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Author(s)	Shimoaka, Takafumi; Tanaka, Yuki; Shioya, Nobutaka; Morita, Kohei; Sonoyama, Masashi; Amii, Hideki; Takagi, Toshiyuki; Kanamori, Toshiyuki; Hasegawa, Takeshi
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Surface Properties of a Single Perfluoroalkyl Group on Water Surfaces Studied by Surface Potential Measurements

Takafumi Shimoaka [a], Yuki Tanaka [a], Nobutaka Shioya [a], Kohei Morita [b],

Masashi Sonoyama [b], Hideki Amii [b], Toshiyuki Takagi [c], Toshiyuki Kanamori [c],

Takeshi Hasegawa*[a]

[a] Laboratory of Solution and Interface Chemistry, Division of Environmental Chemistry, Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

[b] Division of Molecular Science, Faculty of Science and Technology, Gunma University, Kiryu, Gunma 376-8515, Japan

[c] National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

E-mail address: [TS] shimoaka@scl.kyoto-u.ac.jp [YT] yuki@env.kuicr.kyoto-u.ac.jp

[NS] nobutaka@env.kuicr.kyoto-u.ac.jp [KM] t09301167@gunma-u.ac.jp

[MS] sonoyama@gunma-u.ac.jp [HA] amii@gunma-u.ac.jp [TT] t.takagi@aist.go.jp

[TK] t.kanamori@aist.go.jp [TH] htakeshi@scl.kyoto-u.ac.jp

1   ***Corresponding Author:** Prof. Takeshi Hasegawa

2   Postal address: Laboratory of Solution and Interface Chemistry, Division of

3   Environmental Chemistry, Institute for Chemical Research, Kyoto

4   University, Gokasho, Uji, Kyoto 611-0011, Japan

5   Phone: +81 774 38 3070

6   FAX: +81 774 38 3074

7   E-mail: htakeshi@scl.kyoto-u.ac.jp

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10   **Highlights:**

11   ● Dehydration about the head group is a key to understand surface potential changes.

12   ● A single perfluoroalkyl group is stabilized on a water surface.

13   ● A long perfluoroalkyl chain makes a stiff molecular domain on the water surface.

14

Abstract: A discriminative study of a single perfluoroalkyl (Rf) group from a bulk

material is recently recognized to be necessary toward the total understanding of Rf

compounds based on a primary chemical structure. The single molecule and the bulk

matter have an interrelationship via an intrinsic two-dimensional (2D) aggregation

property of an Rf group, which is theorized by the stratified dipole-arrays (SDA) theory.

Since an Rf group has dipole moments along many C–F bonds, a single Rf group would

possess a hydrophilic-like character on the surface. To reveal the hydration character of

a single Rf group, in the present study, surface potential (ΔV) measurements are

performed for Langmuir monolayers of Rf-containing compounds. From a comparative

study with a monolayer of a normal hydrocarbon compound, the hydration/dehydration

dynamics of a lying Rf group on water has first been monitored by ΔV measurements,

through which a single Rf group has been revealed to have a unique "dipole-interactive"

character, which enables the Rf group interacted with the water 'surface.' In addition,

the SDA theory proves to be useful to predict the 2D aggregation property across the

phase transition temperature of 19 °C by use of the ΔV measurements.

1   **Introduction:** Perfluoroalkyl (Rf) compounds exhibit unique "bulk characters"

2   represented by the high water- and oil-repelling property, low dielectric permittivity, and

3   low solubility in a solvent, which have long been used extensively for many practical

4   chemical products.[1] When a local structure of the Rf group is taken into account,

5   however, uniformed understanding of the bulk properties is difficult. For example, the

6   C–F bond has a large dipole moment due to the largest electronegative character of

7   fluorine,[2,3] which should attract water molecule via the dipole-dipole interaction. This

8   fact seems inconsistent with the hydrophobic surface property on Rf compounds.

9   Recently, a novel chemical theory, i.e., the stratified dipole-arrays (SDA) theory, has

10   been proposed for fully understanding the material characters, which discriminates a

11   'single molecular character' from the 'bulk one.'[4]

12   This theory is based on the dipole-dipole interaction[5] of the Rf groups having a

13   helical structure.[1,6,7] In Rf compounds, the Rf chains are aggregated tightly by

14   two-dimensional dipole-dipole interaction arrays, in which all the dipoles corresponding

15   to CF_2 groups are linearly aligned in the head-to-tail manner. The tight aggregation

16   readily explains most of the bulk characters comprehensively[4]. Fortunately, this theory

17   readily covers the conventional polarizability-based theory[8] to account for the low

18   permittivity. Since the intrinsic difference between an Rf group and a normal

4

1 hydrocarbon is attributed[9] to the difference between the dipole-dipole interaction and

2 the dispersion force,[5] respectively, the SDA theory built on the dipole-dipole interaction

3 has become very important. In particular, the SDA theory is the only theory accounting

4 for the discontinuity of the melting point[4] at the length of -C_8F_{17} as well as the

5 fluorophilic effect[10] and the low electric permittivity, which are not found in a normal

6 hydrocarbon material.

7   Some of the 'single molecular characters' predicted by the SDA theory have

8 experimentally been confirmed via the adsorption of 'molecular water' on a stretched

9 polytetrafluoroethylene (PTFE; known as Teflon®) tape by using ^{1}H NMR[11]. A PTFE

10 tape is made of bundled fibrils of polymeric Rf chains with the SDA packing. If the

11 tape is mechanically stretched, then the SDA packed fibrils are partly disaggregated,

12 and a single-molecule character of an Rf chain faces to the air. Since a single Rf group

13 possesses strong dipole moments on the surface due to the C–F bonds, molecular water

14 having a large dipole should be adsorbed on the surface via the dipole-dipole

15 interaction. The ^{1}H NMR study reveals that the adsorption is due to the dipole-diploe

16 interaction in fact by the chemical shift and T_1 analyses.

17   Judging from an electrodynamics theory,[9] both stretched and un-stretched PTFE

18 tapes should exhibit 'hydrophobicity' to a water 'droplet' (not molecular water), since

5

1 the polarization density (summation of dipole moment in a macroscopic scale)

2 becomes nearly zero for both cases. In fact, a large contact angle is commonly obtained

3 for both cases[11].

