CHEMISTRY LETTERS, pp. 1049-1052, 1991.

Well Defined Organic Surfaces Flat at the Molecular Level. Control of Surface Chemical Groups by Bipolar Surfactant Monolayers on Step-Free Mica Surfaces

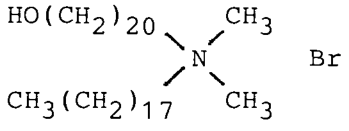
Masakatsu HATO,* Hiroyuki MINAMIKAWA, and Kaoru OKAMOTO
Surface Engineering Laboratory, Research Institute for
Polymers and Textiles, 1-1-4-Higashi, Tsukuba, Ibaraki 305

A new method for preparing well defined organic surfaces flat at the molecular level has been presented. This allows precise control of the composition of hydrophilic and hydrophobic groups at the surfaces.

In recent years, there has been a considerable increase in interest in "molecular-level investigations" of solid/liquid interface, i.e., "buried interface".$^{1)}$ However, as solid/liquid interfaces are much harder to be probed than their solid/vacuum counterparts,$^{1)}$ approaches to the "molecular-level investigations" are not so straightforward as might be wished. In view of this, well defined organic surfaces flat at the molecular level should provide us with a powerful means to address various problems on "buried interface".

Being flat at the atomic level,$^{2,7)}$ freshly cleaved mica surfaces, if modified by organic monolayers in a controlled manner, may be used as a potent substrate to realize flat organic surfaces.$^{2)}$ However, in general, monolayers on step-free mica surfaces so far prepared were not stable enough for the reliable physical properties to be determined.$^{3)}$ Moreover, no method which allows control of the kinds and composition of surface chemical groups has yet been established. In this communication, we will report on a new method which allows preparation of stable and well defined organic surfaces flat at the molecular level.

A bipolar surfactant, 20-hydroxyicosyldimethyloctadecylammonium bromide, HADMOA(20), has been synthesized$^{4)}$ as a unit molecule to modify mica surfaces.



$$\mathrm{HO(CH_2)_{20}}(\mathrm{CH_3(CH_2)_{17}})\mathrm{N}(\mathrm{CH_3})_2\ \mathrm{Br}$$

HADMOA(20)

Monolayers of pure HADMOA(20) at water-air interface were expanded (5.5 °C — 25 °C). However, two-component monolayers of HADMOA(20) and arachidic acid (AA) formed solid condensed monolayers in which the two components were miscible. When the mole fraction of AA (X_a) exceeded 0.5, monolayers having an average molecular cross-sectional area of 0.195-0.22 nm^2/alkyl chain, which is comparable to that of close packed long chain fatty substances[5)] could be obtained at 5.5 °C and 20 mN/m. The solid condensed monolayers were then transferred to step-free mica substrate (Muscovite, 2 cm × 2 cm in size, 2-4 μm in thickness) by a Langmuir-Blodgett technique[6)] by lifting the mica substrate adhered on a thick mica sheet (backing sheet), with a velocity of 5 mm/min at a surface pressure of 20 mN/m. Compression rate and subphase temperature was 0.005-0.02 nm^2/min and 5.5 °C respectively. The transfer ratio was 0.99 ± 0.04 for all cases studied. Step-free mica substrates were prepared by an adaptation of the procedures proposed by Israelachvili for surface forces measurements.[7)] All the experiments were carried out in a class 100 clean cabinet.

Roughness of the monolayer-covered mica surfaces, thickness and refractive index of the monolayers on the mica substrate were determined by a multiple-beam interferometry[8)] at 22.5 °C, using an ANUTECH Surface Forces Apparatus MkII(SFA).[9,10)] The distance resolution of the interferometry is of ca. 0.2 nm.[8)] First, the exposed surfaces of the substrates on the backing sheet were silvered in an evaporator. They were peeled off the backing sheet and glued on a pair of silica discs. The mica substrates covered with the monolayers were then placed in the SFA at the cross cylindrical configuration. The two surfaces were brought into molecular contact and the wave length of Fringes of Equal Chromatic Order[8)] at the contact position was measured. By repeating the procedures for more than 20 samples, the monolayer-covered mica surfaces were estimated to be flat within 5.0 nm, and may be expressed as "flat at the molecular level".

The thickness and the refractive index of the monolayers were 2.6 ± 0.4 nm and 1.43 ± 0.04 at 22.5 °C for all cases studied ($0.5<X_a<0.84$). The 2.6 nm is close to the extended molecular length of 2.8 nm for both AA and HADMOA(20). The refractive index of 1.43 is close to that of n-hexadecane(1.4325, 25 °C),[11a)] or of 1-octanol(1.427, 25 °C).[11b)]

Table 1 lists the normalized pull-off force (F/R) between monolayer-covered mica surfaces in pure water (pH=5.8-6.6), which has been measured by the SFA using a nonrolling and shear-free double cantilever spring. The advancing contact angle of water (θ_a) and interfacial tension between monolayer/water interface (γ_{sl}) were also listed. γ_{sl} was estimated assuming the equation proposed by Johnson, Kendall, and Roberts,[12)]
$\gamma_{sl} = F/(3\pi R)$, where R is the mean radius of curvature of the surfaces.

Table 1. F/R, θ_a, and γ_{sl} of monolayer-covered mica surfaces (22.5 °C)

Monolayer composition (X_a)	θ_a /deg	(F/R) /mN m^{-1}	γ_{sl} /mN m^{-1}
Bare mica	2 ± 2	47 ± 10	5 ± 1
0.50	82 ± 2	190 ± 30	20 ± 3
0.75	95 ± 1	380 ± 50	40 ± 5

Table 1 indicates that with the increase in the mole fraction of AA (X_a), i.e., the increase in the surface fraction of the hydrophobic CH_3CH_2- groups, the contact angle increased and γ_{sl} approached a typical interfacial tension value of ca. 50 mN/m for hydrocarbon/water interface, indicating that the surfaces were fully composed of CH_3CH_2- and $HOCH_2$- groups.

