excitation. A small fraction of the dissociated molecules re-form the C–O bond on the time scale of 200 fs. The nascent photoproduct is found to vibrationally relax in a few picoseconds and to isomerize on the time scale of ≥100 ps. Further experiments need to be conducted to achieve a more complete understanding of the reaction mechanism, especially the dependence of the dynamics on solvent molecular structure and temperature.

Submicron-Range Attraction between Hydrophobic Surfaces of Monolayer-Modified Mica in Water

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Abstract: Very-long-range attraction extending to a separation close to 300 nm was observed between uncharged mica surfaces that are modified by hydrophobic layers of a polymerized ammonium amphiphile. The force distance profile in pure water is expressed by an exponential function composed of intensity parameter and decay length. Their values determined from the deflection method are 1.7 ± 0.5 mN/m and 62 ± 4 nm, respectively. The same parameters obtained from the jump-in method, 0.59 mN/m and 72 nm, agree within the experimental error. This hydrophobic layer is prepared by the Langmuir–Blodgett (LB) deposition in the *down-stroke* mode (transfer ratio: 0.8) and is stable enough to allow us to study salt effects on the attraction, practically for the first time. The intensity parameter decreases to 0.25 mN/m (from deflection) and 0.18 mN/m (from jump-in) with increasing NaBr concentrations to 10 mM, whereas the decay length remained unchanged at around 60 nm. Interestingly, hydrophobic surfaces prepared by monolayer transfer in the *up-stroke* mode (transfer ratio: 1.0) display the attraction which extends in pure water to only ca. 30 nm, although their pull-off forces are the same as those for the down-stroke preparations (200–300 mN/m, which corresponds to the interfacial energy of 21–32 mJ/m²). Therefore, the long-range attraction is very sensitive to small structural differences of the hydrophobic surface. The unprecedented long-range attraction cannot be readily accommodated previous explanations which are based on conventional hydration force and cavitation. The concept of "vicinal water" by Drost-Hansen can be an alternative basis of the observed attraction. We propose that the structural correlation of interfacial water extend to the submicron range, if the interface is sufficiently large, molecularly smooth, and strongly hydrophobic. The enhanced structural correlation leads to long-range attraction.

Introduction

"The hydrophobic effect" is commonly used to express specific properties of nonpolar molecules in water. The "hydrophobic" attraction between nonpolar (hydrophobic) molecules and surfaces in water cannot be fully accounted for by continuum theories of van der Waals forces.[1-3] Interactions between macroscopic hydrophobic surfaces are treated as an extension of these molecular effects. However, recent reports suggest that interactions between nonpolar surfaces in water are more complicated than have been thought. In particular, Drost-Hansen postulated formation of ordered water structures at solid interfaces along with possible existence of long-range order.[4-6] The water molecules on hydrophobic surfaces were considered to become structured in clathrate-like ordering which extends to tens and hundreds (or more) of molecular diameters, while those on polar surfaces were considered to be oriented by dipole–dipole interaction. This effect was thought to affect properties of water near surfaces and physicochemical properties of dispersed systems.

The forces between surfaces can be directly measured by a surface forces apparatus. The force–distance profile is related to the mode of surface interactions. The attractive force, which is much stronger than the conventional van der Waals force and counteracts the electrostatic repulsion, was first reported between hydrophobic adsorbed layers of trimethylcetylammonium bromide

on mica.[7] Although the net interaction was repulsive, the estimated attractive component at distances of several nanometers was two orders of magnitude larger than expected from the van der Waals force, and decreased exponentially with a decay length of 1 nm. More recently, *net* attraction extending to even longer distances was reported.[8,9] In these measurements, surfaces were considered to be more hydrophobic than previous preparations, and the distance where observable attraction appears varied depending on sample preparations. More recently, uncharged hydrocarbon and fluorocarbon surfaces (no observable repulsion) prepared by the Langmuir–Blodgett (LB) technique produced attraction extending to a separation of 80 nm in pure water.[10,11] An exponential function with two decay lengths of 2–3 and 13–16 nm was found to fit the experimental data. The origin of the long-range attraction is not yet fully understood, although several

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mechanisms have been proposed.[12,13] All of these previous force studies suffer from the presence of surface charges probably due to formation of the second layer in the case of the adsorbed monolayers,[7] or due to instability of LB layers especially in the presence of salt.[10,11] Dependence of forces on physical parameters such as salt concentration has not been clearly shown, in spite of the fact that these knowledges are essential to elucidate the origin of forces. Even in the case of hydrophobic surfaces which are previously claimed to be most stable, addition of salts caused ion exchange with cationic amphiphiles and/or ion adsorption to the surface, giving rise to electrostatic repulsion due to surface charges.[11] This electrostatic repulsion was screened by high concentrations of a divalent salt (0.01 or 0.1 M $MgSO_4$), and the net attraction was measured.[13] However, influence of surface charges on the attraction is not known, and salt effects on hydrophobic attraction obtained with monovalent salts and a divalent one are somewhat contradictory.

In the present study, we employed stable monolayers of polymerized ammonium surfactant **1**, and performed direct measurements of forces between LB layers deposited on molecularly smooth mica sheets.[14] Thanks to the improved stability of the monolayer, we could analyze force curves under varied conditions. Several mechanisms including long-range hydration are discussed as a possible origin of the long-range attraction.

Experimental Section

Polymerized ammonium amphiphile **1** ($n = 10000$) was obtained by photoirradiation of aqueous monomer dispersions with a 250-W Hg lamp at 35 °C for 60 min.[15] The degree of polymerization, n, was determined by gel permeation chromatography. Fluorocarbon amphiphile **2** was prepared by following the procedure described before.[16] Water was deionized and doubly distilled by Nanopure II and Fi-streem 46 D glass still system (Barnstead).