4 This implies that the attraction character of a single Rf group to a molecular

5 water should be discriminated from the general concept of hydrophilicity, and the

6 character is thus called "dipole-interactive property" throughout this paper. In the

7 present study, the physical character of a single Rf group is investigated at the air/water

8 interface. Water surface is known to have some hydrogen-bond free (dangling) OH

9 groups,[12] which should be a good field to study a single Rf group on the concept of the

10 dipole-interactive property.

11 A study using a spread monolayer on water (Langmuir (L) film) and the

12 Langmuir-Blodgett (LB) film is a key approach to investigate properties of a

13 two-dimensional (2D) molecular aggregate.[13] In fact, the SDA theory has already

14 proved to be powerful to predict the material property of a compound by the surface

15 pressure (π)–surface area (A) isotherm measurement of the L film and a spectroscopic

16 study of the LB film.[4] For example, according to the theory, a compound containing a

17 short Rf-group ($CF_3(CF_2)_6-$ or shorter) should exhibit the dipole interactive or

18 hydrophilic character, especially when the compound is spread on water: the spread

1   molecules are not aggregated, and they are lying on the water surface.[4] In fact, the

2   monolayer stays on pure water stably, and the lift-off surface area is apparently larger

3   than that of a similar compound having no Rf group.[13] This implies that the short-Rf

4   containing compounds are not dissolving into water, but it is strongly interacted with the

5   water 'surface.' In this manner, a single Rf group should have a unique attracting

6   character with the water surface, which is not found for a normal hydrocarbon.

7   To reveal the unique property of an Rf group on a water surface, in the present

8   study, the surface potential (ΔV)–surface area (A) isotherms are measured for some

9   Rf-containing myristic acid (MA) derivatives having an Rf group with a different length,

10   which are cooperatively discussed with the π–A isotherms. As a result, a notable

11   molecular aggregation property depending on both Rf length and temperature is

12   revealed. Thus far, ΔV–A isotherms have been discussed in terms of molecular

13   orientation change after Gains's textbook.[15] In the present study, however, additional

14   two factors are found necessary: the molecular density change and the dehydration

15   about the head group on the monolayer compression. The dehydration is particularly

16   useful to discuss the dipole-interactive property on the water surface, since the

17   dipole-shielding by the hydration water is broken by the monolayer compression.

18   In addition, the ΔV–A isotherms reveal that bulk properties on the phase

1   transition can also be predicted by the SDA theory. The measurements have all been

2   performed thus far at 15 °C (Phase II) below the transition temperature at 19 °C.[16] If the

3   Rf compounds obey the phase diagram,[16] the SDA theory should readily predict the

4   bulk properties at another temperature above 19 °C (i.e., Phase IV[16]). In the present

5   study, the same analysis is also performed at 25 °C in Phase IV, and the SDA theory has

6   proved to be powerful for explaining the phase transition. This is the first report to our

7   knowledge that the bulk characters of Rf-containing compounds are predicted based on

8   the primary chemical structure.

9

10 **Materials and methods:**

11 **Sample preparation:** Octadecanoic acid (stearic acid, SA, ≥98.5%), tetradecanoic

12 acid (myristic acid, MA, ≥99%) and chloroform (ACS Spectra Grade, ≥99.8%) were

13 purchased from Sigma-Aldrich (St. Louis, MO, USA), and they were used as is without

14 further purification. 11,11,12,12,13,13,14,14,14-Nonafluorotetradecanoic acid (MA–

15 Rf3), 9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluorotetradecanoic acid (MA–Rf5),

16 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluorotetradecanoic acid (MA–

17 Rf7) and 5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-henicosafluorotetra-

18 decanoic acid (MA–Rf9) were synthesized as mentioned in our previous work.[4] Each

1   amphiphilic compound was dissolved in chloroform with a concentration of 0.2–1.0 mg

2   mL^{-1} for preparation of a Langmuir monolayer on water.

3   **π–A and ΔV–A measurements:** The π–A and ΔV–A isotherms were simultaneously

4   measured by using a Biolin Scientific (Espoo, Finland) KSV-NIMA Minitrough

5   Langmuir-Blodgett system equipped with a KSV-NIMA SPOT Kelvin probe. The π was

6   measured by the Wilhelmy method using a paper plate with a width of 1 cm, and ΔV

7   was measured by using the Kelvin probe with a counter electrode made of stainless

8   steel.[17] The Kelvin probe (KP) was located at the position (1) in Chart 1. Each isotherm

9   was measured three times to check the reproducibility. The water subphase and room

10   temperature were both maintained at 15 °C or 25 °C to keep the phase II (<19 °C) or IV

11   (>19 °C), respectively. Pure water subphase was obtained by a Millipore (Molsheim,

12   France) Elix UV-3 pure-water generator and a Yamato (Tokyo, Japan) Autopure

13   WT100U water purifier (a compatible model with Milli-Q). The water exhibited an

14   electric resistivity of 18.2 MΩ cm or higher. The surface tension was 72.5 mN m^{-1} at

15   25 °C, which was measured by using a Kyowa Interface Science Co., Ltd. (Saitama,

16   Japan) DropMaster, DM-501Hy, contact angle meter. The Langmuir monolayer was

17   prepared by spreading the chloroform solution of the amphiphilic compounds on pure

18   water subphase with a size of 75×324 mm^2. Each isotherm was measured with a

1   compression rate of 1.688×10^3 mm^2 min^{-1}.

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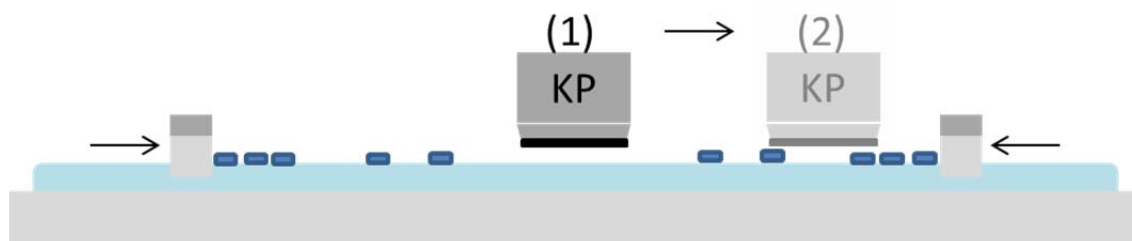
4   Chart 1   The relative position of the Kelvin probe to the trough. The dark blue
5   objects are island domains of a Langmuir film. The surface potential (ΔV) of
6   the film is measured at the position (1) except for the purple dash line in
7   Figure 3a, which is measured at the position (2).

