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# Infrared studies of mixed Langmuir–Blodgett monolayers of octadecyldimethylamine oxide and dioctadecyldimethylammonium chloride with arachidic acid and poly(acrylic acid)

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**Abstract**

Infrared reflection–absorption spectra (IRAS) have been measured for monolayers of octadecyldimethylamine oxide ($C_{18}$DAO), dioctadecyldimethylammonium chloride (2$C_{18}$DAC) and their mixtures with arachidic acid and poly(acrylic acid) prepared by Langmuir–Blodgett (LB) technique on gold-evaporated glass slides. The spectra show that arachidic acid and $C_{18}$DAO or 2$C_{18}$DAC molecules form well-ordered monolayers with trans zigzag conformations. The order of the alkyl chain in $C_{18}$DAO is greatly increased upon the formation of the mixed LB film. The relative intensities of infrared bands due to $CH_2$ and $CH_3$ stretching modes of the hydrocarbon chains indicate that they are tilted with respect to the surface normal in the mixed LB films of arachidic acid and $C_{18}$DAO or 2$C_{18}$DAC. The hydrocarbon chains of $C_{18}$DAO and 2$C_{18}$DAC are disordered in the mixed LB films of poly(acrylic acid) and $C_{18}$DAO or 2$C_{18}$DAC. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Carboxylic acid; Infrared absorption spectroscopy; IRAS; Solid–gas interfaces; Surface structure, morphology, roughness, and topography; Vibrations of absorbed molecules

## 1. Introduction

The fabrication of a close-packed assembly of amphiphilic molecules at the air–water interface by the Langmuir method usually requires suitable subphase conditions, such as ionic content, concentration, pH and temperature [1,2]. It has long been known that improvement in the floating stability and deposition characteristics of amphiphiles with long hydrocarbon chain(s) can be achieved by adding a small amount of cations to the subphase [1,2]. The effects of organic and/or polymeric compounds, soluble in the water subphase, on the stability of amphiphiles at the air–water interface have been studied very intensively [3]. We have investigated the effects of poly(acrylic acid) (PAA), which is soluble in water, on the monolayers of octadecyldimethylamine oxide ($C_{18}$DAO) and dioctadecyldimethylammonium chloride (2$C_{18}$DAC). PAA acts as a Lewis base in the Langmuir trough. It has also been examined

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whether the structure of $C_{18}$DAO and $2C_{18}$DAC monolayers transferred onto gold-evaporated glass slides is susceptible to the presence of arachidic acid, whose chain length is similar to those of the alkyl chains of $C_{18}$DAO and $2C_{18}$DAC.

## 2. Experimental

$C_{18}$DAO and $2C_{18}$DAC employed in the present study were the same as those previously used [4]. Both arachidic acid and PAA (molecular weight 450 000 with a $T_g$ of 106°C) were purchased from Aldrich Chemical Co. and used without further purification. The instrumentation and techniques for the fabrication of Langmuir–Blodgett (LB) films of $C_{18}$DAO and $2C_{18}$DAC on gold-evaporated glass slides were described elsewhere [4].

The infrared reflection–absorption spectra (IRAS) were obtained at a 4 $cm^{-1}$ resolution with a Nicolet Magna 550 IR spectrometer with an MCT detector. To generate the spectra with a high signal-to-noise ratio, more than 1000 interferograms were added.

## 3. Results and discussion

The surface pressure–area ($\pi$–$A$) isotherms of $C_{18}$DAO on a pure water subphase (1), an equimolar mixture of $C_{18}$DAO and arachidic acid on the same subphase (2), and $C_{18}$DAO on a water subphase containing PAA of $2.4 \times 10^{-5}$ M (in monomeric unit concentration) (3) are shown in Fig. 1. All the isotherms exhibit clearly the transition from the gas-like structure to liquid-condensed, and eventually to the solid-like structure with an increase in the surface pressure. In order to investigate the stability of isotherm curves, cycles of compressions and expansions have been repeated. The isotherm traces were found to change little during the cycles. Extrapolating the linear portions, corresponding to the solid-condensed phase, to zero surface pressure, the intercepts are given as 0.63 $nm^2$ $molecule^{-1}$ for the $C_{18}$DAO film on the pure water subphase, 0.22 $nm^2$ $molecule^{-1}$ for the mixed film of $C_{18}$DAO and arachidic acid on the same subphase,

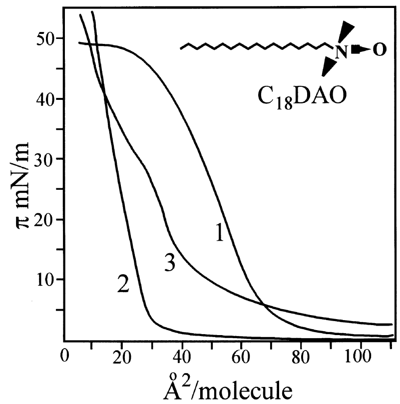


Fig. 1. $\pi$–$A$ isotherms for monolayers of $C_{18}$DAO on a pure water subphase (1), its equimolar mixture with arachidic acid on the same subphase (2), and $C_{18}$DAO in a PAA-containing water subphase (3). In this figure and Fig. 2 the surface area shows the occupied area by the two surfactants, giving only an average value of the mixture.