C₁₆H₃₃OC₂H₄O C CHNHC C₁₀H₂₀ N⁺C₂H₄O C ·CH

1

C₁₀F₂₁CH=CHC₉H₁₈O C CHNH C C₁₀H₂₀·N⁺CH₃

2

C₈F₁₇C₂H₄O C CHNH C CH₂·N⁺·CH₃

3
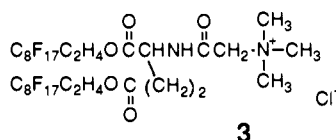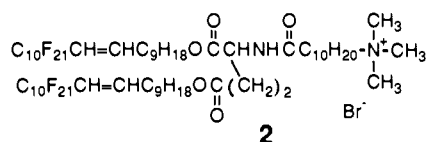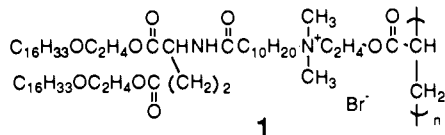
A computer-controlled film balance system (San-esu Keisoku, FSD 50) was used for measuring surface pressure as a function of molecular area (the trough size was 150 × 600 mm) and for LB deposition. Spreading solutions of amphiphiles (1 mg/mL) were prepared in a mixture of benzene/dichloromethane/ethanol (8 : 1 : 1, v/v). The LB deposition was performed at surface pressures of 35.0 ± 0.2 mN/m for **1** and 45.0 ± 0.2 mN/m for **2**, and a deposition rate of 10 mm/min in the vertical mode onto mica which are glued to silica disk lenses prior to deposition.

Force measurements were carried out by using a Surface Forces Apparatus Mark 4 (ANUTECH). Modified mica sheets on cylindrical lenses (radius, $R \approx 20$ mm) are mounted as crossed cylinders in the apparatus. When the surfaces are coated with an LB film that is

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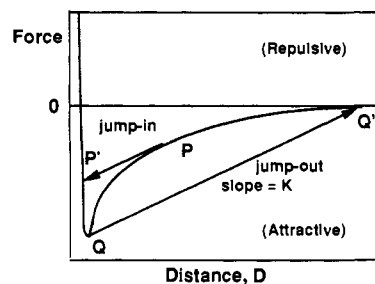

Figure 1. Schematic drawing of force measurements. Forces between two surfaces can be measured from deflection of the spring only in the region where $dF/dD < K$. When the gradient force is positive and exceeds the stiffness, $dF/dD \geq K$, at a separation of P, instability occurs, leading to jumps. Therefore, it is possible to obtain force profiles from distances where jump-in occurs by varying the spring stiffness (K). In the surface separation process, the spring is elongated up to the tension which equals adhesive forces. The surface will then jump apart a long way from Q to Q'. Pull-off forces are obtained from the distance QQ', and indicate intensities of adhesion between two surfaces.
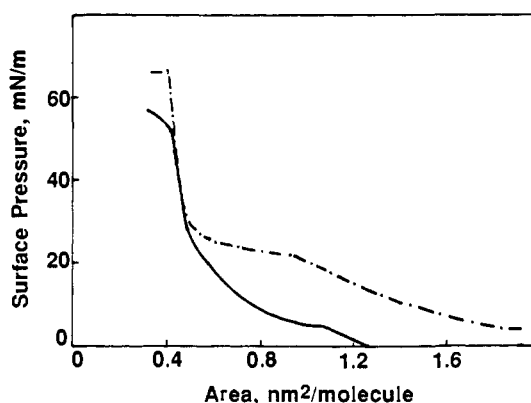

Figure 2. Surface pressure–molecular area isotherms of amphiphile **1** (—) and its precursor monomer (-·-) on pure water at 20.0 ± 0.1 °C.

transferred in the down-stroke mode, the mica sheets are kept under water during the whole mounting process. The surface separation D is measured by use of multiple-beam interferometry. The force (F) is determined from deflection of a double cantilever spring (spring constant K: ~100–400 N/m) on which one surface is mounted, and from the jump-in and jump-out distances (Figure 1). The measured force is normalized by mean radius R of the surface curvature. This quantity is proportional to the free energy of interaction of flat surfaces G_f according to the formula, $F/R = 2\pi G_f$.

Results

Long-Range Attraction between Polymerized Amphiphile 1.

Forces between bare mica surfaces were measured in pure water. The interaction is repulsive in the whole separation range down to 3 nm at which the surface jumps to contact. This behavior agrees well with previous observations.[17] Mica surfaces in pure water are negatively charged owing to dissociation of potassium ion from the cleavage plane, and the repulsion has been ascribed to a long-range repulsive double-layer force. The pull-off force was determined to be 55 ± 15 mN/m from the jump-out distance. This corresponds to an interfacial energy (γ) of 5.8 ± 1.6 mJ/m² which is calculated from the formula, $F/R = 3\pi\gamma$.[17]

Polymerized amphiphile **1** forms a stable monolayer on pure water as shown in Figure 2 together with the surface pressure – molecular area isotherm of the precursor monomer. These monolayers provide similar limiting areas in the condensed phase, indicating that an ordinary molecular orientation is maintained in the condensed phase of polymerized monolayer **1**. The monolayer of **1** was transferred successfully in the *down-stroke* mode

(17) There is controversy as to whether the interfacial energy $\gamma = F/3\pi R$ or $F/4\pi R$. The latter formula gives γ to be ca. 30% smaller than that obtained by the former. The values γ described in the text were calculated as $F/3\pi R$: Herder, C E. *J. Colloid Interface Sci.* **1991**, *143*, 1–8.