8

9   The isotherms were measured on pure water (ca. pH 5.8) to make the potential

10   measurements free from a chemical interference due to a pH modifier. For only MA, the

11   isotherms were measured at pH 2.0; otherwise the shorter compound than SA is

12   dissolved into the subphase.[15] The isotherms of a MA monolayer were measured on a

13   subphase of pH 2.0 involving hydrochloride to prevent the dissolution of the monolayer

14   into the subphase.[12]

15

16   **Results and Discussion:** The variation of ΔV during the monolayer compression (ΔV–

17   A) is discussed with related to the corresponding π–A isotherm. A ΔV–A isotherm of a

18   Langmuir monolayer (L film) is often discussed in terms of only the molecular

19   orientation change of a chemical group having a large dipole moment.[18] In the following

1 sections, we show that a ΔV–A isotherm reflects two other factors, molecular density

2 and dehydration about a polar head group, as well as the orientation change, which has

3 an apparent correlation with the π–A isotherm. Before discussing the Rf-containing

4 compounds, L films of commonly known stearic acid (SA) and MA are thus used to

5 show the newly found key factors.

6 **ΔV–A isotherm of a Normal Carboxylic Acid:**

7   Figure 1a presents π–A and ΔV–A isotherms of an L film of SA measured at

8 25 °C. The π–A isotherm has a typical shape consisting of the well-known three regions:

9 the gaseous and liquid condensed (G/LC), LC (or "tilted condensed") and solid (S, or

10 "un-tilted condensed") phase regions.[19,20] The electric dipole moment of SA is localized

11 near the C=O group, but the moment (1.50 D)[21] is tilted to have the upward component

12 (Figure 1c). Thus, the dipole moment can readily be monitored by the Kelvin probe

13 even when the molecule has a perpendicular stance to the water surface.[15] In fact, ΔV

14 positively appears in the S phase. Note that the ΔV-A isotherm seems not synchronous to

15 the π–A curve (Figure 1a). In particular, ΔV begins to increase at ca. $A = 0.35$ nm^2

16 molecule^{-1}, which is apparently larger than the lift-off of π (ca. 0.25 nm^2 molecule^{-1}) in

17 the G/LC region.
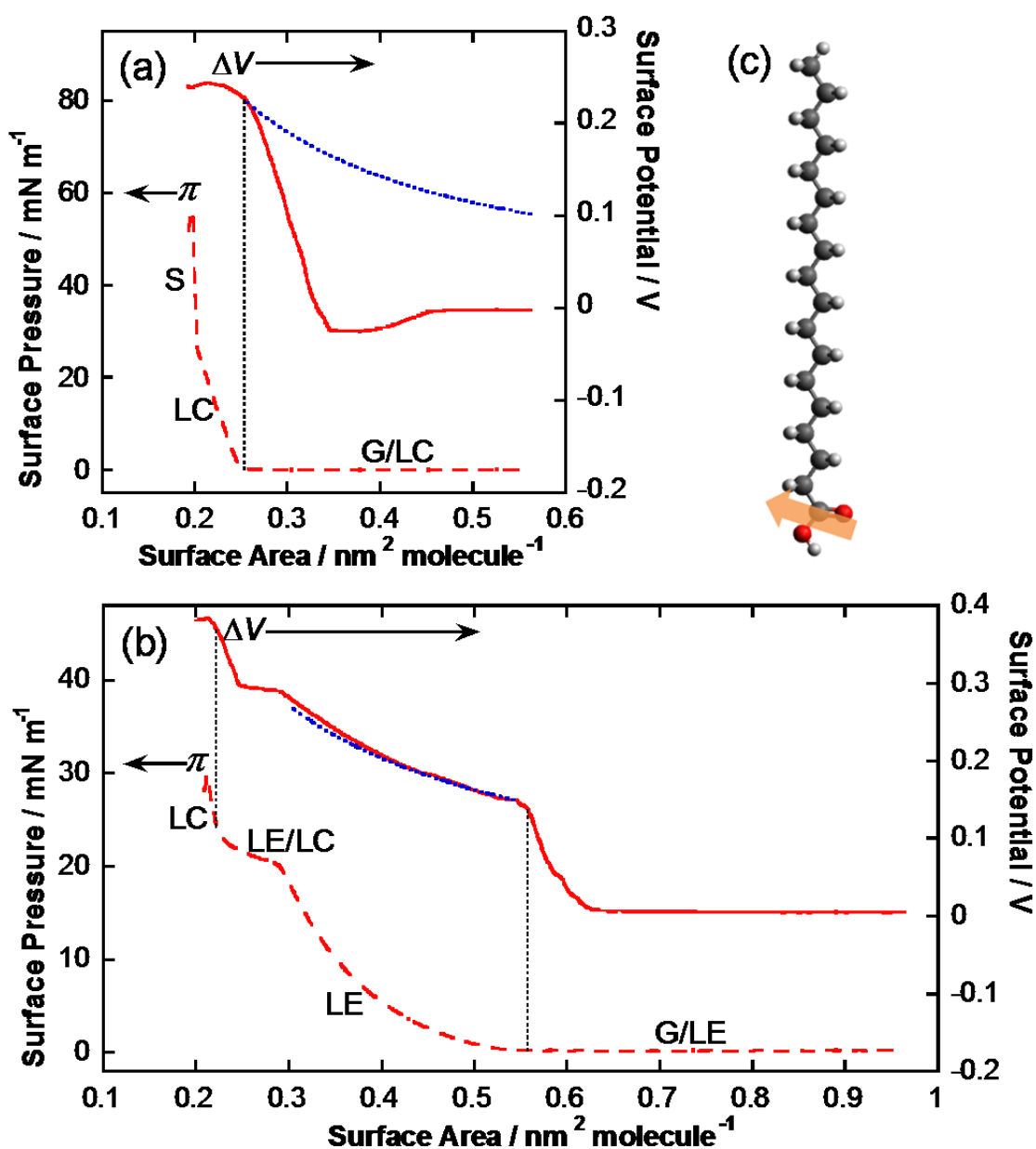
Figure 1.   The π–A (dashed red line) and ΔV–A (solid red line) isotherms of a Langmuir monolayer of (a) stearic acid (SA) and (b) myristic acid (MA) measured at 25 °C. The blue dotted line in the panel (a) and (b) is a calculated "density curve" (see the text for detail). (c) A molecular schematic of stearic acid. The orange arrow represents the molecular dipole moment calculated by a quantum chemical calculation.

