Taylor & Francis
Taylor & Francis Group

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

ISSN: 1058-725X (Print) (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl19

Quantitative Estimation of Molecular Orientation in Langmuir-Blodgett Films of Octadecyldimethylamine Oxide and Dioctadecyl-dimethylammonium Chloride

Takeshi Hasegawa , Diyas A. Myrzakozha , Toyoko Imae , Jujiro Nishijo & Yukihiro Ozaki

To cite this article: Takeshi Hasegawa , Diyas A. Myrzakozha , Toyoko Imae , Jujiro Nishijo & Yukihiro Ozaki (1998) Quantitative Estimation of Molecular Orientation in Langmuir-Blodgett Films of Octadecyldimethylamine Oxide and Dioctadecyl-dimethylammonium Chloride, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 322:1, 227-232, DOI: 10.1080/10587259808030228

To link to this article: http://dx.doi.org/10.1080/10587259808030228

Published online: 24 Sep 2006.

Mol. Cryst. Liq. Cryst., Vol. 322, pp. 227–232
Reprints available directly from the publisher
Photocopying permitted by license only

Quantitative Estimation of Molecular Orientation in Langmuir–Blodgett Films of Octadecyldimethylamine Oxide and Dioctadecyldimethylammonium Chloride

TAKESHI HASEGAWA,[a] DIYAS A. MYRZAKOZHA,[b] TOYOKO IMAE,[c] JUJIRO NISHIJO[a] AND YUKIHIRO OZAKI[b]
[a]Kobe Pharmaceutical University, Kobe , Japan; [b]School of Science, Kwansei Gakuin University, Nishinomiya, Japan; [c]Faculty of Science, Nagoya University, Nagoya, Japan

Received 6 April 1998; accepted 27 April 1998

The molecular orientation in the Langmuir–Blodgett (LB) films of octadecyldimethylamine oxide (C_{18}DAO) and dioctadecyldimethylammonium chloride ($2C_{18}$DAC) was estimated by a newly proposed calculation method for the infrared reflection-absorption (RA) spectral data. The Y- and X-type multilayer LB films of both compounds were prepared respectively as LB(Y) and LB(X) for the RA measurements. There found a large difference in thermal stability between the LB(Y) and LB(X) films for both compounds. Above all, the 9-monolayer LB(Y) films showed a structurally heterogeneous property. The molecular orientation in the heterogeneous structure was explored by introducing a new analyzing method. The method revealed that the first monolayer directly deposited on a gold surface had a specific molecular structure arising from the interaction with the substrate. The structure is different from that in the rest layers. The LB(X) films were found to be thermally very stable; the thermal recovery was notably good comparing to the LB(Y) films.

Keywords Langmuir–Blodgett films; molecular orientation; infrared Reflection–Absorption spectra; thermal property; deposition type; octadecyldimethylamine oxide; dioctadecyldimethylammonium chloride

INTRODUCTION

Octadecyldimethylamine oxide (C_{18}DAO; Fig. 1) and dioctadecyldimethylammonium chloride ($2C_{18}$DAC; Fig. 1) have been investigated with an expectation that they may form unique molecular assemblies having new membrane property, since the head-groups are remarkably small comparing with those of ordinary detergents. One of the authors, Imae, revealed[1] that the Langmuir (L) films of C_{18}DAO contained a large amount of water molecules around the head-groups even at room temperature by using π-A isotherm and LB-AFM (atomic-force microscope) techniques. However, such hydration has never observed on the LB films of $2C_{18}$DAC[2]. This difference on the hydration property of the head-groups is considered to bring different interactions with a metal substrate when the L films are transferred on the substrate to form LB films.

We then constructed LB films of both compounds on gold substrates that can easily be subjected to the infrared reflection-absorption (RA) measurements to evaluate the molecular orientation. We studied the thickness, temperature and film-type dependencies on the film structure for C_{18}DAO and $2C_{18}$DAC. The structure was quantitatively explored by a new theoretical estimation algorithm. The algorithm was proposed in the line of a progress of the calculation method by Hasegawa et al. for the uniaxial multilayer LB films[2].

EXPERIMENTS

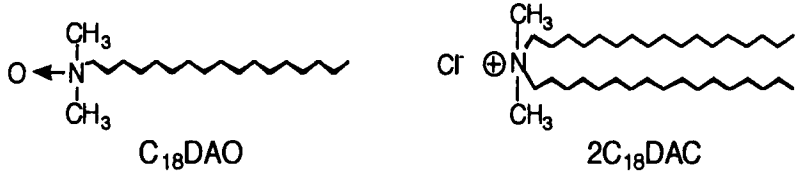

FIGURE 1 Molecular structures of C_{18}DAO and $2C_{18}$DAC

C_{18}DAO was prepared as previously described elsewhere[1]. $2C_{18}$DAC was purchased from Tokyo Kasei Co., Ltd. The Y- and X-type LB films were prepared respectively by the LB and horizontal-lifting (HL) methods. The film type was confirmed by the contact angle measurements of the surfaces of the LB films. The infrared RA measurements were performed on a Nicolet Magna 550 with MCT detector at a resolution of 4 cm^{-1}. The angle of incidence of the *p*-polarized infrared ray was set at 80° from the surface normal.

RESULTS AND DISCUSSION

The LB films of both compounds were first prepared by the LB method on gold-evaporated glass slides to form Y-type films. The thickness of the films was varied from one- to nine-monolayers. We noticed for C_{18}DAO LB films that the band intensity of antisymmetric and symmetric CH_2 stretching vibration modes did not change linearly with the thickness. Example RA spectra are shown in Fig. 2 for one- and three-monolayer (ML) LB films.

