

## FT-IR Reflection-Absorption Spectra of Langmuir-Blodgett Films of Stearic Acid-d<sub>35</sub> on Silver

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*Received June 17, 1993*

1-, 3-, 5-, and 7-Monolayer Langmuir-Blodgett (LB) films of stearic acid-d<sub>35</sub> were fabricated on Ag-coated glass slides from the monolayer on the water surface at the surface pressure of 30 mN/m. Fourier transform infrared (FT-IR) reflection-absorption spectra (RAS) of these LB films were recorded. The spectrum of the 1-monolayer LB film was typical of the stearate-d<sub>35</sub> ion adsorbed on the Ag surface. The spectra of thicker LB films exhibited features characteristic of acid salt species, indicating that the Ag atoms of the substrate easily diffuse into the multilayered LB film as cations.

KEY WORDS: FT-IR reflection-absorption spectra (RAS) / Langmuir-Blodgett (LB) film / Deuterated stearic acid / Silver (Ag) substrate / Acid salt / Acid soap

### INTRODUCTION

Since Professor Emeritus Tohru Takenaka started the structural study of built-up films by using a dispersion-type infrared spectrophotometer in early 70's,<sup>1)</sup> our laboratory has continued and developed the molecular spectroscopic study for more than two decades. During the period, 'built-up film' was renamed as 'Langmuir-Blodgett (LB) film' and has attracted much attention because it can be arranged as organic super-lattices with planned structure and new functions. Also, instrumental developments including Fourier transform infrared (FT-IR) spectroscopy and the laser Raman spectroscopy using the charge coupled device (CCD) detector have enabled us to observe the infrared<sup>2)</sup> and Raman<sup>3)</sup> spectra of LB films at the monomolecular-layer level. Although we have extended the range of investigations to various functional materials,<sup>4-6)</sup> and much information about the molecular structure and orientation in thin LB films has been accumulated, many fundamental problems are still left unsolved.

In a previous paper,<sup>7)</sup> we have recorded the FT-IR reflection absorption (RA) spectra of LB films of stearic acid on the Ag substrate. Therein, we have found that the first monolayer in direct contact with the Ag surface gives no intensity for the C=O stretching band, irrespective of the number of monolayers. We have tentatively ascribed it to the image

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dipole effect, as in the case of ATR study of stearic acid on Ge.<sup>2)</sup> However, our careful examination of the band progression from 1400–1200  $\text{cm}^{-1}$  due to the  $\text{CH}_2$  wagging modes revealed the possibility of the presence of Ag stearate. Dote and Mowery have also demonstrated that metal stearates are partly formed in 1-monolayer LB films of stearic acid on Au and Al.<sup>8)</sup>

In the present work, therefore, we have investigated the FT-IR RA spectra of LB films of stearic acid- $\text{d}_{35}$  which has a clear window in the region of  $\text{COO}^-$  stretching frequency of Ag stearate on the Ag substrate.

### EXPERIMENTAL

Stearic acid- $\text{d}_{35}$  (98% purity) was purchased from Cambridge Isotope Laboratories and used without further purification. LB films were prepared by methods described in detail elsewhere.<sup>7)</sup> Briefly, the monolayer on the pure water subphase was compressed to a surface pressure of 30mN/m in the super liquid (LS) phase of the surface pressure ( $\pi$ )-area ( $A$ ) isotherm<sup>9)</sup> and then transferred onto an Ag-evaporated (100-nm thick) slide glass. FT-IR RA spectra with p-polarized radiation through a Hitachi wire-grid polarizer were recorded on a Nicolet 710 spectrophotometer equipped with a Harrick Model RMA-1DG/VRA reflection attachment at an angle of incidence of 85°. The spectral resolution was 4  $\text{cm}^{-1}$  and the number of interferogram accumulations was 3000.

### RESULTS AND DISCUSSION

Figure 1 shows the transmission spectra of collapsed monolayers of stearic acid- $\text{d}_{35}$  collected onto the  $\text{CaF}_2$  and Ge plates. The observed frequencies are tabulated in Table 1.