1   In this region, the monolayer compression corresponds to the collection of the

2   island domains as confirmed by the Brewster angle microscopic study,[22] which accounts

3   for no increase of the surface pressure ($\pi \approx 0$). The domain is actually an aggregate of

4   loosely packed SA molecules, but the aggregation property is apparently larger than MA

5   because of the difference of the chain length. [23]

6   Once ΔV begins to increase, the slope should be influenced by changes of the

7   molecular density and the orientation. Before attaining the LC region (i.e., in the G/LC

8   region), fortunately, the orientation change can be ignored. To consider the density

9   change, a theoretical "density curve" is calculated by Eq. 1.

10          $\Delta V_{\text{density}} = \Delta V_0 A_0 / A$.   (1)

11   A is the surface area and A_0 is the end area of the G/LC region exhibiting V_0. The point,

12   (A_0, ΔV_0) is read from the isotherm to be (0.254, 0.225), and the calculated density

13   curve is presented by the blue dotted curve in Figure 1a. As a result, the density curve

14   cannot quantitatively explain the ΔV–A curve at all, which straightforwardly implies

15   that the third factor should be considered. To explain the sudden appearance of ΔV at

16   about 0.35 nm^2 molecule^{-1}, not only the hydrocarbon chain of SA, but also the head

17   group should also be taken into account.

18   When the carboxylic group is fully hydrated, the dipole moment is effectively

1   shielded by the dipoles of surrounding water molecules. This explains that ΔV exhibits

2   nearly zero at a surface area larger than ca. 0.35 nm^2 molecule^{-1}. On a further

3   compression, ΔV runs up to 0.23 V *before π increases*. This sudden appearance of ΔV is

4   understandable by considering the removal of the hydration water by the monolayer

5   compression. In other words, the dehydration about the carboxylic group is induced by

6   the monolayer compression, after which the molecules are aggregated resulting in the

7   increase of π. Therefore, the lift-off of π is always found at the surface area where the

8   increase of ΔV finishes. In the S region, no potential change is monitored, which is

9   reasonable when considering that almost no change in the density, orientation and

10   dehydration is expected in the very little change of the surface area.

11   In this manner, by considering the dehydration process, the variations of π and

12   ΔV on the compression are comprehensively explained. The relative position of the

13   increase of π and ΔV is thus found very useful to discuss the dehydration; whereas the

14   absolute value of ΔV is not so important.

15   On this fundamental mechanism, the isotherms of an L film of MA are next

16   discussed. When a monolayer of MA is compressed on pure water (pH 5.8), the π–A

17   isotherm shifts to a smaller area due to the dissolution of the molecules into the

18   subphase because the carboxylic group of MA are partially ionized[24]. To prevent the

1 matter, the isotherms of only MA were measured at pH 2.0. A π–A isotherm of the MA

2 at pH 2.0 is a little bit shifted to a larger area than that on pure water. Fortunately,

3 however, ΔV–A curve also exhibits the same shift. Therefore, the discussion of the

4 relative position between the π–A and ΔV–A isotherms is impervious to pH.

5 The isotherms are presented in Figure 1b. The π–A isotherm of the MA

6 monolayer involves the LE and LE/LC phases in addition to the SA isotherm. This is

7 because the molecular aggregation property of MA, having shorter alkyl chain, is

8 weaker than that of SA.[19]

9 In the case of MA, ΔV keeps nearly zero until ca. 0.63 nm^2 $molecule^{-1}$ and

10 suddenly increases up to 0.15 V before π increases (Figure 1c). This can be explained

11 by the dehydration model as found for SA. In the LE region, ΔV increases almost along

12 the density curve (blue dotted curve in Figure 1c, calculated by Eq. 1 with (A_0, ΔV_0) =

13 (0.544, 0.150)), which suggests that the potential change can simply be attributed to the

14 increase of molecular density only.

15 The LE/LC region is known to correspond to the molecular orientation change

16 during the film compression.[19] ΔV in the LE/LC region keeps almost a constant value.

17 This means that a decrease of ΔV due to the orientation change cancels the density

18 contribution. The decrease is attributed to the orientation change of MA having the

1   carboxylic group.

2   At the near end of the LE/LC region, ΔV rapidly increases again. In the LC

3   regions, the trends of the ΔV–A and π–A isotherms are almost the same as those of SA.

4   Therefore, the rapid increase is again attributed to the dehydration of the carboxylic

5   group. As a conclusion, the dehydration of MA is suggested to occur twice stepwise

6   during the compression.

7   **Analysis of MA–Rfn monolayers via Surface Potential Isotherms at 15 °C (Phase**

8   **II):** The π–A isotherms of MA–Rf7 and MA–Rf9 (Figure 2a) in the present study are

9   identical to those in the previous papers, including partially fluorinated alkanes,

10   alcohols,[4, 25–29] in which no gas and LE region appear in the curves followed by a steep

11   increase of π. This apparently implies that the MA–Rf7 and MA–Rf9 commonly have a

12   spontaneous aggregation character.[4] To discuss the ΔV–A isotherms of MA–Rfn (Figure

13   2a and 3), the molecular dipole moment of the compounds should be noted. Whereas the

14   molecular dipole moment of SA and MA is nearly localized at the C=O group, MA–Rfn

15   has a large dipole moment *along the Rf–R bond* represented as the large arrow in Figure

16   2b and the contribution of C=O is minor as a whole.[1] Since the molecules of MA–Rf7

17   and MA–Rf9 in a monolayer at 15 °C (Phase II) are oriented perpendicular to the water

18   surface,[4,28] the dipole moment with a 'downward' direction should have a large

1   surface-normal component to yield a large 'negative' ΔV.