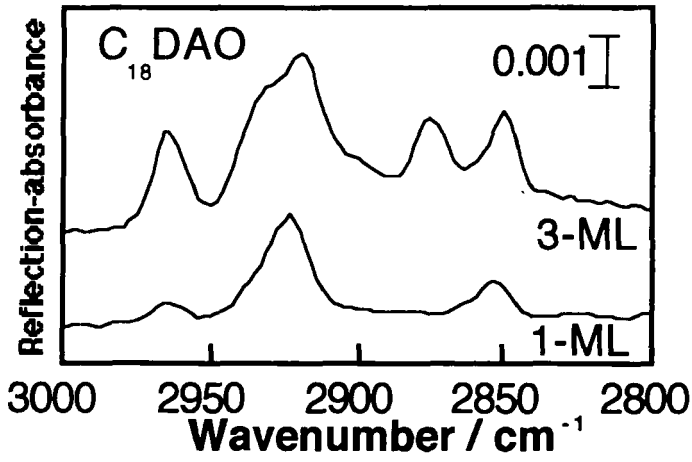

FIGURE 2 IR RA spectra of LB films of C_{18}DAO

Although the thickness of 3-ML LB film was three time greater than 1-ML

LB film, the bands intensity of the antisymmetric CH_2 stretching vibration at 2918 cm^{-1} were almost comparable to each other. This non-linearity was considered to be caused by the specific property of the first monolayer. Judging from the CH stretching vibration bands in the RA spectra, 1-ML LB film is found to have disordered film structure. The accumulated LB(Y) film, on the other hand, may consist of a disordered monolayer and upper layers with greatly improved organized-structure. In other words, the LB film showing the non-linearity has a heterogeneous structure as a whole.

In order to investigate the heterogeneous structure, a new method for theoretical estimation of the molecular orientation was introduced. The structurally heterogeneous LB(Y) film was assumed to have two distinctive phases which are the first and the rest monolayers. Since the first monolayer was separated from the other layers in the analysis, the two unknown molecular orientation angles were introduced for one RA spectrum. With this physical model, we cannot determine the two angles rigidly. However, if we assume a certain angle for one orientation angle, the range of the other angle would be determined with a deviation bar. Thus, both angles could be expressed using the deviation bars. For the calculation, a calculation algorithm[3] taking the uniaxial anisotropy into account was applied.

The calculated mean centered value gradually changed with the number of layers and explained the change of average molecular orientation in the LB(Y) films. The results showed that the first layer had clearly different film structure from the upper layers. It was also found that the accumulation of the upper layer contributed to have the first layer more organized. In the case of $2C_{18}DAC$, the band intensity change against the number of layer was almost linear, but the fitted straight line to the observed values did not pass through the zero point at all. This shift of the linearity was also explained by the unique film structure of the first monolayer. It was likely that the $2C_{18}DAC$ LB(Y) film has better organized film structure than the $C_{18}DAO$ LB(Y) film.

The thermal behavior of the LB(Y) films was more notable. The 9–

monolayer C_{18}DAO LB(Y) film showed melting temperature at about 60 °C. However, below this melting temperature, a clear phase transition was found at 50 °C by our new analytical procedure. This temperature is consistent with the transition temperature between isotropic and anisotropic phases in aqueous C_{18}DAO solution[4]. At this temperature, only the first layer showed a clear disorder while the upper layers remained the ordered structure. This strongly indicated that the first layer was affected by the heating earlier than the upper layers. The upper layers are considered to have stable structure due to the inter- or intra-layer interaction. In the case of the $2C_{18}$DAC, there found no apparent transition temperature in the temperature range from 20 to 110 °C.

The film-type (Y or X) dependence of the LB films on the film structure was also investigated. The corresponding LB(X) films to the LB(Y) films described above were prepared by the HL method. In this case, the non-linearity was not apparent for both C_{18}DAO and $2C_{18}$DAC LB(X) films. We then analyzed the molecular orientation in them by a simple homogeneous structure model.

The RA spectrum of a 7-layer C_{18}DAO LB(X) film showed notable temperature dependence. This relatively homogeneous LB(X) film showed a phase transition at 50 °C and melted at over 70 °C. In the case of the LB(Y) film, it melted at 60 °C. Therefore, it seems that the C_{18}DAO LB(X) film is more thermally stable than the LB(Y) films. This difference was considered to affect the stability of the two-dimensional crystal in the LB films.

For the $2C_{18}$DAC LB(X) films, there found more marked difference in thermal stability between the two film types. The film structure of the LB(X) films was unstable at a low temperature region (below 50 °C), while that of the LB(Y) film was very stable. However, above 50 °C, the LB(X) showed a remarkable thermal stability. It was also proved by the annealing experiment. After cooling down the LB(X) film from 110 °C, the RA spectrum showed good recovery in both band intensity and frequency.

The temperature dependence of the LB(X) films was then quantitatively

analyzed. It was clarified that the LB(X) films had worse molecular orientation at room temperature than LB(Y) films. However, with the increase in temperature, the LB(X) film proved to show notable thermal stability. The tilt angle of the hydrocarbon chain in the LB(X) films did not exceed 20° from the surface normal even when the temperature went up to 110 °C.

REFERENCES

[1.] O. Mori and T. Imae, *Langmuir* **11**, 4779 (1995).
[2.] O. Mori and T. Imae, *J. Colloid Interface Sci.* **198**, 11 (1998).
[3.] T. Hasegawa, S. Takeda, A. Kawaguchi, J. Umemura, *Langmuir*, **11**, 1236 (1995).
[4.] T. Imae, M. Sasaki and S. Ikeda, *J. Colloid Interface Sci.* **131**, 601 (1989).