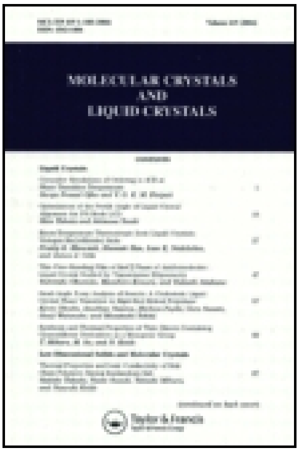

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INFRARED SPECTROSCOPIC STUDY OF SELF-ASSEMBLED AND LANGMUIR-BLODGETT NONADECANOIC ACID MONOLAYERS ON SILVER

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Abstract Self-assembled (SA) and Langmuir-Blodgett (LB) monolayers of nonadecanoic acid on the surface of silver have been investigated by reflection-absorption Fourier transform infrared spectroscopy. The molecule was chemisorbed on silver very favorably as nonadecanoate after losing the carboxylic proton. Although both the LB and SA monolayers consisted of fully extended trans zigzag molecular chains assembled in a crystalline state, the carbon chains of SA monolayers seemed to assume a more perpendicular stance with respect to the silver surface than those of LB monolayers.

INTRODUCTION

It has been generally recognized that the monolayers prepared by the self-assembly (SA) method are very similar to those prepared by the Langmuir-Blodgett (LB) technique. However, direct comparative studies of their structural details have scarcely been reported[1,2].

Recently, we have investigated the SA and LB monolayers of stearic and arachidic acids adsorbed on silver by infrared spectroscopy[3,4]. Although both the SA and LB monolayers consisted of fully extended trans zigzag carbon chains, a closer examination indicated that the SA monolayers should possess a more ordered crystalline structure than the LB monolayers. In order to know whether such a minute structural difference observable for even-numbered carbon chain acids exists also for odd chain acids, we have performed the infrared reflection-absorption (IRA) spectroscopic investigation on the LB and SA monolayers of nonadecanoic acid, a prototypical odd chain acid, anchored to the silver surface.

EXPERIMENTAL

The silver substrates were prepared by the resistive evaporation of silver on batches of previously chromium coated glass slides, and the substrates prepared in the same batch were used equally for the deposition of LB and SA monolayers.

To prepare the LB monolayers, 10^{-2} M nonadecanoic acid in chloroform was spread initially onto the water subphase at 20°C. After evaporation of the solvent, the monolayer was compressed at a constant rate of 1.0 mm min^{-1} up to a surface pressure of 30 mN m^{-1}. Maintaining the surface pressure at 30 mN m^{-1}, the condensed film was transferred to the silver surface by raising the immersed substrate at a rate of 1.0 mm min^{-1}. The SA monolayer was prepared by dipping the silver substrate into 10^{-3} M nonadecanoic acid in ethanol. The solution was initially bubbled with nitrogen, and the whole SA system was kept in the nitrogen purged dry box during the film deposition.

The infrared spectra were taken with a Bruker IFS 113v FT-IR spectrometer. To record the IRA spectra, the angle of incidence for the p-polarized light was set at 85°. Each spectrum was obtained by averaging 2048 interferograms at 4 cm^{-1} resolution. All IRA spectra have been reported as the $-\log(R/R_o)$, where R and R_o are the reflectivities of the sample and the bare clean silver substrate, respectively.

Unless otherwise specified, all chemicals and gases were reagent grade and used as received. Triply distilled water, of resistivity greater than 17.5 MΩ cm, was used throughout in the preparation of the LB monolayers.

RESULTS AND DISCUSSION

The adsorption of nonadecanoic acid on the silver surface occurred very favorably in the liquid state. The IRA spectra of the films obtained within 1 h of immersion were hardly different from those obtained after 8 days of immersion, suggesting that complete monolayers could be formed rather easily by contacting the silver substrate with the acid solution.

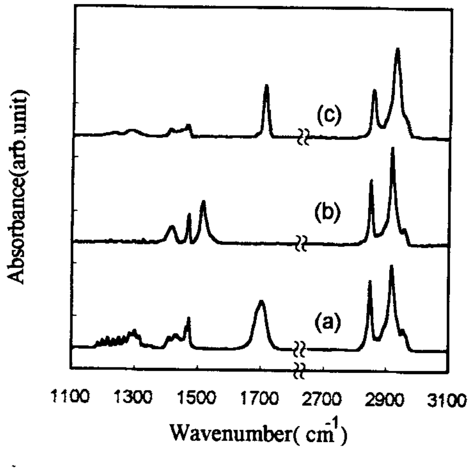

FIGURE 1 Transmission IR spectra of nonadecanoic acid (NA) (a) and its silver salt (b) in KBr matrices, and NA (c) in carbon tetrachloride.

