsilon_3) = -0.14 \text{ D} \quad (4)$$

which allowed us to obtain $\mu_2^{\text{PC}} = 3.3$ D for the PC head. This value is a little bit larger than that reported by Taylor et al. for DPPC (2.44 D),²⁷ which can be explained by the fact that F8C5PC is a single-chain amphiphile whereas DPPC is a double-chain lipid. In each case, a change in ΔV may also result from a change in PC hydration. Also, the value of μ_{\perp} for PC must reflect the water structure. Then, this difference may come from experimental conditions such as substrate conditions (electrolyte, pH), compression rates, and so forth.

Ideality of the Mixture. The two-component mixed monolayer system composed of F8C5OH and F8C5PC was studied in order to assess the impact of the molecular structure of the amphiphiles on their miscibility in the monolayer and on the state of the monolayer. For this purpose, the π - A , ΔV - A , and μ_{\perp} - A isotherms of the F8C5PC/F8C5OH mixed monolayers were measured for various F8C5OH molar fractions (X_{F8C5OH}) (298.2 K, 0.15 M NaCl subsolution). The results are shown in Figure 2. For $X_{\text{F8C5OH}} = 0.9$ and 0.7, π - A isotherms display a transition pressure which increases with decreasing X_{F8C5OH} . Although it is difficult to ascertain the transition pressure at lower mole fractions, this is a first indication

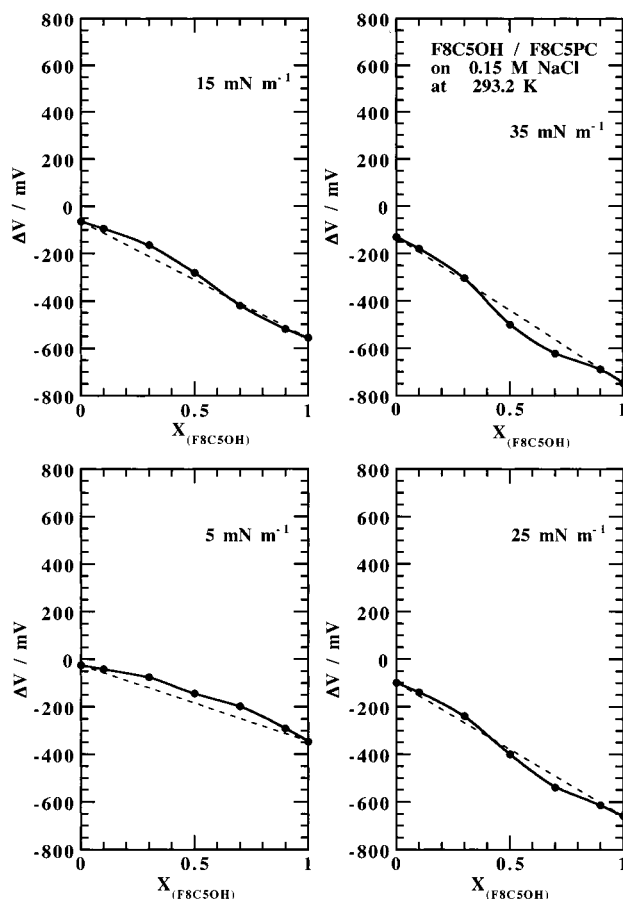


Figure 4. Surface potential (ΔV) of the mixed F8C5PC and F8C5OH system as a function of F8C5OH at four different pressures. The dashed lines were calculated by assuming the additivity rule, and the solid circles represent experimental values.

that F8C5PC and F8C5OH are at least partially miscible in the mixed monolayers.

An understanding of the interactions between F8C5PC and F8C5OH is provided by examining whether the variation of the mean molecular area as a function of X_{F8C5OH} satisfies the additivity rule or not. A comparison between experimental mean molecular areas (closed circles) and mean molecular areas (dashed lines) calculated assuming an ideal mixing is given in Figure 3 at four surface pressures (5, 15, 25, and 35 mN m^{-1}). For all surface pressures, it clearly shows a negative deviation between the theoretical and experimental curves, indicating some interactions between F8C5OH and F8C5PC. These interactions may likely result from attractive interactions between PC and OH polar heads.