2
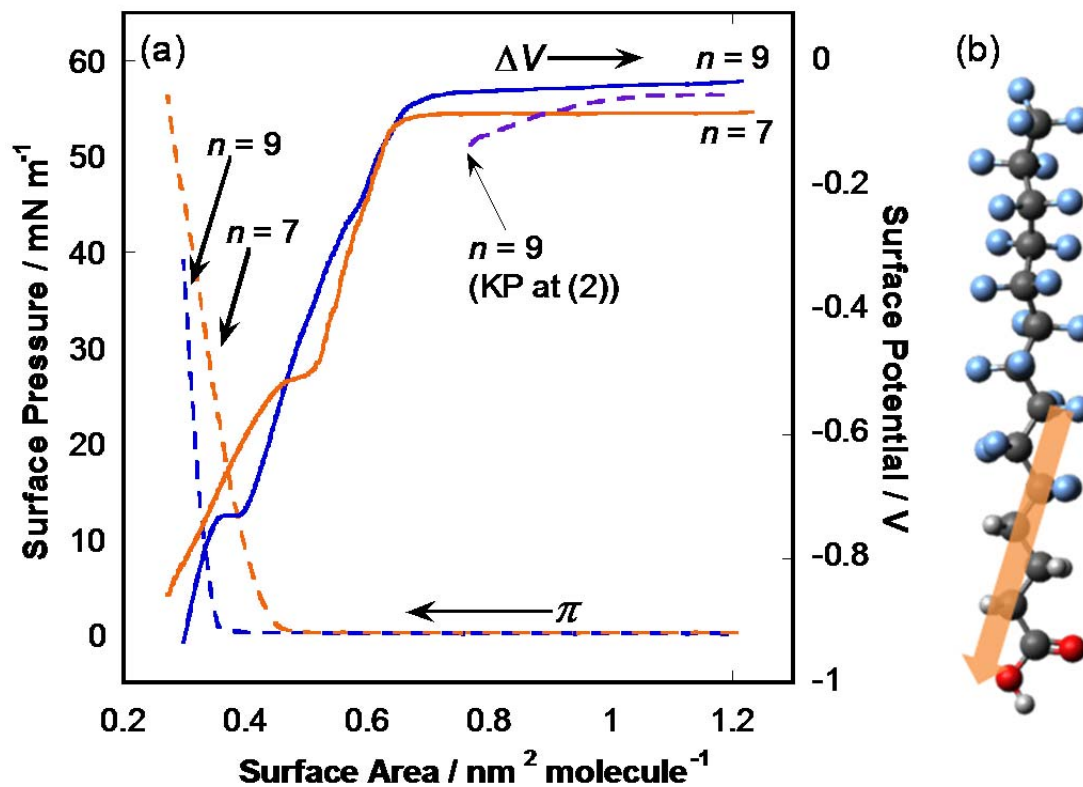
Figure 2.   (a) The π–A (dashed line) and ΔV–A (solid line) isotherms of Langmuir
monolayers of MA–Rf7 (orange) and MA–Rf9 (blue) at 15 °C (phase II).
The ΔV–A isotherm of MA–Rf9 displayed in purple is measured with the
KP at the position of (2) in Chart 1. (b) A molecular schematic of MA–Rf9.
The orange arrow represents the molecular dipole moment. The blue atoms
are fluorines.

10

11   In fact, as the monolayer is compressed, ΔV changes to a very large negative

12   value (Figure 2a), which is specific to a diblock (Rf–R) compound.[27, 30] ΔV is constant at

13   nearly zero at a surface area larger than ca. 0.70 nm^2 molecule^{-1}. In the case of SA and

1   MA, the constant potential at nearly zero was attributed to the hydration of the

2   carboxylic group. As for MA–Rf9, a more primitive phenomenon readily explains it,

3   that is, the inhomogeneous distribution of the island domains. According to the SDA

4   theory, the MA–Rf9 molecules aggregate spontaneously, and a *stiff* island domain are

5   generated.[4] When a monolayer of MA–Rf9 is compressed by the moving barrier, the

6   stiff domains should be accumulated near the barrier; whereas the domains near the

7   Kelvin probe at the position (1) in Chart 1 would be left un-compressed at the initial

8   stage.

9   To confirm this speculation, the same measurements were carried out by

10   displacing the Kelvin probe to the position (2) in Chart 1. As expected, ΔV decreases

11   earlier (the purple dashed line in Figure 2a), which proves that the stiff domains near the

12   barriers are collected to arrive at the position (2) earlier. The inhomogeneity model has

13   thus been confirmed readily. MA–Rf7 (orange curve) exhibits a similar process, but the

14   initial constant potential is a little shifted to a negative value, which will be discussed in

15   detail in the next section.

16   During the decrease of ΔV, an "apparent plateau" appears just before the lift-off

17   of π for both MA–Rf7 ($A \approx 0.5$) and MA–Rf9 ($A \approx 0.4$). The relative position of the

18   change of π and ΔV straightforwardly implies that the cancel of the decreasing potential

1   should be attributed to the dehydration of the carboxylic group, since the dehydration

2   generates the positive increase of the potential.

3   In the case of SA and MA, the potential increase due to the dehydration cannot

4   be discriminated from the increasing density, since both changes exhibits positive

5   changes. On the other hand, in the case of an Rf–R diblock compound, the two changes

6   exhibit opposite potential changes, which make the dehydration process clearly visible.

7   On the other hand, the molecules of MA–Rf3 and MA–Rf5 having a shorter Rf

8   chain have a poor aggregation property, which is quite different from MA–Rf7 and

9   MA–Rf9.[4] As found in the isotherms in Figure 3, π exhibits an apparent positive value

10   even at an initial compression, which indicates that molecules are lying on the water

11   surface.[4] As discussed for normal MA shown in Figure 1b, the spread molecules do not

12   make island domains, but they are spread over the water surface homogeneously.