and 0.40–0.50 $nm^2$ $molecule^{-1}$ for the $C_{18}$DAO monolayer on the PAA-containing water subphase. This implies that a more close-packed $C_{18}$DAO monolayer can be formed in the presence of arachidic acid and PAA. Another noteworthy point is that on the pure water subphase the phenomenon of collapse occurs at a surface pressure of about 48 mN $m^{-1}$, but in the presence of arachidic acid or PAA the solid-like $C_{18}$DAO monolayer can be sustained even above 70 mN $m^{-1}$. Similar densely packed $2C_{18}$DAC monolayers can be formed at the air–water interface by adding arachidic acid or PAA (Fig. 2). This implies that the polymeric nature of PAA itself is advantageous regarding the formation of extremely rigid films. Since the protonated nitrogen atoms of $C_{18}$DAO and $2C_{18}$DAC are linked upon interacting with the carboxyl group of PAA, their repulsive interaction would become insignificant so that the densely packed monolayer forms readily at the air–water interface.

The weak-base $C_{18}$DAO and cationic $2C_{18}$DAC, acting as a Lewis base, can be mixed with a weak acid, such as arachidic acid, which has a similar hydrocarbon chain and which readily forms well-ordered LB monolayers. The high stability of mixed LB films may be due to the strong acid–base-type of interaction between the head

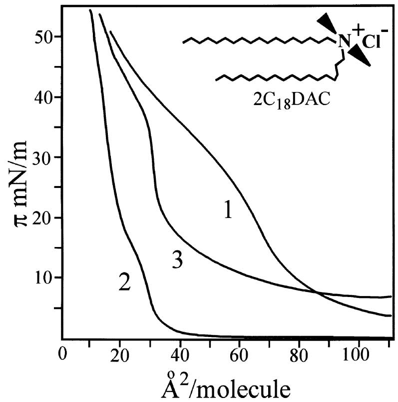


Fig. 2. $\pi$–$A$ isotherms for monolayers of $2C_{18}DAC$ on a pure water subphase (1), its equimolar mixture with arachidic acid on the same subphase (2), and $2C_{18}DAC$ in a PAA-containing water subphase (3).

group of $C_{18}DAO$ and $2C_{18}DAC$ and the carboxyl group of arachidic acid. The mixed LB films of $C_{18}DAO$ and arachidic acid have been studied using the atomic force microscope (AFM) by one of the authors [5]. However, their molecular orientation and structure have never been investigated. Fig. 3 shows the IRAS spectra of the mixed LB films of $2C_{18}DAC$ and arachidic acid (Fig. 3a), $C_{18}DAO$ and arachidic acid (Fig. 3b), $2C_{18}DAC$ and PAA (Fig. 3c), and $C_{18}DAO$ and PAA (Fig. 3d) on gold-evaporated glass slides. These mixed LB films were deposited under a surface pressure of 25 mN m$^{-1}$. Bands near 2920 and 2850 cm$^{-1}$ are due to antisymmetric and symmetric $CH_2$ stretching modes of the hydrocarbon chains. It is well known that the frequencies of the $CH_2$ stretching bands of a hydrocarbon chain are sensitive to the conformational ordering of the chain [6]. When the chain is highly ordered (trans-zigzag conformation), the bands appear at 2918 and 2848 cm$^{-1}$, whereas if conformational disorder is included in the chain they shift upward to 2926 and 2856 cm$^{-1}$, depending upon the content of gauche conformers.

The $CH_2$ stretching bands are located at 2916 and 2849 cm$^{-1}$ in Fig. 3a and b, suggesting that the alkyl chains of $2C_{18}DAC$, $C_{18}DAO$, and arachidic acid are highly ordered in the mixed LB films. A band progression due to $CH_2$ wagging modes appears in the 1400–1200 cm$^{-1}$ region in

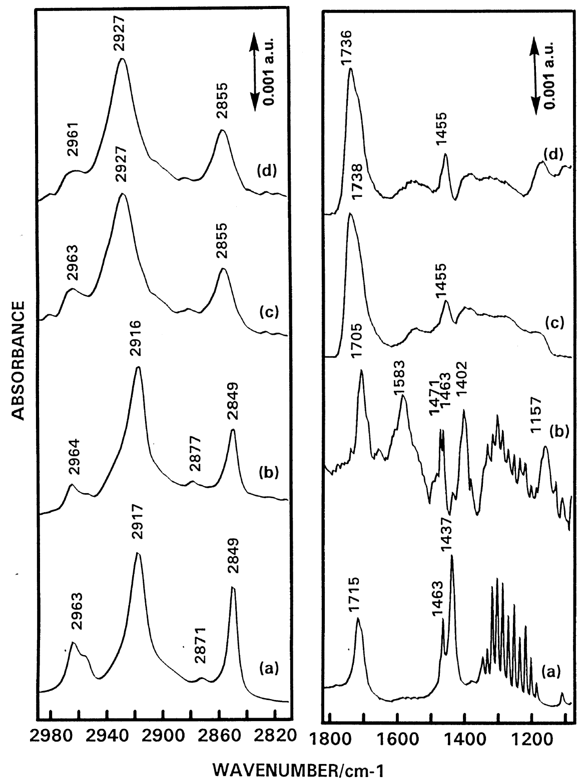


Fig. 3. FTIR reflection–absorption spectra of the mixed LB films on gold-evaporated glass slides. (a) The film of $2C_{18}DAC$ and arachidic acid; (b) the film of $C_{18}DAO$ and arachidic acid; (c) the film of $2C_{18}DAC$ and PAA; (d) the film of $C_{18}DAO$ and PAA.