In Figure 2 we have also examined the influence of X_{F8C5OH} on the ΔV - A and μ_{\perp} - A curves. Both ΔV and μ_{\perp} reflected the π - A behavior; the higher the collapse pressure, the larger the ΔV and μ_{\perp} values. As was observed for monolayers made from pure compounds, μ_{\perp} - A isotherms did not reach limiting values under compression for each mole fraction. The magnitude of the surface dipole moment showed the minimum value for $X_{\text{F8C5OH}} = 0.9$, which reflects the extent of the interaction.

An analysis of the surface potential (ΔV) and of the surface dipole moment (μ_{\perp}) of the monolayer was also made in terms of the additivity rule. For the F8C5PC/F8C5OH mixed system, the results are presented by the solid points in Figures 4 and 5, where the dashed lines show the mean ΔV and the mean μ_{\perp} calculated assuming the additivity

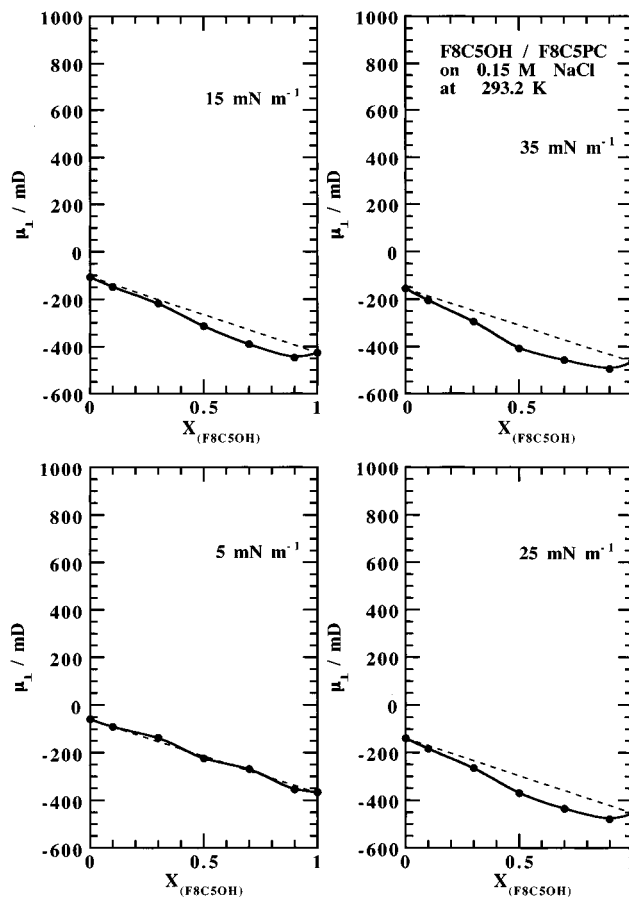


Figure 5. Surface dipole moment (μ_{\perp}) of the mixed F8C5PC and F8C5OH system as a function of F8C5OH at four different pressures. The dashed lines were calculated by assuming the additivity rule, and the solid circles represent experimental values.

rule. The variations of μ_{\perp} at various surface pressures (15, 25, and 35 mN/m) showed a significant negative deviation.

Two-Dimensional Phase Diagram. Two-dimensional phase diagrams of F8C5PC/F8C5OH monolayers were constructed by plotting the values of collapse pressures as a function of F8C5OH mole fractions. A representative phase diagram at 278.2 K is shown in Figure 6. On this figure, M indicates a mixed liquid monolayer formed by F8C5PC and F8C5OH and Bulk denotes a solid phase ("bulk phase" may be called "solid phase"). The collapse pressure π^c determined at each mole fraction is indicated by a filled circle, where the dashed line shows $\xi = 0$.

The coexistence phase boundary between the expanded phase of the F8C5PC/F8C5OH mixture and the bulk phase can be theoretically simulated by the Joos equation³¹

$$1 = x_1^s \gamma_1 \exp[(\pi_m^c - \pi_1^c) \omega_1 / kT] \exp[\xi(x_2^s)^2] + x_2^s \gamma_2 \exp[(\pi_m^c - \pi_2^c) \omega_2 / kT] \exp[\xi(x_1^s)^2] \quad (5)$$

where x_1^s and x_2^s denote the mole fractions at the surface of components 1 and 2 and π_1^c and π_2^c are the collapse pressures of components 1 and 2. π_m^c is the collapse pressure of the mixed monolayer at given compositions of the surface x_1^s and x_2^s . ω_1 and ω_2 are limiting areas at the collapse points. γ_1 and γ_2 are the surface activity coef-

