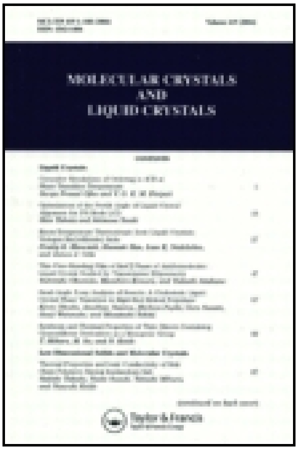

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Structure-Dependent Wettability of Hydrophobic Monolayer

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STRUCTURE-DEPENDENT WETTABILITY OF HYDROPHOBIC MONOLAYER

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Abstract Hydrophobic monolayer films of dimethyldioctadecyl-ammonium bromide (DMDOA) deposited on mica by Langmuir-Blodgett (LB) method have been studied using Wilhelmy plate type wetting measurements, and atomic force microscopy (AFM). The structural change of DMDOA monolayer was observed when exposed to salt solution. The effect of exposure time to aqueous KBr salt solutions (immersion time) was especially investigated on surface morphology and wettability of DMDOA films. AFM images have shown that the surface coverage of DMDOA monolayer is decreased with increase in KBr concentration, or in immersion time to KBr solution. The wetting measurements have demonstrated that the hydrophilicity of DMDOA sample is increased with decrease in surface coverage. Drastic hydrophilisation was observed between 60% and 50% covered DMDOA samples.

INTRODUCTION

Well-defined hydrophobic surfaces are interesting for many research applications, including direct measurements of interaction forces between such surfaces in aqueous solutions. The monolayer of dimethyldioctadecylammonium bromide (DMDOA) deposited on mica has been used for these applications because of its hydrophobic surface. The limited stability of deposited hydrophobic films in contact with various liquids has been recognized for long time. However, this subject has not received very much attention.

In our current work, it was found that structural change on the DMDOA monolayer was induced by contact with aqueous solutions.[1] This structural change is caused by DMDOA molecules peeling off from the sample immersed in aqueous solution. For further elucidation of this structural change, we investigated the effect of salt concentration and immersion time with respect to the morphology of DMDOA monolayer. The morphology was studied using atomic force microscope (AFM). AFM is one of the suitable technique to estimate the surface coverage of thin films. The hydrophilicity was studied using Wilhelmy plate type wetting measurements for DMDOA sample immersed in salt solutions with different exposure time. We reveal, in this paper, the relationship between the wettability and the morphology of DMDOA monolayer.

EXPERIMENTAL

Preparation of DMDOA and purification of water were carried out in the same manners described in the previous paper.[2] Singly distilled chloroform was used as solvent for DMDOA solution. Brown muscovite mica sheets were purchased from Watanabe Shoko Co. Tokyo. The rectangular mica plate (2cm x 4cm x 20-50μm) as the substrate for DMDOA monolayer was cleaved just before deposition.

Depositing the DMDOA monolayer on mica surface was carried out by Kyowa Kaimen Kagaku Model HBM surface film balance at room temperature. The DMDOA solution was spread over the air/water interface and left for 20 minutes to evaporate chloroform. The monolayer was deposited onto mica at 25mN/m by LB method with deposition rate of 5mm/min. The transfer ratio of monolayer onto mica was 0.95-1. The DMDOA monolayer on mica was dried up in the laminar flow cabinet overnight.

The dynamic contact angle was measured by Wilhelmy plate method. The contact angle relaxation and DMDOA film stability were evaluated by keeping the meniscus at a constant position for an extended period of time, both during advancing and receding runs, at the same time preventing evaporation by keeping the measurement cell sealed and humid. After immersion, the wettability of the former meniscus position was probed by additional immersions using pure water. The wetting measurements were carried out at a temperature of 22-23°C, where the surface tension of pure water is about 72.5mN/m.

The DMDOA samples were imaged with a NanoScope III atomic force microscope (Digital Instruments, Santa Barbara, CA). All images were taken in contact mode using silicon nitride tips. Surface coverage was calculated using the height histogram of a given image. We computed the surface coverage by doubling the integrated intensity of the "high" half of this peak.[3]

RESULTS AND DISCUSSION

Figure 1 shows the series of AFM images of DMDOA samples immersed in KBr solutions for 1h, and 24h. From many AFM imagings, any aggregated structure or multi-layered structure has not been observed. The height difference between dark and bright area in these images is 2.0-2.1nm, corresponding to the thickness of a DMDOA monolayer. Hence, the dark area in these images should be the region of bare mica. It is obvious that the surface coverage of DMDOA samples is decreased with an increase in the concentration, or immersion time. The size of holes caused by peeling off of DMDOA molecules increases as the surface coverage decreases. The AFM images of the DMDOA sample immersed in dilute solutions (≤ 0.1mM) show isolated holes in DMDOA monolayer ("pond" structure);the images of the sample immersed in concentrated solutions (≥ 1mM) for 24h show isolated island in continuous exposed mica ("island" structure).

