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Very Strong Long Range Attractive Forces between Stable Hydrophobic Monolayers of a Polymerized Ammonium Surfactant[1)]

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Direct measurements of forces between stable hydrophobic monolayers are performed, revealing very long-range attraction which extends to a separation of 300 nm in pure water. The attraction decreases in the presence of NaBr, while the pull-off force changes only moderately.

Importance of accurate, direct measurements of interactions between various surfaces has become widely acknowledged since introduction of Surface Forces Apparatus designed by Israelachvili.2,3) However, there are still disagreements among experiments and theories, even concerning basic forces such as hydrophobic interactions. In recent years, direct measurements have been made for forces between hydrophobic surfaces prepared by adsorption of monolayers4,5) and by Langmuir-Blodgett (LB) deposition.6-9) These studies indicated the presence of attractive forces that are stronger than expected from van der Waals forces.10) However, its satisfactory explanation has not been given. All of these previous studies suffered from the presence of surface charges due to probable formation of the second layer in the case of adsorbed monolayers, and due to instability of LB layers especially in the presence of salts.8,9,11) Their detectable force ranges differed from 10 nm4) to 70 nm.7) Dependence of forces on physical parameters such as salt concentration has not been clearly shown, although these knowledges are essential to understand the origin of forces. Needs of studies on apparently stable, clean hydrophobic surfaces were repeatedly mentioned in previous studies.

In order to circumvent the difficulties described above, the present investigation utilizes stable monolayers of a polymerized ammonium surfactant, and performs direct measurements on forces between LB layers deposited on molecularly smooth mica sheets.

Polymerized ammonium surfactant, **1**, (n = 10000) was obtained by photoirradiation of an aqueous surfactant dispersion with a 250-W Hg lamp at 35 °C for 60 min.[12] A solution of **1** (1 mg ml^{-1}) in a mixture of C_6H_6:CH_2Cl_2:EtOH (8:1:1) was spread on water and the surface pressure-area (π-A) isotherm was examined by a computer controlled film balance (Sanesu-Keisoku, FSD 50). A stable monolayer is formed as shown in Fig. 1. The pressure increases steeply at a molecular area of about 0.4 nm^2 $molecule^{-1}$, which corresponds to the molecular cross section of two normal alkyl chains and indicates close packing of long hydrocarbon chains.

Force measurements were carried out by using a Surface Forces Apparatus Mark 4 (ANUTECH).[2,13] Molecularly smooth mica sheets are glued on cylindrical silica lenses (radius ≈ 20 mm) and mounted in the apparatus. The surface separation D is measured by use of multiple-beam interferometry. The force (F) is determined from a deflection of a double-cantilever spring (spring constant K ≈ 100 N m^{-1}) on which one surface is mounted. The measured force is normalized by the mean radius of curvature of the surfaces R, and the value of F R^{-1} is plotted as a function of surface separation.

Forces between mica surfaces without any modification were measured in pure water (Fig. 2). The interaction is repulsive in the whole separation range down to 3 nm where the surfaces jump together to contact (the largest repulsion of 3 mN m^{-1} at this separation). This behavior agrees well with a previous observation.[14] The repulsion was ascribed to a long-range repulsive double-layer force,since mica surfaces in pure water possess weak negative charges due to dissociation of potassium ion from the cleavage plane. On the other hand, the adhesive force between bare mica surfaces due to van der Waals force is determined to be 55 ± 15 mN m^{-1} from the jump-

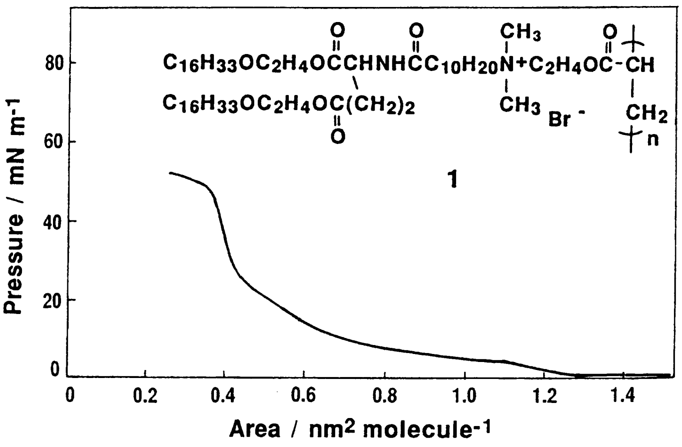

Fig. 1. The π-A isotherm of monolayer **1** on pure water at 20.0 ± 0.1 °C.