Attraction between Hydrophobic Surfaces of Mica

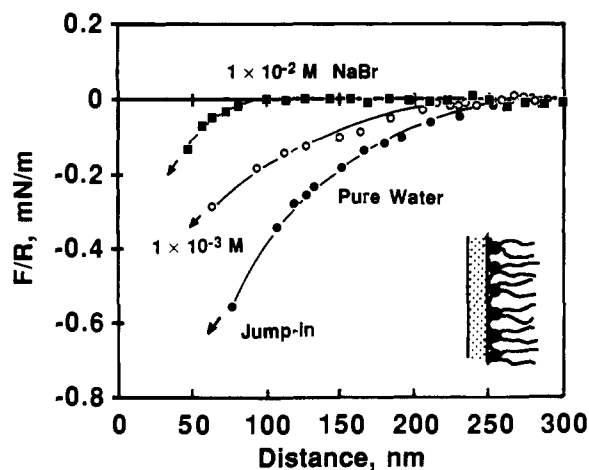*J. Am. Chem. Soc., Vol. 114, No. 27, 1992* 10929

Figure 3. Attractive forces between monolayers of **1** on mica transferred at 35 mN/m in the down-stroke mode in water at various NaBr concentrations, and at spring stiffness (K) of ~100 N/m.

onto bare mica surfaces (transfer ratio: 0.8), although the bare mica surface was highly hydrophilic as indicated by its low contact angle of water of 3.2 ± 0.1° (Kyowa-Interface Sci., CA-DT-A goniometer). Forces between these modified surfaces were quite different from those between unmodified ones. Very-long-range attraction extending to a separation of about 300 nm was found between these surfaces in pure water as shown in Figure 3, and the surfaces jumped-in to contact from a separation of 76 nm (spring constant, K ~ 100 N/m). The pull-off force was 280 ± 80 mN/m (interfacial energy γ: 30 ± 8 mJ/m^2), which is close to those reported for hydrophobic surfaces.[18] Air bubbles can attach to this surface with contact angles of about 90°.[19] Therefore, we conclude that the surface modified with **1** in the down-stroke mode is essentially hydrophobic as the polymerized cationic head group of **1** prefers to attach to negatively charged mica surfaces through multiple ionic interactions. We noticed during this transfer process that water rose on mica and formed the meniscus of a contact angle much lower than 90°, then moved to form the meniscus of ca. 90°. Apparently, the monolayer is transferred to form the hydrophobic surface by intermittent slippage.

This hydrophobic surface is quite stable, and allows us to study the salt effect on the attractive force (Figure 3). The distance where detectable force appears decreased from ca. 260 nm in pure water to ca. 90 nm in 10 mM aqueous NaBr. A similar decrease from 76 nm to 45 nm was found for the jump-in distance. On the other hand, the pull-off force changed only slightly from 280 ± 80 mN/m (γ: 30 ± 8 mJ/m^2) to 190 ± 20 mN/m (γ: 20 ± 2 mJ/m^2). Double-layer repulsion was not detected at any salt concentration, indicating that the surfaces were maintained essentially uncharged.[20]

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(19) The advancing contact angles of a water droplet on mica surfaces modified with monolayer **1** are 84 ± 6° for a down-stroke mode preparation, and 94 ± 1° for a up-stroke one. These values indicate that the surfaces are similarly hydrophobic, although their small difference seems to reflect transfer ratios of two preparations (0.8 for the down-stroke; 1.0 for the up-stroke preparation). Whether the contact angle is a good index to judge the hydrophobicity of these surfaces in water is questionable, because a down-stroke preparation has been withdrawn from water. The condition for undisturbed monolayers (no passing through air–water interface) was not satisfied any longer. Therefore, the contact angle of air bubbles to the surface prepared by the down-stroke deposition mode while keeping it under water is a more reliable measure of surface hydrophobicity.

(20) In 10 mM NaBr solution, net attraction was sometimes not clear before the surface jumped in to contact, and occasionally even weak repulsion less than 0.1 mN/m (F/R) was seen in this separation range. We think that attractive force profiles obtained from jump-in distances are not influenced significantly by this range of weak repulsion. Prolonged incubation in this solution for 1 day increased the repulsion to ~0.6 mN/m, indicating that even this polymerized monolayer was not extremely stable at high salt concentrations.
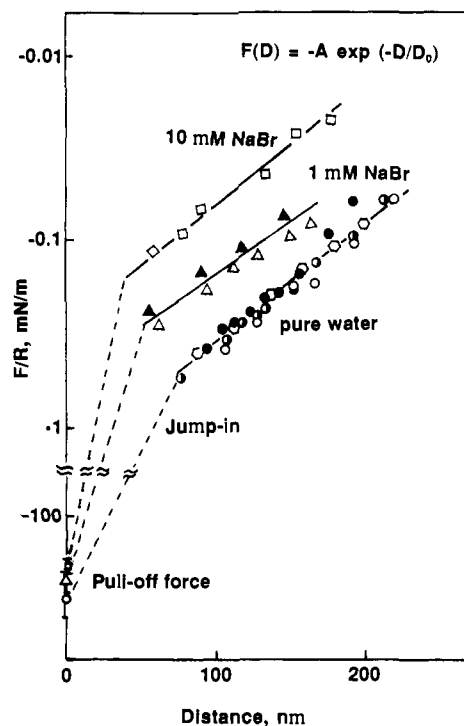