From the foregoing results, it can be concluded that the molecules in the two-component monolayers on the mica surfaces were closely packed and took nearly perpendicular configuration with respect to the mica surfaces. Therefore, the monolayer modified mica surfaces can be viewed as chemically heterogeneous surfaces composed of two-dimensional array of close packed hydrophobic CH_3CH_2- and hydrophilic $HOCH_2$- groups (Fig.1).

Figure 2 gives the time dependence of the advancing contact angle of water(θ_a) on the monolayer-covered mica surfaces under saturated vapor conditions. The results for pure AA and dimethyldioctadecylammonium bromide (DMDOA) monolayers on mica surfaces were also plotted by dashed lines. It is clear that on the two component monolayers, θ_a was almost constant, while θ_a on the pure DMDOA or AA monolayers decreased quickly with time. DMDOA or AA molecules escaped from the mica surface by spreading through the water-air interface.3) On the other hand, the two component monolayers were much more stable and the spreading and/or dissolution of the molecules observed in the DMDOA or AA monolayers did not take place. Therefore, the θ_a on the two component monolayers has definite physical meanings and can be considered as the Young contact angles.13)

The following relation was found to hold between θ_a and the mole fraction of $HOCH_2$- groups at the surface $f_{HO}[=(1-X_a)/(2-X_a)]$,

$$\cos\theta_a = -0.309 + 1.309\, f_{HO} \quad (0 < f_{HO} < 0.33) \qquad (1)$$

This equation may be formally obtained by substituting the experimental values of $\theta_{HO}=0$ and $\theta_{CH}=108$ into the Cassie equation, $\cos\theta_a = f_{HO}\cos\theta_{HO} + (1-f_{HO})\cos\theta_{CH}$. θ_{HO} and θ_{CH} is the θ_a value of pure $HOCH_2$- and CH_3CH_2- surface, respectively. More detailed discussion on the present results will be published in a separate paper.

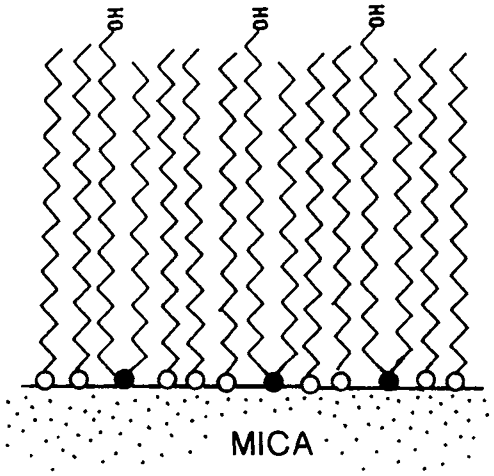


Fig.1. Schematic illustration of an idealized version of the two component monolayers on step-free mica surfaces.

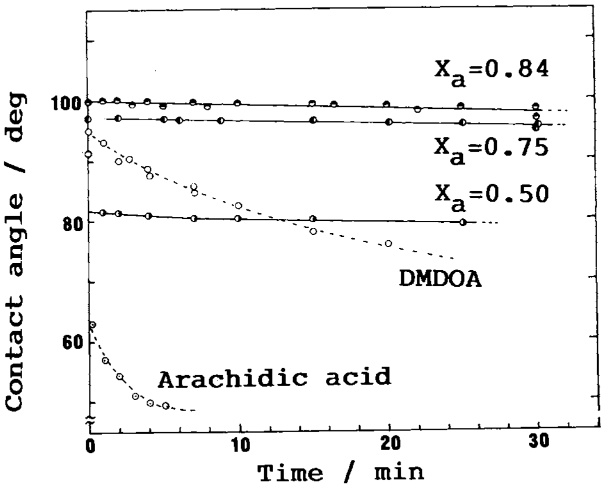


Fig.2. Advancing contact angle of water on the monolayer-covered mica surfaces as a function of time.

References

1)"Report of the Research Briefing Panel on Science of Interfaces and Thin Films", National Academy Press, Washington, D.C. (1986).

2)G.L.Gaines,Jr., J. Phys. Chem., **61**,1408 (1957).

3)Per M.Claesson,C.E.Blom,P.C.Heder and B.W.Ninham, J. Colloid Interface Sci., **114**, 234 (1986).

4)S.R.Sandler and W. Karo, "Organic Functional Group Preparation," Academic Press, N.Y. (1983), Vol.1, p.380.

5)G.L.Gaines, "Insoluble Monolayers at Liquid-Gas Interfaces," InterScience, N.Y. (1966).

6)K.B.Blodgett and I.Langmuir, Phys. Rev., **51**,964 (1937).

7)J.N.Israelachvili, J. Colloid Interface Sci., **44**,259 (1973).

8)S.Tolansky, "Multiple-Beam Interferometry of Surfaces and Films," Dover, New York (1970).

9)D.Tabor and R.H.S.Winterton, Proc.R.Soc. London, Ser.A, **312**,435 (1969).

10)J.N.Israelachvili, and G.E.Adams, J.Chem.Soc.,Faraday Trans.1, **74**,975 (1978).

11)a) J.Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, N.Y. (1950), pp.112-113; b) "Handbook of Chemistry and Physics," 54th ed, CRC Press, Cleveland (1973), E-219.

12)K.L.Johnson,K.Kendall, and A.D.Roberts, Proc.R.Soc. London, Ser.A, **324**,301 (1971).

13)A.W.Neumann, Adv. Colloid Interface Sci., **4**, 105 (1974).

(Received March 14, 1991)