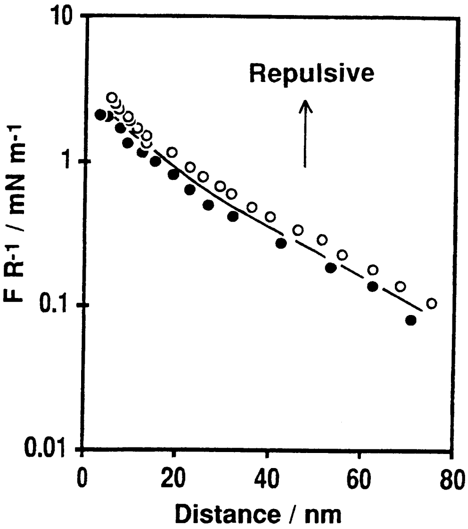

Fig. 2. Forces between mica surfaces in pure water.

out distance when two surfaces pull-off. This figure also agrees well with the previously reported value of 45 ± 20 mN m^{-1}.15)

Coating of the surfaces with LB films of **1** changes the interaction drastically. Figure 3 shows the forces between mica surfaces modified by LB deposition of **1** at a surface pressure of 35 mN m^{-1} in the down-stroke mode (transfer ratio: 0.8). Mica sheets were mounted in the apparatus while being kept under water. Surprisingly, we observed a measurable attraction at a long distance close to 300 nm in pure water. The surfaces jump into contact from a separation of 76 nm. These distances are considerably longer than those previously reported.7) Absence of repulsive forces at any separation indicates that this surface is neutral: the ammonium group of monolayer **1** must be bound to negative mica surfaces by electrostatic attraction, exposing the hydrophobic side towards water, though LB deposition is performed in the down-stroke mode. The adhesive force (pull-off forces) between these hydrophobic layers is determined to be 189 ± 17 mN m^{-1}.

This hydrophobic surface is stable, and allows us to study the salt effect on the attractive forces(Fig. 3). The jump-in distance decreases to 45 nm in 10 mM (M = mol dm^{-3}) NaBr, while the pull-off force changes moderately to 160 ± 12 mN m^{-1}. Repulsive forces are not detected at any salt concentration, indicating that the surfaces are maintained uncharged.

Phenomenologically, these force curves can be described in the form of $F(D) = -A \exp(-D/D_0)$. Table 1 summarizes A and D_0 values obtained at different salt concentrations. The data reveal that the decay length D_0 is virtually independent of salt concentrations, while A is dependent.

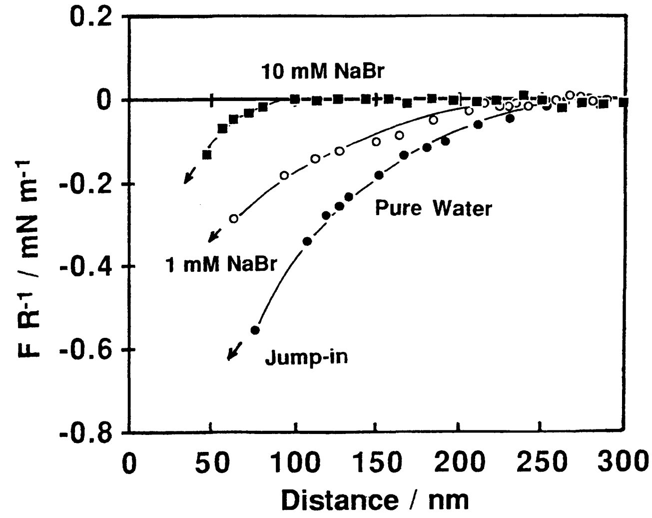

Fig. 3. Attractive forces between monolayers of **1** in water.

Table 1. Attractive forces between hydrophobic surfaces

Medium	$F(D) = -A \exp(-D/D_0)$		Pull-off force
	A / mN m^{-1}	D_0 / nm	mN m^{-1}
pure water	1.7 ± 0.5	62 ± 4	189 ± 17
1 mM NaBr	0.40 ± 0.14	63 ± 17	166 ± 11
10 mM NaBr	0.25	42 ± 22	160 ± 12

An attraction extending nearly to 300 nm has never been demonstrated. Our current observations clearly demonstrate that it is difficult to explain the hydrophobic interaction only in terms of the conventional van der Waals interaction whose maximum measurable range of D is 20-30 nm. Other forces like structural (hydration) forces$^{5,16)}$ and cavitation$^{17)}$ need to be considered in order to understand the hydrophobic interaction at both of macroscopic and molecular levels. Stable monolayers of polymerized surfactants provide an ideal system for further investigation of this interaction.

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