In order to help interprete the IRA spectra, the transmission spectra of nonadecanoic acid and its silver salt were recorded in KBr matrices. The IR spectrum of nonadecanoic acid dissolved in carbon tetrachloride was also taken with a prism liquid cell. The corresponding spectra are shown in Fig. 1(a), (b), and (c), respectively. The peak positions and their appropriate vibrational assignments are collectively summarized in TABLE 1. Significant spectral differences are observed in the 1800-1100 cm^{-1} region. The ν(C=O) band appears distinctly at 1703 cm^{-1} in Fig. 1(a) and at 1711 cm^{-1} in Fig. 1(c), but completely absent in Fig. 1(b). Instead, the $\nu_s(COO^-)$ and $\nu_{as}(COO^-)$ bands are observable, respectively, at 1418 and 1517 cm^{-1} in Fig. 1(b). This implies that silver atoms should be symmetrically bonded to the carboxylate group when forming the silver salt. The so-called progressional bands are also seen distinctly in the acid spectrum (Fig. 1(a)) in the 1350-1150 cm^{-1} region. Such bands are known to occur from coupling between twisting and wagging of CH_2 units trans to each other[7]. Although weak, the corresponding bands are again identifiable in the salt spectrum, reflecting that the alkyl chains in the silver salt also consist of a trans zigzag structure.

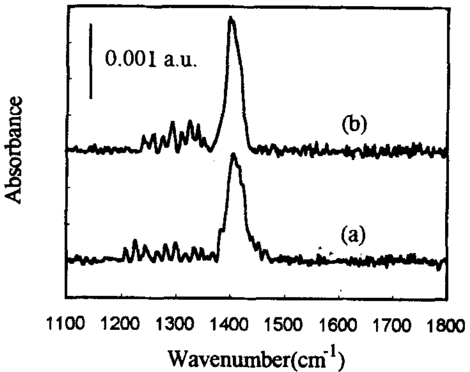

FIGURE 2 IRA spectra of LB (a) and SA (b) monolayers in 1800-1100 cm^{-1} region.

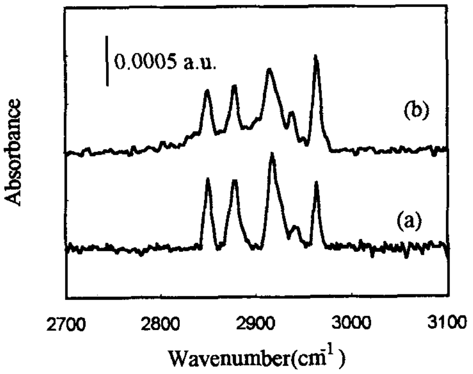

FIGURE 3 IRA spectra of LB (a) and SA (b) monolayers in 3100-2700 cm^{-1} region.

Fig. 2(a) and (b) represent, respectively, the IRA spectra of LB and SA monolayers of nonadecanoic acid on the silver surfaces in the 1800-1100 cm^{-1} region. The spectral pattern for the LB monolayers is very close to that of the SA monolayers. In both spectra, the C=O stretching band which appears at ca. 1700 cm^{-1} in Fig. 1(a) and (c) is completely absent. This absence, together with the presence of the symmetric stretching bands of the COO^- group at 1405 cm^{-1} in Fig. 2(a) and at 1403 cm^{-1} in Fig. 2(b), dictates that nonadecanoic acid is adsorbed on silver as nonadecanoate after losing the carboxylic proton. However, the anti-symmetric stretching band of the COO^- group is hardly seen in the IRA spectra. Referring to the

IRA selection rule[8], this indicates that the two oxygen atoms of carboxylate group of the adsorbed species should lie parallel to the silver surface. Further, the distinct appearance of $\nu_s(COO^-)$ band in Fig. 2 suggests that the carboxylate group should be bound to the silver surface via its oxygen lone pair electrons rather than the π orbitals. This may imply that the Ag-COO$^-$ bonding feature in the adsorbed state is much the same as that in the silver salt even though the bond strength in the adsorbed state is weaker than that in the salt state. Nonetheless, it is noteworthy to observe the progressional bands in the 1350-1150 cm^{-1} region for both the LB and SA spectra. This dictates that both monolayers should consist of fully extended close-packed structure, implying the twisting of the methylene units infeasibly to occur during the monolayer formation.

TABLE 1 Vibrational mode assignments of nonadecanoic acid(NA)[a]

$C_{18}H_{37}CO_2H$	$C_{18}H_{37}CO_2Ag$	SA NA/Ag	LB NA/Ag	Assignment[b]
		2964	2964	CH_3 asym str
2955(2958)[c]	2955			CH_3 asym str
		2938	2938	CH_3 sym str[d]
2917(2928)	2917	2918	2918	CH_2 asym str
2871(2878)	2873	2878	2878	CH_3 sym str
2849(2854)	2850	2850	2850	CH_2 sym str
1703(1711)				C=O str
	1517			COO$^-$ asym str
1472(1468)	1472		1471	CH_2 sci def.
1464			1464	
1431(1414)				C-O str+OH def
	1418	1403	1405	COO$^-$ sym str
			1384	CH_3 sym def
1150-1350	1150-1350	1150-1350	1150-1350	CH_2 wag + twist

[a]Wavenumbers in cm^{-1}. [b]Assigned based on ref. 5 and 6. [c]Values in parentheses correspond to the solution state. [d]In Fermi resonance with overtone of CH_3 asym def., and crystalline transition.

