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Quantitative Analysis of Molecular Orientation of Structurally Heterogeneous Langmuir-Blodgett Films by Infrared Reflection-Absorption Spectra

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Infrared reflection-absorption (RA) spectra were measured for Langmuir-Blodgett (LB) films of octadecyl-dimethylamine oxide ($C_{18}DAO$) and dioctadecyl-dimethylammonium chloride ($2C_{18}DAC$) on gold-evaporated slide glasses. The RA spectra showed unique relations between the reflection-absorbance and the number of layers of the LB films. Since the RA spectrum of the monolayer LB film showed different properties from the upper layers especially for the $C_{18}DAO$ LB film, this layer was separated from other layers in the molecular orientation analysis. We then proposed a new schematic model comprising a four-phase architecture (IR//air/LB2/LB1/gold) to explain the RA spectra (LB1 refers to the first monolayer only). The results by the new model indicated that the first monolayer directly on the substrate had different film structure from that of the upper layers. These relations could not be figured out by a simple three-phase model (IR//air/LB/gold) that ignored the heterogeneous architecture in the film phase. The present structurally heterogeneous property was also recognized in the temperature-dependent RA spectra of the LB films.

INTRODUCTION

Infrared RA spectrometry (1) has become one of the most powerful measurement techniques of vibrational spectroscopy especially for ultra-thin films on metallic substrates. The application of this technique has been restricted, however, to structurally homogeneous LB films thus far. In other words, all of the layers in the LB films are assumed to have uniform film structure. For the analysis of the layer-location dependent molecular orientation in LB films or heterogeneous LB films, the deuteration method has been the most popular method to investigate the film structure of a specific layer in the stratified multi-layer films (2). The deuteration method is not appropriate for every LB film, especially when deuteration is difficult. In the present study, we have attempted to explore quantitative molecular orientation in a specific layer as well as that in the remaining layers simultaneously from one RA spectrum. The results showed that the first monolayer directly on the metal substrate has a different film structure from that of the remaining layers.

EXPERIMENTAL

$C_{18}DAO$ and $2C_{18}DAC$ were synthesized as described previously (3). $C_{18}DAO$ has one hydrocarbon chain with dimethylamine oxide, while $2C_{18}DAC$ has two hydrocarbon chains with a positively charged dimethylammonium chloride (Fig. 1).
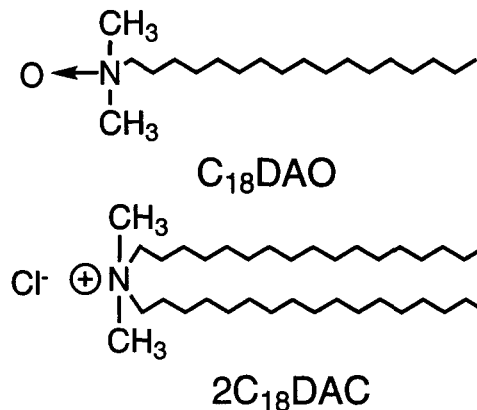

FIGURE 1. Chemical Structures of $C_{18}DAO$ and $2C_{18}DAC$

Chloroform solutions of the two compounds were individually spread on the water surface to prepare Langmuir (L) films. The L film was compressed by a Teflon® coated aluminum barrier at a compression speed of 15 cm² min⁻¹ from an area of 900 cm². They were transferred to a gold evaporated slide glass by the conventional LB technique at 35 mN m⁻¹ at neutral pH. The water subphase was maintained at 25°C by a water circulator.

The infrared *p*-polarized RA measurements of the LB films were performed on a Nicolet Magna 550 FTIR spectrometer with an MCT detector at a resolution of 4 cm⁻¹. The number of scans was 1000 for each measurement. The temperature-dependent RA measurements of the LB films were performed from 35°C to 110°C.

RESULTS AND DISCUSSION

The infrared RA spectra of the $C_{18}DAO$ LB films depended on the number of layers as follows: For the monolayer film, the symmetric CH_3 stretching vibration mode ($v_s(CH_3)$) was almost invisible whereas the symmetric CH_2 stretching vibration mode ($v_s(CH_2)$) was intense in the CH stretching region (2800~3000 cm^{-1}). For the 3-layer LB film, however, the $v_s(CH_3)$ mode was clearly visible, and was comparable to the $v_s(CH_2)$ mode. This suggests that the film structure was better organized during the accumulating process. The lower shift of the $v_s(CH_2)$ mode from 2853 to 2850 cm^{-1} (respectively, for the monolayer and 3-layer LB films) also supports this organization. For more accumulated LB films, it was remarkable that the band intensity change of the $v_s(CH_2)$ mode was not proportional to the number of layers.

In the case of the $2C_{18}DAC$ LB film, the RA spectra depended on the number of layers showed a little different behavior from the previous spectra. The band intensity profile of this LB film was almost linear. However, the fitted straight line did not pass through the zero point.

