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 (2C_{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 2C_{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 2C_{18}DAC. The hydrocarbon chains of C_{18}DAO and 2C_{18}DAC are disordered in the mixed LB films of poly(acrylic acid) and C_{18}DAO or 2C_{18}DAC.

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 (2C_{18}DAC). PAA acts as a Lewis base in the Langmuir trough. It has also been examined...
whether the structure of C18DAO and 2C18DAC 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 C18DAO and 2C18DAC.

2. Experimental

C18DAO and 2C18DAC employed in the present study were the same as those previously used [4]. Both arachidic acid and PAA (molecular weight 450 000 with a Tg 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 C18DAO and 2C18DAC 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 (p–A) isotherms of C18DAO on a pure water subphase (1), an equimolar mixture of C18DAO and arachidic acid on the same subphase (2), and C18DAO on a water subphase containing PAA of 2.4 × 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 nm² molecule⁻¹ for the C18DAO film on the pure water subphase, 0.22 nm² molecule⁻¹ for the mixed film of C18DAO and arachidic acid on the same subphase, and 0.40–0.50 nm² molecule⁻¹ for the C18DAO monolayer on the PAA-containing water subphase. This implies that a more close-packed C18DAO 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 C18DAO monolayer can be sustained even above 70 mN m⁻¹. Similar densely packed 2C18DAC 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 C18DAO and 2C18DAC 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 C18DAO and cationic 2C18DAC, 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. \( n-A \) 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).

The mixed LB films of 2C\(_{18}\)DAC 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\(_3\) wagging modes appears in the 1400–1200 cm\(^{-1}\) region in 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 \( n-A \) 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 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 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 ($\approx 1737$ cm$^{-1}$) of the band is close to the frequency ($\approx 1743$ 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