Distance, nm

Figure 4. Attractive forces between monolayers of **1** prepared in the down-stroke mode on mica (K ~ 100 N/m) are plotted in a form of exponential functions (solid lines). Hexagons and circles for data in pure water represent reproducibility among different preparations. Dotted lines show that the surface jumps in to contact.
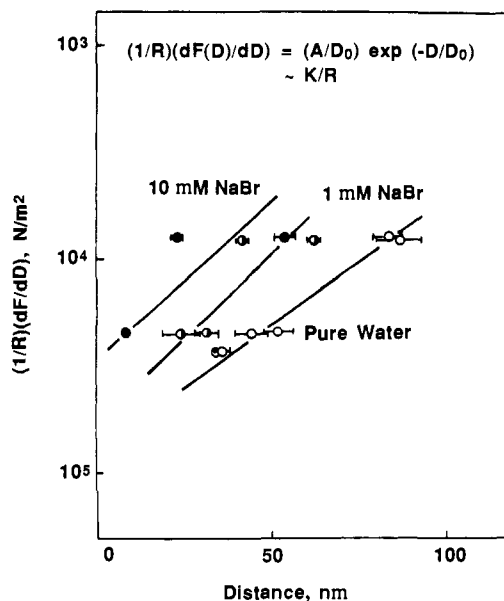

Distance, nm

Figure 5. Attractive force profiles obtained from the jump-in distance for monolayers of **1** transferred at 35 mN/m in the down-stroke mode on mica. Jump-in distances observed at various spring stiffness are plotted following eq 3′. In order to compare force profiles of Figures 3 and 4 easily, numbers of the ordinate in this figure increases downward. The figure summarizes data obtained over six independently prepared samples.

Phenomenologically, these force curves can be described in the form of:

$$F(D)/R = -A \exp(-D/D_0) \qquad (1)$$

where A denotes the intensity factor corresponding to the force at $D = 0$ and D_0 is the decay length.

Figure 4 plots the force curves according to eq 1 as well as the pull-off forces. These forces were calculated from deflection of

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Table I. Attractive Forces between Hydrophobic Surfaces

medium	$F(D)/R =$ $-A \exp(-D/D_0)$		pull-off force, mN m^{-1} (interfacial energy, mJ m^{-2})
	A/mN m^{-1}	D_0/nm	
Monolayers of 1 Transferred in the Down-Stroke Mode (Transfer Ratio: 0.8)			
From Deflection			
pure water	1.7 ± 0.5	62 ± 4	
1 mM NaBr	0.40 ± 0.14	63 ± 17	
10 mM NaBr	0.25	42 ± 22	
From Jump-In			
pure water	0.59	72	280 ± 80 (30 ± 8)
1 mM NaBr	0.34	57	220 ± 50 (23 ± 5)
10 mM NaBr	0.18	61	190 ± 20 (20 ± 2)
Monolayers of 2 Transferred in the Up-Stroke Mode (Transfer Ratio: 0.9)			
From Deflection			
pure water	0.27	20	470 ± 100 (50 ± 11)

Table II. Attractive Forces between Hydrophobic Surfaces of Monolayer 1 Transferred in the Up-Stroke Modes (Transfer Ratio: 1.0)

medium	jump-in distance nm	pull-off force, mN m^{-1} (interfacial energy, mJ m^{-2})
pure water	30 ± 2	190 ± 10 (20 ± 1)
1 mM NaBr	13 ± 2	180 ± 10 (19 ± 1)
10 mM NaBr	12 ± 2	190 ± 10 (20 ± 1)

the spring. Note that the force profiles were measured for several separate samples (Table I). A satisfactory reproducibility is demonstrated. All data points except in the weak force region (<ca. 0.05 mN/m) give straight lines, and values obtained for A and D_0 are 1.7 ± 0.5 mN/m and 62 ± 4 nm, respectively, in pure water. The addition of salt reduces the intensity parameter A to 0.40 ± 0.14 mN/m (1 mM NaBr) and 0.25 mN/m (10 mM NaBr), while the decay length D_0 is virtually independent of salt concentrations.

The attractive mica surface held by the spring jumps to contact with the fixed surface, once the slope of the force–distance curve equals or slightly exceeds the spring constant (K).

$$dF(D)/dD \geq K \qquad (2)$$

Thus, the attractive force can be obtained by plotting spring stiffness as a function of jump-in distance. Usually spring constant (K) and force (F) are normalized by the curvature of mica surfaces. Using eq 1, eq 2 is rewritten as follows:

$$(1/R)(dF(D)/dD) = (A/D_0) \exp(-D/D_0) \geq K/R \qquad (3)$$

$$\log (1/R)(dF(D)/dD) = \log (A/D_0) - (\log e/D_0)D \qquad (3')$$

In Figure 5, jump-in distances (horizontal axis) observed at various spring stiffness are plotted against normalized spring constants $(K/R$, vertical axis). Logarithmic slopes of the attraction, $(1/R)(dF(D)/dD)$, are proportional to the distance D in accordance to eq 3 and 3'. Slopes of these straight lines provide the decay length D_0, and the intensity parameter A is calculated from ordinate intercepts and D_0. The intensity parameter and the decay length thus determined are 0.59 mN/m and 72 nm for pure water, 0.34 mN/m and 57 nm for 1 mM NaBr, and 0.18 mN/m and 61 nm for 10 mM NaBr, respectively (Table I). Parameters obtained by the deflection method and the jump-in method are identical within experimental errors, and A decreases at higher salt concentrations while D_0 remains unchanged. We may emphasize that jump-in distances summarized in Figure 5 have been measured for six independent preparations. It shows satisfactory reproducibility of this very-long-range attraction.