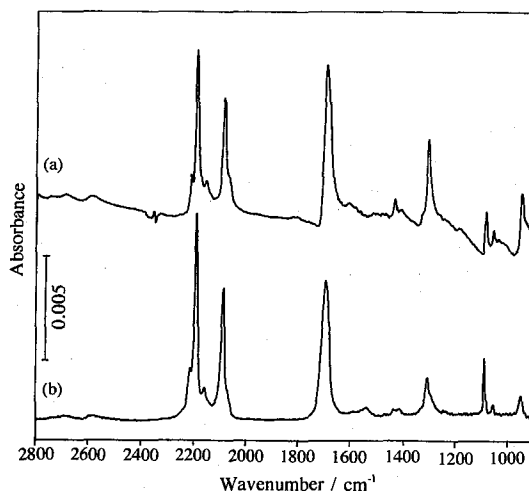


Fig. 1. FT-IR transmission spectra of collapsed films of stearic acid- $\text{d}_{35}$  on (a)  $\text{CaF}_2$  and (b) Ge plates.

Table 1. Infrared spectra and mode assignments of stearic acid-d<sub>35</sub>\*

Collapsed film		CCl <sub>4</sub> solution <sup>8</sup>	LB film (RAS)		Assignment	Reference
/CaF <sub>2</sub>	/Ge		1-ML	7-ML		
2686	2689	w	-	2688	$\nu$ OH	
2588	2586	w	-	2587	$\nu$ OH	
2212	2212	sh	2220	2219	$\nu_a$ CD <sub>3</sub>	10
2192	2191	2200	2192	2192	$\nu_a$ CD <sub>2</sub>	11
2156	2156	-	-	-	$2 \times \delta_a$ CD <sub>3</sub> - $\nu_s$ CD <sub>3</sub>	10
2086	2087	2095	2088	2087	$\nu_s$ CD <sub>2</sub>	11
sh	sh	-	2072	2071	$\nu_s$ CD <sub>3</sub>	10
-	-	-	-	1933	$\nu$ OH (Ag, acid salt)	20
-	-	-	-	1878	$\nu$ OH (Ag, acid salt)	
1694	1695	1710	-	1707	$\nu$ C=O	11
-	1606	w	-	-	-	
-	-	-	-	1586	$\nu_a$ COO <sup>-</sup> (Ag, acid salt)	
1537	-	-	-	-	$\nu_a$ COO <sup>-</sup> (Ge salt)	12
-	-	-	-	1465	$\nu_s$ COO <sup>-</sup> (Ag, acid salt)	
1432	1433	-	-	-	-	
-	-	-	-	1414	$\nu_s$ COO <sup>-</sup> (Ag, acid salt)	
1410	1412	w	-	-	-	
-	-	-	1390	-	$\nu_s$ COO <sup>-</sup> (Ag surface)	
-	-	-	-	1329	- (Ag, acid salt)	
1306	1306	1300	-	-	$\delta$ COH + $\nu_a$ C-C-O	13
-	-	-	1271	1266	-	
-	-	-	-	1242	- (Ag, acid salt)	
-	-	-	-	1214	- (Ag, acid salt)	
-	-	-	-	1167	- (Ag, acid salt)	
1085	1091	1085	1091	1086	$\delta$ CD <sub>2</sub>	10
1056	1057	-	1056	1056	$\delta_a$ CD <sub>3</sub>	10
950	950	-	-	950	$\gamma$ OD	13

\*w: weak, sh: shoulder

The spectra are principally the same with that of the CCl<sub>4</sub> solution<sup>8</sup> (see Table 1). On the CaF<sub>2</sub> plate, which has lower refractive index than the Ge plate, bands are slightly distorted by the anomalous dispersion effect of the refractive index (the Christiansen effect), which indicates that the collected collapsed monolayer is not a uniform film but rather consists of aggregated microcrystals or powders. On careful examination there are slight differences between spectra (a) and (b) in the region 1600-1400 cm<sup>-1</sup>. The relative intensities of the 1432- and 1410-cm<sup>-1</sup> bands are different between the two, and the 1537-cm<sup>-1</sup> band observed in the spectrum (b) is absent in (a). This might come from the surface Ge stearate-d<sub>35</sub> species in the spectrum (b), since the surface Ge arachidate gives 1535 and 1410 cm<sup>-1</sup> as the antisymmetric and symmetric COO<sup>-</sup> stretching frequency.<sup>12)</sup>

Figure 2 demonstrates the FT-IR RA spectra of 1-, 3-, 5-, and 7-monolayer LB films of stearic acid-d<sub>35</sub> on the Ag substrate. The spectral features in the CD stretching region appear to be of highly oriented hydrocarbon chains with stronger intensities of the asymmet-