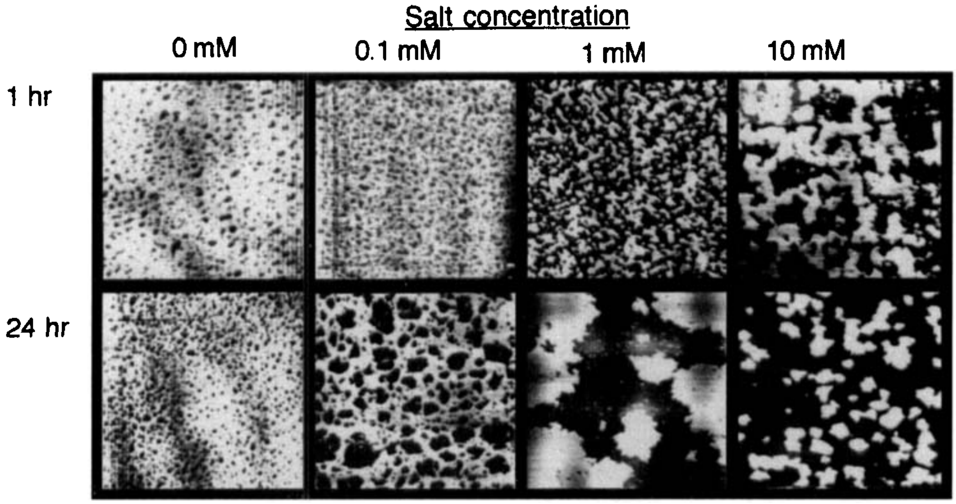

FIGURE 1 The series of AFM images of DMDOA samples immersed in KBr solutions with different concentrations for 1hr, and 24hr. Image size is 5μm x 5μm.

Table 1 shows the coverage and dynamic wetting data of DMDOA samples treated in each conditions. It is shown that advancing (Θa) and receding (Θr) contact angles decrease as the surface coverage decreases. It can be seen that hydrophilisation of DMDOA sample is due to the increase of exposed mica area. The receding contact angles (Θr) for the sample immersed in concentrated solutions (≥ 1mM) for 24h are extremely small (≈0°), while the advancing contact angles (Θa) of the sample immersed in 1mM solution and 10mM solution for 24h are 54±4° and 32±4°, respectively. This suggests that Θr is affected by the continuous exposed mica surface of DMDOA samples forming "island" structure. It should be noted that the surface coverage and Θa are the same, ≈54° for about 30% coverage, for the sample treated in 1mM for 24h ("island" structure) as for

TABLE 1

KBr concentration (mM)	Immersion time (h)	θ a	θ r	coverage (%)
0 (water)	0	108	57	> 90
	1	107	57	86 - 91
	24	105	49	84 - 88
0.1	1	101 ± 2	60 ± 6	75 - 78
	24	96 ± 3	51 ± 5	57 - 63
1	1	58 ± 4 (80)	30 ± 4	51 - 59
	24	54 ± 4	0	29 - 35
10	1	54 ± 5	29 ± 5	21 - 39
	24	32 ± 4	0	14 - 20

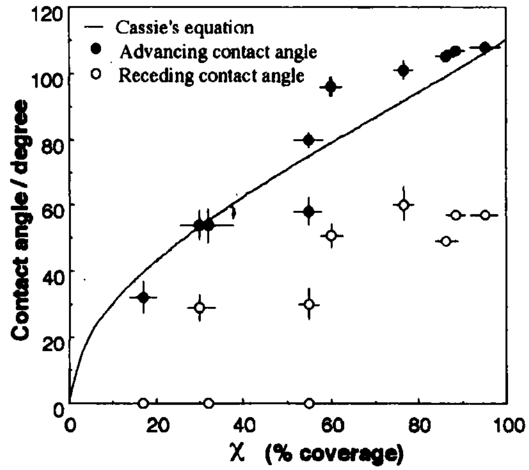

FIGURE 2 Advancing and receding contact angle of water versus the surface coverage measured using AFM. The solid line is a phenomenological line calculated from Cassie's equation.

that treated in 10mM for 1h ("pond" structure), whereas Θr is ≈0° for the sample forming "island" structure and 29±5° for the sample forming "pond" structure. This structural dependence on the difference between Θa and Θr is in consistency with the theoretical calculation and simulation results by Schwartz and Garoff.[4]

The standard first approximation for the contact angle of a liquid in contact with a chemically heterogeneous surface composed of a fraction f_1 of chemical groups of type 1 and a fraction f_2 of groups of type 2 is the Cassie's equation

$$\cos\Theta = f_1 \cos\Theta_1 + f_2 \cos\Theta_2$$

where Θ_1 and Θ_2 are the contact angle of the pure, homogeneous type 1 and type 2 surfaces, respectively. In our case, this can be written

$$\cos\Theta = \cos\Theta_{mica} + X(\cos\Theta_{DMDOA} - \cos\Theta_{mica})$$

where X is the fractional monolayer coverage. This implies a relationship Θ and X. It is interesting to compare our data to this phenomenological equation. Figure 2 shows advancing contact angle and receding contact angle versus the surface coverage of DMDOA sample. In the low- and high-coverage region, advancing contact angles seem to be in agreement with the calculated angles from Cassie's equation. It is noteworthy that drastic hydrophilisation is observed between 60% and 50% covered DMDOA samples. The structure of DMDOA sample ("pond" or "island") would significantly affect the wettability of the sample surface in this region.

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