The attractive interaction was similarly observed when the surfaces were modified in the *up-stroke* mode (ordinary hydrophobic modification mode, transfer ratio: 1.0) and returned into
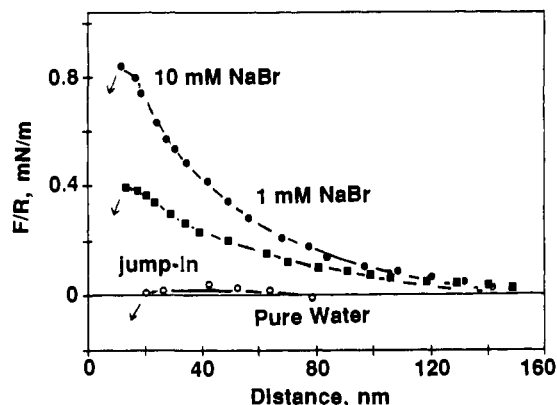
Figure 6. Interaction between monolayers of 1 transferred at 35 mN/m in the up-stroke mode. In pure water, no force operates in the longer separation range, and the surface jumps in to contact from 24 ± 6 nm. Addition of NaBr induces weak repulsion as well as reduction of jump-in distances.
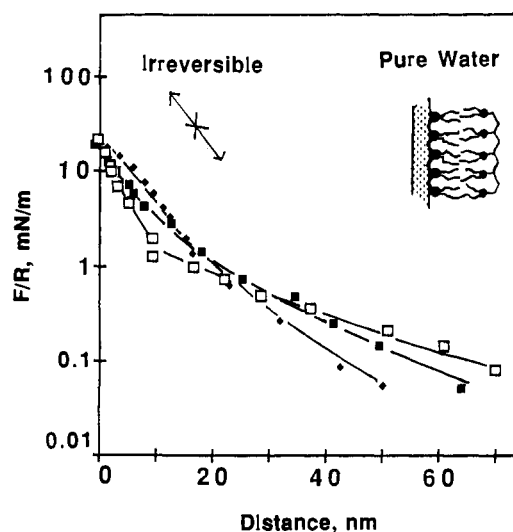
Figure 7. Repulsive forces between bilayers of a polymerized amphiphile 1 on mica in pure water. Different symbols present forces obtained at different positions. A deflection point of open squares is the clearest among five measured spots of two independently prepared samples.

pure water (Figure 6, Table II). The distance range where the attraction appeared was considerably shorter, although it was still very long from conventional pictures of the van der Waals attraction as well as from most of previously measured hydrophobic attraction.[7-9] The attraction caused jump-in of the surface to contact at 24 ± 6 nm.[21] The net interaction was virtually zero at the distance range longer than this jump-in distance. In 1 mM aqueous NaBr, the net interaction turned to weak repulsion in the longer distance range, and the attractive jump-in distance decreased to 15 ± 3 nm. Further addition of salt (10 mM) strengthened the repulsion, but the jump-in distance changed only a little to 12 ± 2 mN/m.

On the other hand, pull-off forces were close to each other among surfaces prepared in both of the up-stroke and down-stroke modes: ~200–400 mN/m (γ: 21–42 mJ/m^2) in pure water as well as in aqueous NaBr.[22] This indicates that surfaces prepared in the two different modes are similar and basically hydrophobic. Therefore, remarkable differences in the extent of long-ranged

(21) Average of two independent preparations. The deviation in the jump-in distances of surfaces prepared in the up-stroke mode is larger than those prepared in the down-stroke mode. This may indicate that the surface structure is disturbed when the sample is returned into water from in air.

(22) Pull-off forces between hydrophobic surfaces prepared in the down-stroke mode tended to vary among different samples (Table I), and the sample-dependent fluctuation was greater than those obtained on the identical sample at different salt concentrations.
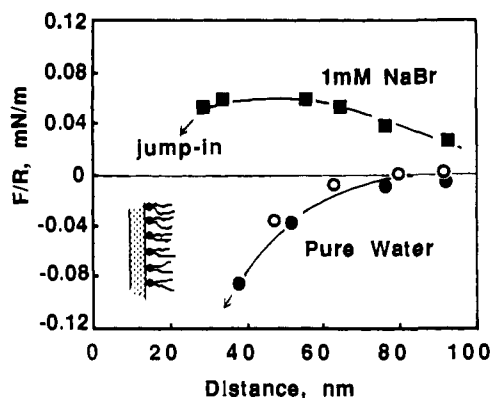
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Figure 8. Interaction between monolayers of **2** transferred at 45 mN/m in the up-stroke mode on mica. Attraction extending to 80 nm acts in pure water, while weak repulsion appears in 1 mM aqueous NaBr.

attraction between the two different preparations must be attributed to relatively small (though important) variations in surface structures.

Interactions between Hydrophilic Layers of Polymerized Amphiphile 1. Bilayers of polymerized amphiphile **1** were prepared by transferring monolayer **1** onto mica first in the up-stroke mode (35 mN/m and 10 mm/min, transfer ratio: 1.0), then in the down-stroke mode (transfer ratio: 0.6). This procedure would produce hydrophilic surfaces. In fact, forces between these bilayer surfaces were repulsive, displaying electrostatic double-layer repulsion similar to that found between hydrophilic surfaces of monomeric ammonium amphiphiles (Figure 7).[23] This force between the hydrophilic surfaces is quite different from the long-range attraction observed between monolayers of **1** deposited in the down-stroke mode. The force curve sometimes displayed breaks at around $D \sim 10$ nm, and the location and sharpness of such breaks differed from one measuring spot to another even on the same surface; the maximum distance where a break was seen was ca. 10 nm. Hydrophilic surfaces of the monomeric precursor of **1** do not exhibit any break in their forces profiles. The polymerized hydrophilic surface appears to be slightly more disordered than the unpolymerized counterpart; however, force profiles are basically similar between monomeric and polymerized surfaces.