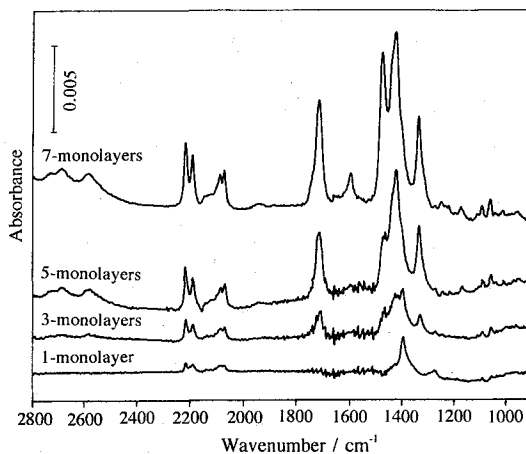


Fig. 2. FT-IR RA spectra of 1-, 3-, 5-, and 7-monolayer LB films of stearic acid- $d_{35}$  on the Ag substrate.

ric ( $2219\text{ cm}^{-1}$ ) and symmetric ( $2071\text{ cm}^{-1}$ )  $\text{CD}_3$  stretching bands than those of the antisymmetric ( $2192\text{ cm}^{-1}$ ) and symmetric ( $2087\text{ cm}^{-1}$ )  $\text{CD}_2$  stretching bands, respectively. In RA spectra of the alternating LB film of the Ba salt of 5-(*p*-dodecyloxyphenyl) pyrazine-2-carboxylic acid and stearic acid- $d_{35}$ , whose chain tilting angle from the surface normal was  $19^\circ$ , the  $\text{CD}_3$  stretching bands appeared weaker (by half) than the corresponding  $\text{CD}_2$  stretching bands.<sup>11)</sup>

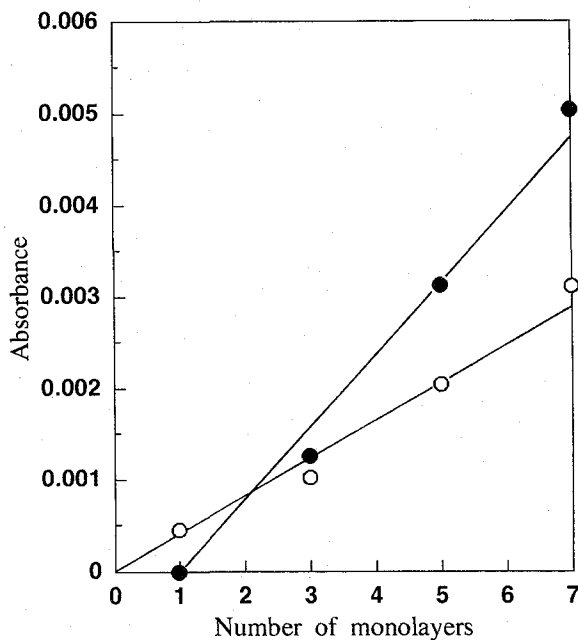


Fig. 3. Absorbances of  $\nu_{\text{s}}\text{CD}_2$  (○) and  $\nu_{\text{C=O}}$  (●) bands plotted against the number of monolayers.

Therefore, the chain tilt is very slight in this case, as in the case of LB films of non-deuterated stearic acid prepared from the LS phase.<sup>7)</sup>

On casual inspection, the spectrum of the 1-monolayer LB film in lower frequency region is apparently different from others: It lacks the C=O stretching band of stearic acid-d<sub>35</sub>, and shows a strong peak at 1390 cm<sup>-1</sup> (see Table 1). In Fig. 3, the absorbance of the C=O stretching band is plotted against the number of monolayers, together with that of the anti-symmetric CD<sub>2</sub> stretching band at 2192 cm<sup>-1</sup>. Although the least-squares line for the antisymmetric CD<sub>2</sub> stretching band passes through the origin, that for the C=O stretching band crosses the abscissa at the 1-monolayer position, indicating that the first monolayer in direct contact with the Ag surface in all LB multilayers has no intensity at the frequency of the C=O stretching mode. The similar phenomenon has been observed in our previous RAS measurements of LB films of non-deuterated stearic acid on Ag.<sup>7)</sup> The frequency of 1390 cm<sup>-1</sup> for the most intense band in the 1-monolayer LB film in Fig. 2 is very close to that (1395 cm<sup>-1</sup>) of the symmetric COO<sup>-</sup> stretching mode of the stearate ion adsorbed on the Ag surface, or adsorbed to the surface adatom.<sup>14)</sup> [Note that the corresponding bands of stearic acid and stearic acid-d<sub>35</sub> on the Au surface appear at 1385<sup>15)</sup> and 1380 cm<sup>-1,8)</sup> respectively.] Therefore, it is evident that stearic acid-d<sub>35</sub> molecules in the first monolayer in direct contact with Ag are fully ionized in this case, forming Ag stearate-d<sub>35</sub>.