If an LB film has completely homogeneous film structure from the bottom to the top layer, the band intensity profile should be a simple linearly proportional relation (4). Our results then suggest that the LB films investigated have a heterogeneous film structure. Since the band intensity for the monolayer LB film is different to the accumulated layers, the first layer is considered to have a specific molecular orientation.

In order to understand of the results, we attempted to apply the conventional 3-phase model (IR//air/LB/gold) calculation to the RA spectra. The calculation procedure was the same as that mentioned previously (5). In the calculation, the optical anisotropy reflecting the molecular orientation was taken into account for the film phase. With this calculation procedure, the molecular orientation angles of the $v_a(CH_2)$ (antisymmetric stretching) and $v_s(CH_2)$ modes (α and β) were quantitatively obtained. These angles were converted to the tilt angle of the hydrocarbon chain (γ) with the following equation (5).

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \qquad (1)$$

The results were, however, insensitive to the change of the band intensity. Although the band intensity itself largely jumped between the monolayer and 3-layer LB films, the calculated molecular orientation almost linearly changed all through the number of layers. The results by the 3-phase model could not clarify the physico-chemical properties of the LB films. This may be because this model ignored the heterogeneous change in the film phase.

We then proposed a 4-phase model. In this model, the film phase was divided into two phases for the first monolayer and the layers named LB1 and LB2 remaining, respectively. The first monolayer was thus separated from other layers. In this model, two unknown molecular orientation angles are introduced for one RA spectrum.

Then, the set of the two solutions would not be obtained rigidly. In the present study, however, we attempted to draw the solutions from one RA spectrum. The solutions of the orientation angles have maximum and minimum values to satisfy the border condition restricted by the observed value and the multiple reflection in the 4-phase system. We then obtained two molecular orientations in the two phases simultaneously from an RA spectrum where the result was expressed as an averaged value with a deviation bar.

The averaged orientation angles showed that the first monolayer in accumulated LB films may have similar film structure to the monolayer LB film, and the upper layers have better organized film structure for the two LB films. In particular, the tilt angle from the surface normal of the hydrocarbon chain in the LB2 phase was getting lower with an increase of the number of layers. Since the LB2 phase does not interact with the substrate directly, only the interaction among the film molecules should have played an important role to stabilize the film phase. Regarding the tilt angle in the LB2 phase, the tilt angle for the $2C_{18}DAC$ LB film was better organized than the $C_{18}DAO$ LB film. This may be because the two-leg (two hydrocarbon chains) molecule is likely to form a more stable molecular assembly than the one-leg molecule. Regarding the LB1 phase, the tilt angle for the $2C_{18}DAC$ LB film was also better ordered than the $C_{18}DAO$ LB film. This may reflect the difference of the net charge of the head-group on the film molecules. Since $2C_{18}DAC$ has a positively charged region in the head-group, this region may help the interaction between the head-group and the stronger gold-evaporated substrate ($C_{18}DAO$ has no net charge).

We also measured temperature dependence of the RA spectra for both LB films. The 7-layer LB film of each compound was used for the experiments. They were sufficiently dried in a desiccator in advance. The RA spectra of the $C_{18}DAO$ LB film showed clear melting temperature at ~ 50°C. The band intensity of the CH_2 stretching modes abruptly began to increase at about 50°C, and increased up to 60°C. Above 60°C, the intensity decreased to a lower value, and kept almost constant value for higher temperature.

On the other hand, the $2C_{18}DAC$ LB film showed no melting temperature in the temperature region between 20°C and 110°C. The band intensity began to increase at 50°C, but it was moderate. Above 70°C, the intensity rapidly increased, and continued to increase up to 110°C.

We also applied the 4-phase model to these RA results. The result indicated that the sufficiently dried LB film of $C_{18}DAO$ had quite ordered film structure, giving an homogeneous property. This stability remained until 40°C. At 50°C, however, the tilt angle of the hydrocarbon chain in the LB1 phase was greatly disordered, leaving the tilt angle in the LB2 phase not so disordered. This means the LB film showed a heterogeneous property at this temperature. At 60°C, the tilt angles of the two phases agreed with each other, again indicating the homogeneous

property. This should correspond to the complete melt of the film. The 4-phase model showed, in this way, that the first monolayer was firstly disordered before the entire film melted at 60°C.

The results for the 2C_{18}DAC LB film were quite different. This film did not show a complete melt, but only the LB1 phase was greatly disordered. The LB film at 35°C after the heating showed fairly good recovery of the film structure.

The difference between the LB films could be explained by the difference of the net charge of the head-groups and the number of the hydrocarbon chains in their molecules. The difference of the net charge should have affected on the property of the LB films more severely than the number-of-layer dependence.

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