Long-Range Attraction between Fluorocarbon Layers. Fluorocarbon amphiphile **2** forms a stable monolayer at the air–water interface, which can be transferred onto mica in the *up-stroke* mode at a surface pressure of 45.0 ± 0.2 mN/m and at a rate of 10 mm/min (transfer ratio: 0.9). Interactions between these LB layers were investigated in order to examine general features of the long-range attraction between hydrophobic surfaces (Figure 8). Purely attractive force, which is appreciable at a separation of ca. 80 nm, was observed in pure water and the surface jumped-in to contact from a separation of 40 nm. This attraction decays exponentially with an intensity parameter A of 0.27 mN/m and a decay length D_0 of 20 nm (see eq 1). The absence of repulsive force indicates that the surfaces are practically uncharged. When 1 mM NaBr was added, repulsion appeared and the jump-in distance was lessened to 25 nm. These pictures are very close to the long-range attraction reported for LB film surfaces of a similar fluorocarbon amphiphile **3** by Claesson and Christenson.[10] These fluorocarbon data obtained in different laboratories implies that the long-range attraction between hydrophobic surfaces is quite general.

Discussion

Long-Range Attraction between Various Hydrophobic Surfaces. Hydrophobic surfaces prepared by transferring monolayer **1** in the down-stroke mode (transfer ratio: 0.8) are stable and display long-range attraction extending to about 300 nm in pure water.

This long-range attraction can be described by an exponential function (eq 1). Intensity parameter A and decay length D_0 obtained for this hydrophobic surface are ~ 1 mN/m and 60–70 nm in pure water, respectively (Table I). Attraction between hydrophobic layers of dioctadecyldimethylammonium bromide **4** transferred at 25 mN/m was reported to decay double-exponentially with decay lengths of 2–3 nm ($A \sim 300$ mN/m, in the shorter separation range) and 13–16 nm ($A \sim 2.5$ mN/m, in the longer separation range).[10,24] Although our decay length is four to five times longer than that of the long-range component of the attraction between layers of **4**, these parameters are in the same orders of magnitude. The origin of attraction must be closely related. Fluorocarbon hydrophobic surfaces exhibit similar attraction ($A = 0.27$ mN/m, and $D_0 = 20$ nm in this work), supporting again the universal presence of this long-range attraction. An intensity parameter (ca. 300 mN/m) of the short-range attraction between layers of **4** is similar to the pull-off forces between hydrophobic layers obtained in this work and others.[10,11] The pull-off force of 300 mN/m corresponds to the interfacial energy (γ) of 32 mJ/m², which is in the range expected for hydrophobic energies.[1] This agreement may indicate that the short-range component of attraction corresponds to the conventional hydrophobic interaction.

This work can provide the first salt dependence data of the long-range attraction, since we do not observe any appearance of the surface charge which may arise from instability of LB layers.[9,11] Direct analysis of the attraction was difficult in the past studies, because the electrostatic repulsion shielded long-range components of the attraction. In our case, the polymerized layer was much stabler and the attraction between these layers was much longer ranged. Thus, it was possible to examine the salt effect without interferences of the electrostatic effect and undesirable overlapping with the short-range component of the hydrophobic attraction. Intensity parameter A was found to decrease with increasing NaBr concentrations from ca. 1 mN/m (pure water) to 0.2 mN/m (10 mM NaBr), whereas decay length D_0 remained the same at around 60 nm (see Table I for detailed values).

The salt effect obtained here is quite different from that previously reported by Christenson et al. for fluorocarbon surfaces.[10] They found that parameter A increased from 2.3 mN/m to 60 mN/m as D_0 decreases from 16 nm to 1.5 nm, with increasing salt concentrations from pure water to 10 mM tetrapentyl-ammonium bromide. However, they measured attraction only in the separation range of up to 20 nm for a 10 mM salt solution. In this limited separation range, the long-range attraction overlaps with the short-range attraction which may be ascribable to the conventional hydrophobic interaction. This results in seemingly large intensity parameters and shorter decay lengths. Our separation range is much larger, and the hydrophobic layers are much more stable. Therefore, we could avoid overlapping of long-range and short-range forces.

Influence of Monolayer Structure on Long-Range Attraction. Long-range attraction between hydrophobic layers of polymerized amphiphile **1** depends on the deposition mode. When monolayer **1** is transferred in the *down-stroke* mode (transfer ratio: 0.8), virtually no electrostatic repulsion exists even in the presence of 10 mM NaBr. In contrast, hydrophobic surfaces prepared in the *up-stroke* mode (transfer ratio: 1.0) lead to much shorter attraction which operates only up to 30 nm in pure water. Repulsion is not observed in the whole separation range. Addition of NaBr (1 to 10 mM) gives rise to repulsive forces, implying that charged units become exposed to water. Several factors may be counted on to explain the higher stability and hydrophobicity of the down-stroke preparation compared to those of the up-stroke one. Samples prepared in the down-stroke deposition are kept under water during the whole mounting processes, making surface structures less disturbed. Moreover, monolayer **1** transferred in the down-stroke mode should be structurally less strained (thus more stable), because molecules can rearrange more freely under water (in the down-stroke mode) than in air (in the up-stroke mode). When the surface pressure applied to the monolayer at

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(24) Intensity parameter A was estimated from Figure 4 of ref 10.