13   The ΔV–A isotherms of the MA–Rf3 and MA–Rf5 monolayers are overlaid on

14   the π–A isotherms in Figure 3. The ΔV curves of MA–Rf3 and MA–Rf5 decrease

15   significantly as compressed, which agrees with the density curve (blue dotted curve; (A_0,

16   ΔV_0) = (1.211, −0.208)). This agreement confirms that the molecules are, in fact,

17   homogeneously spread over the water surface for both compounds.

18
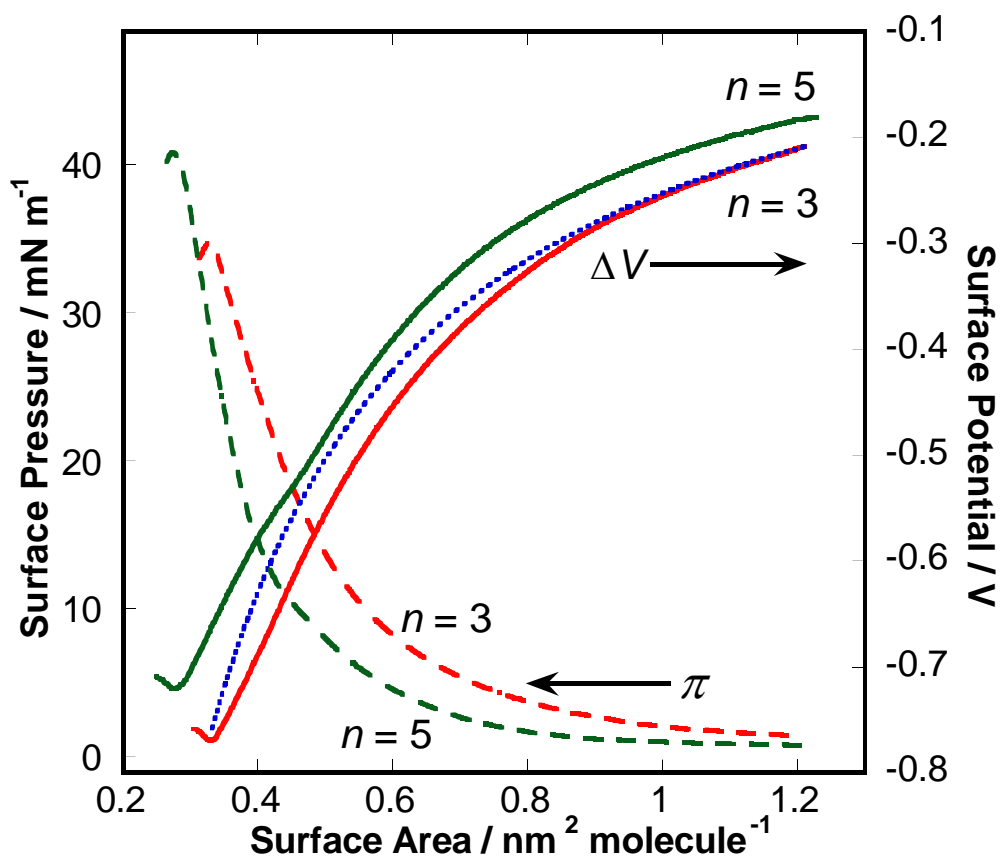
Figure 3.   The π–A (dashed line) and ΔV–A (solid line) isotherms of Langmuir monolayers of MA-Rf3 (red) and MA-Rf5 (green) at 15 °C (phase II). The blue dotted line is a calculated density curve.

Here, we have to pay attention to a fact that ΔV exhibits a fairly large negative value "even before" the monolayer compression, which is apparently larger than that in Figure 2a. If the molecules are lying on the water surface, there is no need to exhibit a negative value considering various molecular rotational orientations of the lying molecule (Figure 4a–c). Water surface is known to have hydrogen-bond free (dangling) OH groups,[12] which can receive a single Rf group via the dipole-dipole interaction. In

1   this manner, a single Rf group lying on the water surface would be highly stabilized via

2   the dipole-interactive property. In addition, a single Rf group is not dissolved into a

3   bulky water, since the Rf group has only the dipole-interactive character, and no

4   hydrogen bonding one, which is unfavorable to break the hydrogen bonding network of

5   the bulky water. As a result, a single Rf group is stably interacted with water 'surface'

6   only.
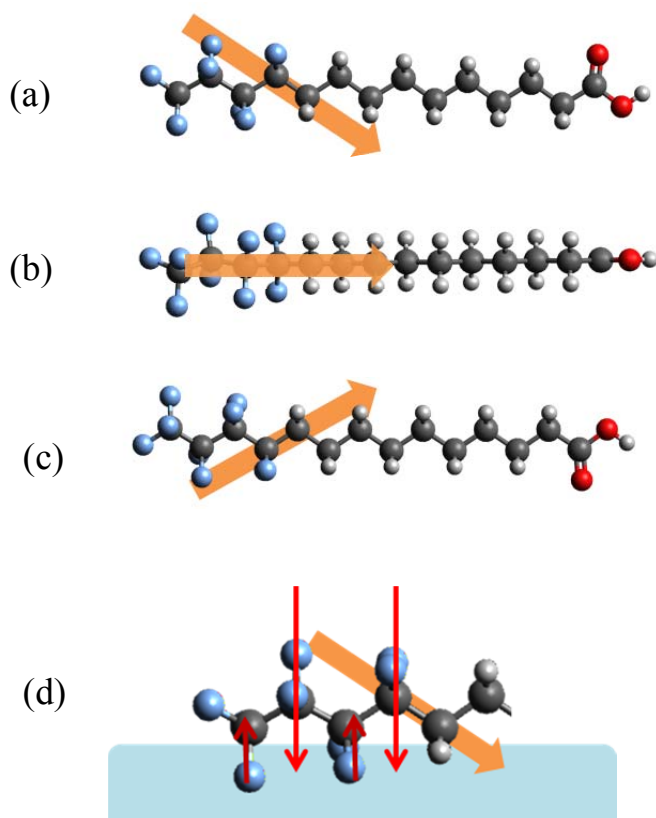
26   Figure 4.   (a)~(c) Three different rotational orientations of a lying MA–Rf3 molecule.
27   (d) A schematic view of a dipole-interactive Rf group in the water surface
28   based on the schematic (a).