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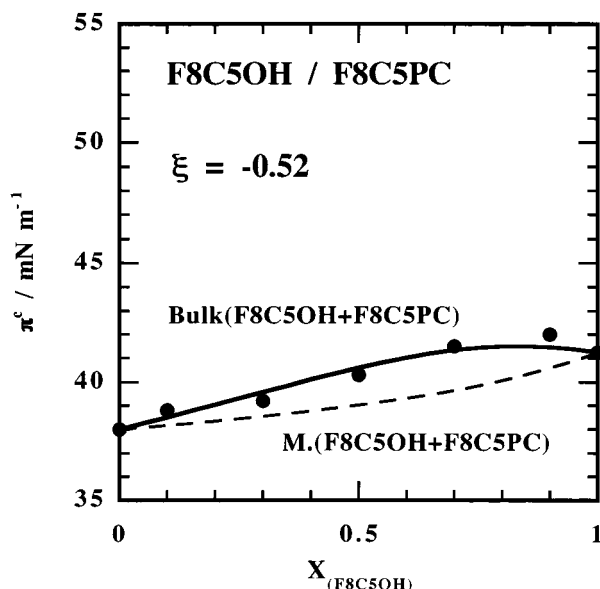


Figure 6. Collapse pressure π^c as a function of the surface composition of the mixed monolayer of F8C5OH. The solid line was calculated according to eq 5, the dashed line was calculated according to eq 5 in the case of $\xi = 0$, and the solid circles represent experimental values.

ficients at the collapse point, and ξ is the interaction parameter. kT is the product of the Boltzmann constant with Kelvin temperature. The solid curve is made coincident with the experimental values by adjusting the interaction parameter in the above equation. The F8C5PC/F8C5OH system produced a negative interaction parameter ($\xi = -0.52$). Such a negative parameter implies that the interaction energy between F8C5PC and F8C5OH (which was calculated to be 210 J mol^{-1}) is higher than the mean energy between similar molecules. That means that the two components are completely miscible, both in the expanded state and in the condensed state. However, their mutual interaction is weaker than the mean of interactions between pure component molecules themselves.¹⁴ Figure 5 shows a common characteristic of mixed monolayers in which ion-ion or ion-dipole interaction takes place. The average area per molecule does not show a large negative deviation from the additivity rule, which may depend on the fact that the two components form an

expanded monolayer. However, a surface potential per molecule must show a deviation from the additivity line, because ion-ion or ion-dipole interaction reduces the average surface dipole per molecule in mixed monolayers.^{32,33}

To ascertain the above phenomena, the miscibility of the F8C5PC/F8C5OH system has to be further studied by other techniques such as ellipsometry, Brewster angle microscopy, and so forth, which will be reported in a future paper.

In conclusion, the new finding of this study is that the single-chain perfluoroalkylated phosphocholine (F8C5PC) and the perfluoroalkylated alcohol (F8C5OH) can be spread as a stable monolayer at 293.2 K on a 0.15 M NaCl subphase. F8C5OH was found to exhibit a LE/LC phase transition, whereas the F8C5PC monolayer is in the LE phase. The nature of the polar head of PC versus OH strongly influenced the surface potentials. The Demchak and Fort model was applied to analyze the surface potentials obtained from F8C5PC and F8C5OH pure and mixed monolayers, and their headgroup (PC) and terminal group (CF_3) dipole moments were determined. It is concluded that the hydrophilic headgroups contribute significantly to the surface potential. Assuming a regular surface mixture, the Joos equation was applied to trace the collapse pressure of a mixed monolayer with miscible components. An interaction parameter ($\xi = -0.52$, that is, an interaction energy of 210 J/mol) was calculated, showing miscibility of the two fluorinated amphiphiles.

Note Added After ASAP Posting

This article was inadvertently released ASAP on 11/16/00 before final corrections were made. Additional information was added to reference 15. Additional reference citations were added on page C, paragraph 2, line 11 and paragraph 4, line 4. This version contains the final corrections.

Acknowledgment. This work was supported by Grant-in-Aid for Scientific Research No. 10554040 from the Ministry of Education, Science, and Culture, Japan, which is greatly appreciated.

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