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the interface is relieved from the deposited monolayer under water, the monolayer packing may relax to a more stable arrangement. The transfer ratio of the down-stroke preparation (0.8) corresponds to the molecular area of **1** on mica of 0.5 nm^2/molecule. This value agrees well with the molecular area, 0.5 nm^2/molecule, extrapolated to zero pressure in the condensed phase at the air-water interface (Figure 2). The larger molecular density of **1** in the up-stroke preparation (0.4 nm^2/molecule for transfer ratio of 1.0) would make the deposited monolayer more strained, i.e., less stable.

An interesting comparison can be made between the present work and former reports which used LB films of dioctadecyldimethylammonium bromide **4**.[9,10] Hydrophobic surfaces of **4** prepared at a deposition pressure of 25 mN/m revealed longer-ranged ($\sim$70 nm) net attraction in pure water.[10] In contrast, surfaces prepared at a higher pressure of 35 mN/m exhibited repulsion in the long separation range, and net attraction appeared only at separations of less than 15 nm.[9] Again less densely covered surfaces are more stable.

Previous Explanation for Long-Range Attraction Data. This work clearly demonstrates the presence of attractive forces operating at the submicron range between hydrophobic surfaces. It is difficult to adopt the idea of "modified van der Waals forces" to interpret this unusually long-ranged attraction. Intensity parameter A of the attraction, 0.2–1 mN/m for **1**, is two orders of magnitude smaller than the pull-off force, 200–400 mN/m, which is attributable to the conventional hydrophobic interaction. Following are possible explanations.

"Bridging" of polymers adsorbed onto two surfaces is known to cause long-range attraction.[25] However, general characteristics of the attraction caused by bridging do not fit our force profiles. In the case of bridging, attraction changes to steric repulsion by further compression of surfaces. If such repulsion exists in our system and is shielded by strong van der Waals attraction at shorter distances, the repulsion should appear at distances less than 20 nm and surface polymers should be deformed to make hydrophobic contact. Such a drastic structural change is questionable. Additionally, the following scaling analysis predicts that the repulsion would appear at distances much longer than 20 nm if it exists. Studies on poly(styrene) and poly(methylstyrene) layers in cyclohexane have revealed that attraction becomes detectable at a separation D of $(2\sim3)r_g$ (r_g: radius of gyration) and reaches a maximum at $D \sim r_g$, and then the force becomes repulsive at $D \sim (2/3)r_g$, without regard to kinds of polymers and their molecular weights.[25] The radius of gyration is not known for our polymer **1**. However, we may tentatively adopt the above scaling behavior. The gyration of radius estimated from the distance where the attraction appears (the value of 260–270 nm in Figure 1 corresponds to $(2–3)r_g$) is 90–140 nm, and the separation where the attraction changes to repulsion ($(2/3)r_g$) is calculated to be 60–100 nm. This distance is too large compared with a separation (<20 nm) where the conventional hydrophobic attraction appears. Furthermore, if bridging of polymerized amphiphiles could occur, the amphiphile must extend toward bulk water exposing ionic groups. This would create electrostatic repulsion and contradict our observation (Figure 3). Thus, the bridging mechanism is unlikely to be the source of the long-range attraction.

"Cavitation" has been pointed out as an origin of the long-range attraction.[10,26] The liquid phase of water is less stable than the vapor phase on the hydrophobic surface which shows contact angles of water of greater than 90°. Vapor cavity is formed under these conditions, and during this process long-range attraction should act between two hydrophobic surfaces.[27] Vapor cavities formed between fluorocarbon layers were photographed.[26] Nevertheless, correlation between cavitation and long-range attraction is still not clear. The presence of charges (ionic groups) should reduce the hydrophobicity of surfaces, but weakly charged

hydrophobic surfaces, of which the contact angle is less than 90°, still display long-range attraction. The macroscopic cavitation should not occur with this weakly charged surface and cannot explain the depression of the long-range attraction caused by salt addition.

The cavitation mechanism may still hold true at the microscopic level where we cannot see cavities by an optical microscope.

Long-Range Correlation of Water Structure on Hydrophobic Surfaces. We need to propose an alternative hypothesis in order to explain the submicron range attractive force we observed. The past postulates of bridging and cavitation are not satisfactory, as we discussed in the preceding section. Changes in the surface hydration structure have been mentioned by Israelachvili and Pashley as a possible cause of the attraction.[7] They observed the attraction which was stronger than that expected as the van der Waals attraction. The attraction extended to several nanometers and was describable by the exponential function, the intensity parameter of which was 110 mN/m. Since this value is close to the free energy of an interaction pair of small hydrophobic molecules in water, they have ascribed the attraction between hydrophobic surfaces to the conventional hydrophobic interaction which arises from the structural rearrangement of water molecules. Recent reports of longer-ranged attraction detected to 90-nm separation started to contradict with the conventional mechanism of surface hydration,[10,26] because a generally held view of hydration of solid surfaces often limits its range to several molecular diameters to several nanometers.[28,29]

It is, however, known that interfacial (vicinal) water has properties that differ from those of bulk water.[4–6,28–31] For instance, the heat capacity of vicinal water is approximately 1.25 cal/(g K) on surfaces of porous glass, zeolite, diamond, and charcoal. The ordered water structure was estimated to extend into the bulk liquid for a considerable distance (0.02 μm[28] to 0.1 μm[5]). This distance is much larger than that assumed for the hydration force by previous reports.[10,26] The structural order should disappear with distances from surfaces because of thermal motion. It was suggested that the ordering on a hydrophobic surface would decrease with extending distances less rapidly than that on a polar surface.[5]

Etzler[31] has proposed a statistical thermodynamic model which suggests that vicinal water differs from the bulk, and that hydrogen bonding between water molecules is enhanced by proximity to solid surfaces. This model has a common feature with clathrate formation in which a hydrophobic molecule is surrounded by the hydrogen-bonded water network.[1] However, the structural correlation will be lessened in long-range separation from the surface compared with that near the surface. A similar phenomenological model of hydration was reported recently to interpret the long-range attraction.[32]