1   The lying molecular scheme (Figure 4d) works well for explaining the potential

2   isotherms. In this model, one side of the lying Rf group is attached to the water surface,

3   and the rest half remains un-hydrated. This partial hydration model implies that each

4   dipole moment on the hydrated side is shielded, and the negative potential should

5   appear as a total irrespective of the rotational molecular orientation on the water surface.

6

7   **Prediction of Phase Transition by the SDA theory:** The analytical discussion made

8   above is for a fixed temperature of 15 °C, i.e., Phase II. In the present section, the bulk

9   material properties of monolayers in Phase IV[12] are predicted on the SDA theory.

10   The SDA theory provides a criterion[4] whether the spontaneous two-dimensional

11   molecular aggregation of Rf groups takes place or not, which depends on the twisting

12   angle of the Rf group reflecting the Rf length (Table 1). When the theoretical twisting

13   angle is 90° or larger, they are expected to aggregate spontaneously.[4] When referring to

14   Table 1, below 19 °C, MA–Rfn is spontaneously aggregated for $n = 7$ and 9 (marked by

15   bold in Table 1); whereas only MA–Rf9 should be aggregated above 19 °C. This implies

16   that only MA–Rf7 would exhibit an apparent change in both π–A and ΔV–A isotherms

17   when the measurement temperature is changed from 15 °C to 25 °C.

18

Table 1   Theoretical twisting angle of both ends of the CF_2 groups in an Rf group as a function of the number of CF_2 groups (Rf length) in Phases II and IV.

No. of CF_2	Twisting angle / °	
	Phase II (<19 °C)	Phase IV (>19 °C)
3	Un-twisted	Un-twisted
5	60	51
7	**90**	77
9	**120**	**103**

Figure 5 presents the π–A and ΔV–A isotherms of MA–Rfn monolayers on water at 25 °C. ΔV–A isotherms (solid lines) are particularly sensitive to the Rf length and temperature. As theoretically predicted on the SDA theory, only the ΔV–A isotherm of MA–Rf7 (orange curve) is significantly changed from that in Figure 2a; whereas the rest curves are kept almost unchanged. The potential decrease below the surface area of 0.9 nm^2 molecule^{-1} in Figure 5 is more apparent than that of Figure 2a. The early decrease implies that the molecules at 25 °C are more homogeneously spread on water than 15 °C. The decrease is suppressed at 0.7 nm^2 molecule^{-1} or smaller, which indicates that dehydration happens in this region because π begins to increase after the suppress finishes in an exchanging fashion. In this manner, only the MA–Rf7 monolayer exhibits different aggregate properties in both π–A and ΔV–A isotherms as predicted by the SDA theory.
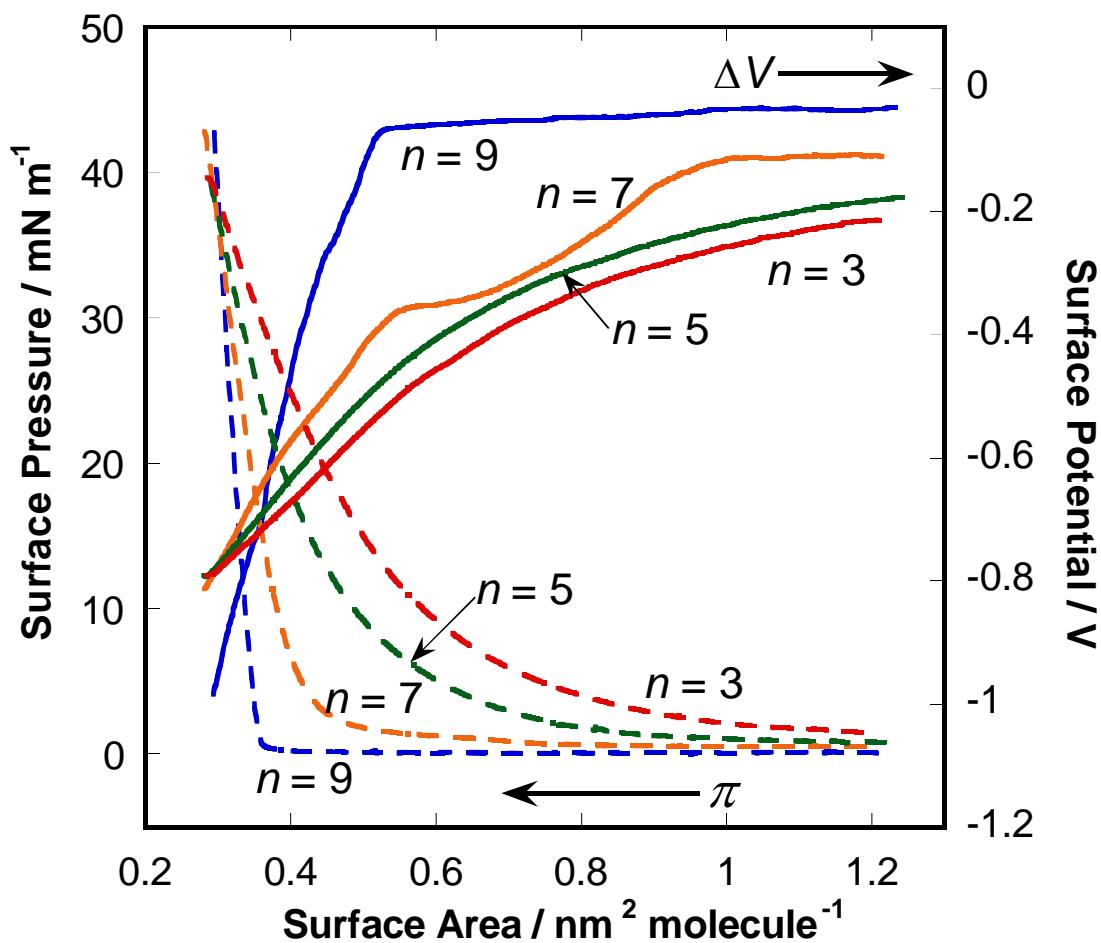
Figure 5. The π–A (dashed line) and ΔV–A (solid line) isotherms of Langmuir monolayers of MA–Rf3 (red), MA–Rf5 (green), MA–Rf7 (orange) and MA–Rf9 (blue) at 25 °C (phase IV).