In the spectrum of the 3-monolayer LB film in Fig. 2, the 1390-cm<sup>-1</sup> band remains and new peaks at 1414, 1465 and 1329 cm<sup>-1</sup> appears and grows with increasing the number of monolayers. Surprisingly, these frequencies are different from those of the stearic acid-d<sub>35</sub> (see Table 1). In the 7-monolayer LB film, the band assignable to the antisymmetric and symmetric stretching modes of Ag stearate-d<sub>35</sub> appears at 1586 and (1465, 1414) cm<sup>-1</sup>. In non-deuterated Ag stearate, the corresponding bands appear at (1563-7, 1521) and (1473, 1418) cm<sup>-1</sup>, respectively, although the 1473-cm<sup>-1</sup> band is overlapped with the CH<sub>2</sub> scissoring band.<sup>16,17)</sup> In the 7-monolayer LB film, the C=O stretching band also appears at 1707 cm<sup>-1</sup>, coexisting with the COO<sup>-</sup> stretching bands mentioned above. This indicates the presence of the acid salt or acid soap species. In 1:1 (=H:M) acid salts, MHX<sub>2</sub>, M being alkali metal, of monocarboxylic acid, HX, the two structural types, A and B, exist.<sup>18)</sup> In type A, two X molecules are crystallographically equivalent and linked with a very short symmetrical hydrogen bond, giving a very low frequency like 850 cm<sup>-1</sup> for the antisymmetric O-H stretching mode.<sup>19)</sup> In type B, the acidic radicals in the formula, M<sup>+</sup>X<sup>-</sup>, HX, are crystallographically distinct, one of them can be recognized as the anion and the other as in the neutral molecule. In acid soaps with longer hydrocarbon chains, they take various phases (structures), depending upon their hydrogen content.<sup>20)</sup> In the hydrogen rich L<sub>2</sub> phase, the infrared spectral feature is similar to that of type B, mentioned above, giving no significant changes in the frequency of the C=O stretching mode of the acid (HX) and the COO<sup>-</sup> stretching modes of the carboxylate (M<sup>+</sup>X<sup>-</sup>).<sup>21)</sup> Its characteristic is the appearance of new bands at around 2500 and 1900 cm<sup>-1</sup>. In Fig. 2, a broad band appears at 1933 cm<sup>-1</sup> in the multilayer LB films. Bands are also present at 2587 and 2688 cm<sup>-1</sup> in these LB films, but these bands already exist in the spectra of stearic acid (Fig.1) and the possibility of the overlapping with acid salt bands in this region remains. The spectral feature in the 7-monolayer LB film in Fig. 2 are also similar to the 1:1 acid salt of sodium laurate-lauric acid system.<sup>22)</sup> There is a possibility that the upper layer spectra are due to the different polymorphs of stearic acid-d<sub>35</sub>. However, it is

not natural that the LB film compressed to the high pressure LS phase is different in structure from the collapsed film. Therefore, above discussion leads to the conclusion that Ag atoms of the substrate easily diffuse into upper LB monolayers which is far (15 nm in the 7-monolayer LB film) apart from the substrate, forming acid salt. The spectra in Fig. 2 were recorded within 3-24 hrs after film preparation. They were re-measured after 113 days, giving no spectral change at all. Thus, the film structure of these LB films are very stable.

#### ACKNOWLEDGMENT

S. R. P. wishes to thank Professor Emeritus Tohru Takenaka of this institute for his kind accommodation to visit and work at this institute. This work was supported by the Grant-in-Aid for Scientific Research 03640406 from the Ministry of Education, Science and Culture, Japan.

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