The $\nu_s(COO^-)$ band in Fig. 2(b) is more intense and sharper than that in Fig. 2(a). Assuming that the packing density of LB monolayers is similar to that of SA monolayers, this indicates that the C_1-C_2 axis of nonadecanoate in the SA monolayers should be more perpendicular to the silver surface than that in the LB monolayers. Further, the bands attributable to the CH_2 and CH_3 deformation are clearly seen at 1471 and 1384 cm^{-1}, respectively, in Fig. 2(a) while being barely seen in Fig. 2(b). This suggests that the CH_2 planes assume more parallel stance with respect to the metal surface in the SA monolayers than in the LB monolayers while the H_2C-CH_3 axis is directed more perpendicularly to the surface in the LB monolayers than in the SA monolayers. The present argument implies that the carbon chains in the SA monolayers should take more perpendicular orientation than those in the LB monolayers. This can be confirmed further from the spectral pattern in the C-H stretching region.

The IRA spectra of LB and SA monolayers on the silver surfaces in the C-H stretching region are shown in Fig. 3(a) and (b), respectively. In both spectra, the peak known to arise from a Fermi resonance interaction between the symmetric stretching vibration and the overtone of anti-symmetric deformation of the methyl group in a crystalline state[9] appears distinctly at 2938 cm^{-1}. In conjunction with the progressional bands, this indicates that the monolayers are composed of fully extended trans zigzag molecular chains assembled in a crystalline state. Since the peak positions of C-H stretching bands are hardly different between the LB and SA spectra, the packing density of LB monolayers is thought much the same as that of SA monolayers, as assumed previously. Besides, it is seen that the relative peak intensities in the IRA spectra are significantly different from those in the salt spectrum (Fig. 1(b)). In the surface spectra, the stretching bands of CH_3 group become as strong as those of CH_2 groups. On the other hand, the spectral pattern of LB monolayers is observed somewhat different from that of SA monolayers. In the LB monolayers, the $\nu_s(CH_3)$ band at 2878 cm^{-1} is more intense than the $\nu_{as}(CH_3)$ band at 2964 cm^{-1}, while the latter is more distinct in the SA monolayers. As mentioned previously, this dictates that the H_2C-CH_3 bond in the LB monolayers should possess a more perpendicular stance with respect to the silver surface than that in the SA monolayers.

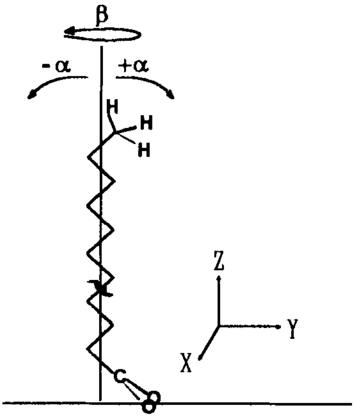

FIGURE 4 Angles of chain tilt (α) and chain twist (β).

For a more quantitative comparison to be made, the IRA spectral pattern in the C-H stretching region was simulated by using the Hansen's model[10], based on the complex refractive indices of silver metal[11] and silver nonadecanoate salt as well as the directions of the transition dipole moments in the CH_2 and CH_3 stretching vibrations[12]. Theoretical IRA spectra were obtained as a function of tilt and twist angles, defined, respectively, as the angle between the direction of CCC backbone and the surface normal and the angle between the CCC backbone plane and the surface normal plane (see Fig. 4). The simulated IRA spectrum best fit to the experimental one was found when the tilt and twist angles were set, respectively, at -4° and 4° for the LB monolayers and at 3° and 3.5° for the SA monolayers. The present calculation reveals that the direction of tilt, albeit small, is different between the LB and SA monolayers of nonadecanoic acid. A rather similar structural difference has been observed already for the LB and SA monolayers of stearic and arachidic acids[3,4].

Summarizing, this work reveals that well-ordered monolayers of nonadecanoate can be readily prepared on the silver surface by the SA method. The orientation of alkyl chains in the SA monolayers is concluded to be somewhat different from that in the LB monolayers. From the fact that the $\nu_s(COO^-)$ band is more inhomogeneously broadened upon the formation of LB monolayers than that of SA monolayers, the SA monolayers are conjectured to possess a more ordered crystalline structure than the LB monolayers. Since much the same observation can be made on the monolayers of stearic and arachidic acids, a minute structural difference observable between the LB and SA monolayers seems to be rendered to the difference in the method of film deposition rather than to the difference in the molecular characteristics.

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