We may assume that the enhanced hydrogen bonding of the vicinal water near hydrophobic surfaces is the source of unusually long-range attraction. The water phase would become more stable as the two hydrophobic surfaces approach and the hydrogen bonded structure grows. This gives rise to attractive forces. The conventional hydration structure appears in the short-range of surface separation. As other possibilities, enhanced hydrogen bonding may mediate attraction between the hydrophobic surfaces, or the attraction may be induced by specific orientation of dipoles of the structured vicinal water. The exponential decay of the attractive force and the absence of the salt effect on the decay length are consistent with structuring of the vicinal water which decay predominantly by thermal motion.[3] We found that the range of the attractive force was much extended in the case of uniformly hydrophobic surfaces. Growth of the hydrogen bond

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network on hydrophobic surfaces will be favored when the surface is uniform and smooth. The importance of the surface hydrophobicity in bringing about long-range attraction has been pointed out by previous workers.[8,10] It is clear that our monolayer modified mica which is sufficiently large, molecularly smooth, and strongly hydrophobic is the prerequisite for the observed long-range attraction. Numerous physiological anomalies at the biological

surface were referred to the structuring of the vicinal water.[5,28] We consider that the observed attractive force has significant bearing on biological functions at cell surfaces.

Monte Carlo Simulations for the Interactions of Metal Complexes with the Silicate Sheets of a Clay: Comparison of Binding States between Tris(1,10-phenanthroline)metal(II) and Tris(2,2'-bipyridyl)metal(II) Chelates

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Abstract: Monte Carlo simulations are used to compare the binding states of tris(1,10-phenanthroline)metal(II) ([M(phen)$_3$]$^{2+}$) and tris(2,2'-bipyridyl)metal(II) ([M(bpy)$_3$]$^{2+}$) bound to a clay. A pair of [M(phen)$_3$]$^{2+}$ or [M(bpy)$_3$]$^{2+}$ complexes is placed on the model surface of a silicate sheet. The surface is composed of linked [SiO$_4$]$^{4-}$ and [AlO$_4$]$^{5-}$ tetrahedra. The binding energy is obtained as the sum of the interaction energies of the metal complexes with the sheet and the intermolecular energy between the metal complexes. The stable binding state is examined in terms of the free energy at 300 K as a function of the intermolecular distance, r_{M-M}. For [M(phen)$_3$]$^{2+}$, a racemic pair has the minimum free energy at r_{M-M} = 9.2 Å, and an enantiomeric pair has the minimum free energy at r_{M-M} = 13.4 Å. The mean binding energy (E) for the racemic pair is 1.5 kJ/mol lower than that for the enantiomeric pair. The results indicate that the racemic mixture forms a more compact and stable pair than does the pure enantiomer. For [M(bpy)$_3$]$^{2+}$, racemic and enantiomeric pairs have the minimum binding free energy at nearly the same values of r_{M-M}: r_{M-M} = 9.3 Å for a racemic pair and 9.5 Å for an enantiomeric pair. E is 25.3 kJ/mol lower for the racemic pair than for the enantiomeric pair. Thus a pair of the metal complexes form a dimer with similar compactness irrespective of the chirality of the complexes. These results are compared with experimental observations of the chirality effects on the adsorption behaviors of these metal complexes by a clay.

Introduction

Clay minerals are phyllosilicates with layer structures. For the 2:1 class of clays, a layer is composed of an octahedral sheet sandwiched by two tetrahedral sheets.[1] The surface of a tetrahedral sheet is characterized by a two-dimensional network structure, as confirmed by electron diffraction analyses and AFM observations.[2,3]

Recently, the remarkable effect of chirality on the amount of adsorption of a metal complex by a clay has been reported.[4–6] For example, when [M(phen)$_3$]$^{2+}$ (phen = 1,10-phenanthroline) and [M(bpy)$_3$]$^{2+}$ (bpy = 2,2'-bipyridyl) are adsorbed, the maximum amount of adsorption is different between a racemic mixture and a pure enantiomer. The racemic mixture of [M(phen)$_3$]$^{2+}$ (M = Fe and Ru) is adsorbed to about a 2-fold excess of the cation-exchange capacity (CEC), while the enantiomer is adsorbed at levels within the CEC.[7] In the case of [M(bpy)$_3$]$^{2+}$ (M = Ru), a counter anion affects the adsorption behaviors drastically. At low ionic strength, the racemic mixture is adsorbed at levels within the CEC, while the enantiomer of the same chelate is adsorbed in 1.5–2.5-fold excess of the CEC. At high ionic strength, both the racemic mixture and enantiomer of [M(bpy)$_3$]$^{2+}$ are adsorbed in excess of the CEC.[8]

A clay is a unique material in the sense that such an enormous difference in the adsorption amount is not observed for other ion

exchangers, such as ion-exchange resins and zirconium phosphate.[4] The above results are considered to be an indication that the bound metal complexes interact with their neighbors in a stereoselective way, leading to the difference in the packing structures between a racemic mixture and a pure enantiomer. It is also suspected on the basis of a simple molecular model that the geometrical matching between the molecular size of a metal complex and the network structure of a silicate sheet is essential to achieving these stereoselective interactions.[4] These properties have opened the way to utilizing a clay–metal complex adduct as an adsorbent in optical resolution and asymmetric syntheses.[5,6]

Extensive work has been done to validate the above postulate. No decisive experimental evidence, however, has so far been presented.[9] In this work, the adsorption of metal complexes by

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