Reproducibility of ΔV–A isotherm measurements is another useful index to check the homogeneity of the monolayer. When a monolayer of homogeneously spread molecules is compressed, the ΔV–A measurements shows a good reproducibility; whereas a monolayer of island domains shows a poor reproducibility.[31] Figure 6 shows

1   three traces for each π–A and ΔV–A isotherm of MA–Rf3 and MA–Rf7. As shown in

2   Figure 6a, MA–Rf3 at 15 °C shows an extremely high reproducibility, and the same

3   trend is also found at 25 °C (data not shown), which is consistent with a fact that a short

4   Rf compound does not shown an apparent aggregation.[4] On the other hand, MA–Rf7

5   shows a good reproducibility at 25 °C; whereas the reproducibility is lost at 15 °C in the

6   area range of 0.4~0.6 nm^2 $molecule^{-1}$, which straightforwardly implies that the

7   molecules are aggregated to generate island domains at 15 °C, while they are spread

8   homogeneously at 25 °C. The results are perfectly consistent with the theoretical

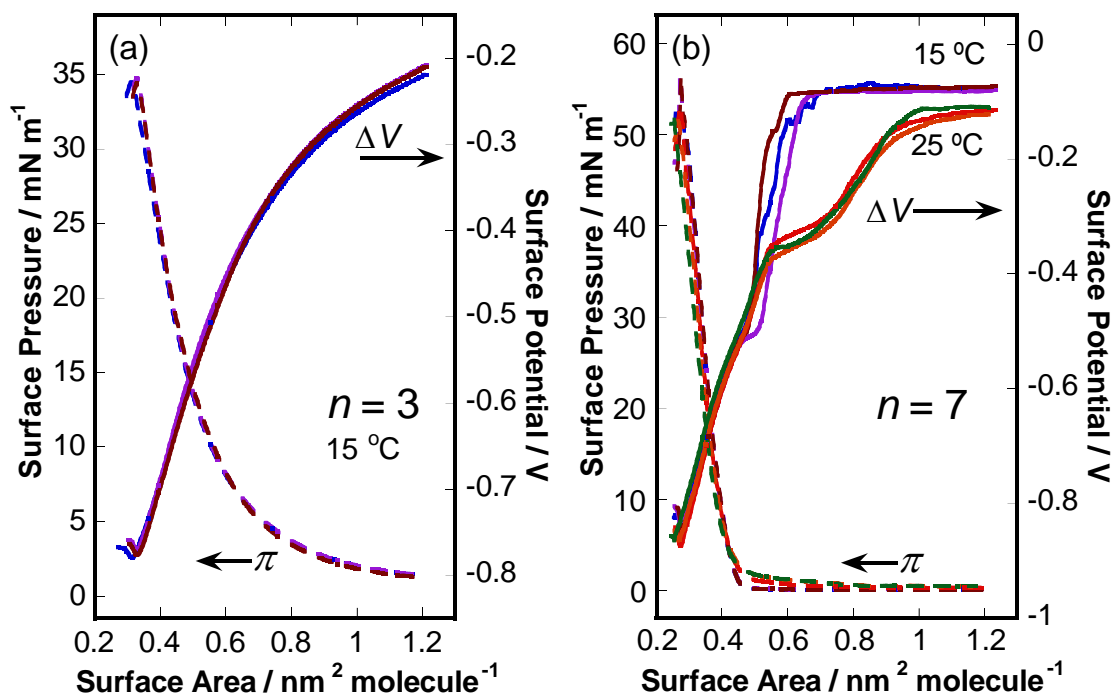9   prediction on the SDA theory (Table 1).

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12

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Figure 6. The π–A (dashed lines) and ΔV-A (solid lines) isotherms of the monolayers of (a) MA–Rf3 and (b) MA–Rf7. Three repeatedly measured results are overlaid for checking the reproducibility. Only the results at 15 °C are presented for better visibility in (a), since no difference was found for both 15 °C and 25 °C.

The reader may be interested in the results of MA-Rf9 at 25 °C, since the suppression of the potential decrease during the monolayer compression is not obvious (Figure 5) when comparing to the results at 15 °C. On closer inspection, however, the suppression gradually appears along the potential decrease. Since the reproducibility of this isotherm was high, the hydrated water should smoothly and gradually be removed at 25 °C on the compression probably due to a high molecular mobility at a higher temperature.

1   **Conclusion:** Through the comparative study of the surface potential (ΔV)–surface area

2   (*A*) isotherm of a monolayer of a carboxylic acid involving a normal alkyl and a

3   perfluoro alkyl (Rf) group with a different length, the dehydration process is found to be

4   a key to understand the isotherms, which is a progress to the conventional discussion on

5   only the molecular density and orientation changes [15]. The 'dehydration' effect would

6   be useful for understanding the properties of a Langmuir monolayer of a wide range of

7   compounds, not only for Rf compounds. In particular for an Rf containing diblock

8   compound, the dehydration process is apparently visible in the isotherm, which greatly

9   helps us to discuss the surface pressure (π)–*A* isotherm, too. As a result, the ΔV

10   measurements have proved to be powerful to discriminate whether the compound has a

11   spontaneous molecular aggregation property or not. In addition, a lying Rf-R diblock

12   molecule has been revealed to have a "dipole-interactive property" on the Rf group. A

13   "single" Rf group is interacted with the water surface, but it is not dissolved in the bulky

14   water. In other words, the water surface has proved to have a unique chemical field to be

15   interacted with an Rf group. Regardless, a further molecular orientation study is

16   expected to fully confirm the discussion in this study. To do that, we are planning an

17   additional study using the polarization modulation-infrared reflection- absorption

18   spectrometry (PM-IRRAS) technique, which can measure IR spectra of a Langmuir

1   monolayer on the water surface in situ [23,24].

2

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