Fig. 3a and b. The band progression may be due to the hydrocarbon chain of arachidic acid.

It was reported that the hydrocarbon chain is fairly disordered in a one-layer LB film of $C_{18}DAO$ on a gold-evaporated glass slide [4]. Therefore, the observation in Fig. 3b shows that the addition of arachidic acid to the molecular assemblies of $C_{18}DAO$ increases greatly the order of the alkyl chain. This conclusion is in good agreement with the observation in the $\pi$–$A$ isotherm in Fig. 1.

The intensities of the two $CH_2$ stretching bands are strong compared with those of $CH_3$ stretching bands near 2960 and 2875 cm$^{-1}$. This indicates that the alkyl chains are tilted from the normal direction with respect to the substrate in the mixed LB films. Other evidence for the tilt of the alkyl chains is the appearance of the out-of-plane component of the $CH_3$ asymmetric stretching mode at 2958 $cm^{-1}$. If the chains were nearly perpendicular to the substrate surface, only the in-plane component of the $CH_3$ asymmetric mode would appear at 2966 $cm^{-1}$.

A band near 1710 $cm^{-1}$ in Fig. 3a and b is assigned to a C=O stretching mode of arachidic acid. The frequencies of this band indicate that almost all the carboxylic groups in the mixed LB films are involved in the hydrogen bonds. Probably, in the mixed LB film of $2C_{18}DAC$ and arachidic acid they form the hydrogen bonds between the neighbouring hydrocarbon chains in a lateral fashion.

The situation is complicated for the mixed LB film of $C_{18}DAO$ and arachidic acid because bands due to the antisymmetric and symmetric $COO^-$ stretching modes also appear at 1583 $cm^{-1}$ and 1402 $cm^{-1}$ respectively. In addition, a band assigned to the N–O stretching mode is shifted from 1278 to 1157 $cm^{-1}$ upon going from the LB film of $C_{18}DAO$ to the mixed LB film [4]. Therefore, hydrogen bonds between (i) the carboxylic groups, (ii) the carboxylic acid and carboxylate groups, (iii) the carboxylic group and N–O group and (iv) the carboxylate group and $HO–N^+$ group may be considered. From the present infrared study, it is rather difficult to determine which is the major hydrogen bond in the mixed LB film. However, Mori and Imae [5], based upon an AFM study, suggested that the arachidic acid and $C_{18}DAO$ form mixed domains in the films. Therefore, the hydrogen bonds (iii) and (iv) may contribute greatly to the spectrum (Fig. 3b).

PAA was selected to demonstrate how water-soluble polymeric compounds can be transferred onto the metal surface by means of the LB technique. The mixed LB films of $2C_{18}DAC$ and PAA and of $C_{18}DAO$ and PAA show the $CH_2$ stretching bands at 2927 and 2855 $cm^{-1}$. These bands contain contributions from PAA as well as $2C_{18}DAC$ or $C_{18}DAO$. However, there is little or no band intensity near 2918 and 2848 $cm^{-1}$, indicating that the alkyl chains are disordered in the films. An intense feature near 1737 $cm^{-1}$ is due to a C=O stretching mode of the carboxylic group of PAA [7]. Although the peak top frequency ($\sim$1737 $cm^{-1}$) of the band is close to the frequency ($\sim$1743 $cm^{-1}$) of the C=O stretching band of the free carboxylic groups of PAA in a cast film [7], the band is very broad. Therefore, it seems that some of the carboxylic groups of PAA are involved in the hydrogen bonds in the mixed LB films.

## References

[1] A. Ulman, An Introduction to Ultrathin Organic Films, From Langmuir–Blodgett to Self-Assembly, Academic Press, New York, 1991.
[2] G. Roberts, Langmuir–Blodgett Films, Plenum Press, New York, 1990.
[3] G.A. Somorjai, Chemistry in Two Dimensions: Surfaces, Cornell University Press, Ithaca, NY, 1981.
[4] D.A. Myrzakozha, T. Hasegawa, J. Nishijo, T. Imae, Y. Ozaki, Langmuir, in press.
[5] O. Morie, T. Imae, Langmuir 11 (1995) 4779.
[6] J. Umemura, D.G. Cameron, H.H. Mantsch, Biochim. Biophys. Acta 32 (1980) 602.
[7] J. Dong, Y. Ozaki, K. Nakashima, Macromolecules 30 (1997) 1111.