

# Langmuir–Blodgett Films Containing Carotenoid Dye.

## I. Preparation and Characterization of Ethyl $\beta$ -Apo-8-carotenoate/Cadmium Stearate LB Films

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**ABSTRACT:** This article describes the preparation and characterization of ethyl  $\beta$ -apo-8-carotenoate dye/cadmium stearate mixed Langmuir–Blodgett films. The Wilhelmy plate method, FTIR spectroscopy, and contact angle measurements were the principal techniques utilized. Incorporation of cadmium stearate was observed to be critically important to the formation of ethyl  $\beta$ -apo-8-carotenoate/cadmium stearate mixed monolayers in the highly condensed and easily transferable states. Surface pressure (P)–area (A) isotherm measurements on the mixed monolayers with varying compositions, showed that highly condensed monolayers can be formed at the air/water interface from mixtures containing as much as 20 mol % of the carotenoid dye. The mixed monolayers were successfully transferred onto the solid substrates as “Y-type” film by the vertical lifting method. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 779–785, 1997

**Key words:** Langmuir–Blodgett films; preparation; characterization; isotherm; carotenoid dye

### INTRODUCTION

Interest in Langmuir–Blodgett (LB) films has recently undergone a dramatic growth, particularly as a result of their potential applications as components of microelectronics devices, high resolution photoresists for microlithography, and nonlinear optical components.<sup>1–3</sup> A major trend in LB film research is to move from simple saturated fatty acids, which function as insulating layers, to functional surface-active compounds, which are electrochemically or photochemically active.

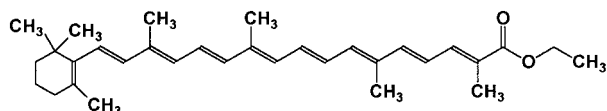
Carotenoids have recently been found to display efficient optical second harmonic generation both in the solid state and in solution.<sup>4,5</sup> The authors have postulated that highly ordered special

carotenoid dye with long conjugated double bonds, such as ethyl  $\beta$ -apo-8-carotenoate (EA8C) (Fig. 1) would have a potential for technically useful electroactive materials after doping with iodine or acids because it has the extended  $\pi$ -electron overlap along its highly conjugated structure.

It is, therefore, necessary to develop techniques for processing EA8C into highly ordered structures, such as LB films. But mainly due to its rigid elongated structure, EA8C alone is not able to form stable and transferable monolayer on the water subphase for LB films. It has been previously shown that the addition of fatty acid, such as stearic acid to the polymer solution increased the ability of the stable monolayer formation.<sup>6</sup> It is also well known that the collapse pressure of the fatty acid is greater for the subphase containing divalent metal ion than for the pure water subphase. The increase in collapse pressure was explained in view of the fact that the presence of a

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**Figure 1** The chemical structure of ethyl  $\beta$ -apo-8-carotenote (EA8C).

divalent metal ion causes two adjacent carboxylic acid head groups of fatty acids to bind together to one divalent metal ion, resulting in a more compressible monolayer with higher pressures.

Based upon these earlier observations, we have come to expect that the addition of divalent metal salts of fatty acids to EA8C would increase the stability of the monolayer and, thus, the fabrication of dye-containing electroconductive LB films would be possible. The fatty acid molecules would simply act as a processing aid by dispersing the EA8C molecules and rendering the resultant surface film flexible enough to be transferred into multilayers via the vertical dipping technique. The objective of this work was to find experimental variables, including chemical compositions, subphase pH, and the nature of divalent metal cation, for fabricating EA8C into LB films with highly ordered structures.

## EXPERIMENTAL

### Chemicals

EA8C (Fluka), stearic acid (TCI), cadmium chloride (Tokyo Kasei), barium chloride (Tokyo Kasei), chloroform (ISC), hydrochloric acid, sodium hydroxide, potassium bicarbonate, iodine, and sulfuric acid (Fluka) of a special grade have been used without further purification.

### Trough and Deposition Conditions for LB Films

A moving wall-type LB trough made in our laboratory for the preparation of LB films has been described in the previous publication.<sup>7</sup>

Surface pressure ( $\Pi$ )-area ( $A$ ) isotherms were found from a Wilhelmy plate method.<sup>8</sup> A piece of G7 grade filter paper with 8 mm width was used as the Wilhelmy plate and placed in front of a moving barrier. The force applied to the Wilhelmy plate was measured by using the strain gauge with 8.0 g capacity (Orientec). The subphase pH was adjusted by addition of either 0.1N HCl or 0.1N NaOH solution. The effect of dissolution of CO<sub>2</sub> on the subphase pH values were found to be

so small under our experimental condition that the adjusted pH values of the subphase were considered to be practically constant. The glass (Matsunami) substrate was etched with concentrated KOH-ethanol solution and then rinsed with the deionized water in a ultrasonic cleaner (Branson). Monolayers were compressed to surface pressures of 25–30 mN/m and then deposited onto the glass substrate at a rate of 25 mm/min. The subphase temperature was kept constant at 19°C.

Multilayer thin films of EA8C/cadmium stearate were formed from monolayers created by spreading mixed solutions of stearic acid and EA8C in chloroform onto a subphase of high purity water (resistivity: 18 M $\Omega$ cm) containing 5.0  $\times 10^{-4}$  M cadmium chloride and 1.0  $\times 10^{-4}$  M potassium bicarbonate.

### Measurements of Contact Angle

The contact angle of the cadmium stearate and EA8C/cadmium stearate mixed LB films with the water drop was measured using a contact angle meter G-1 (Erma) at room temperature.

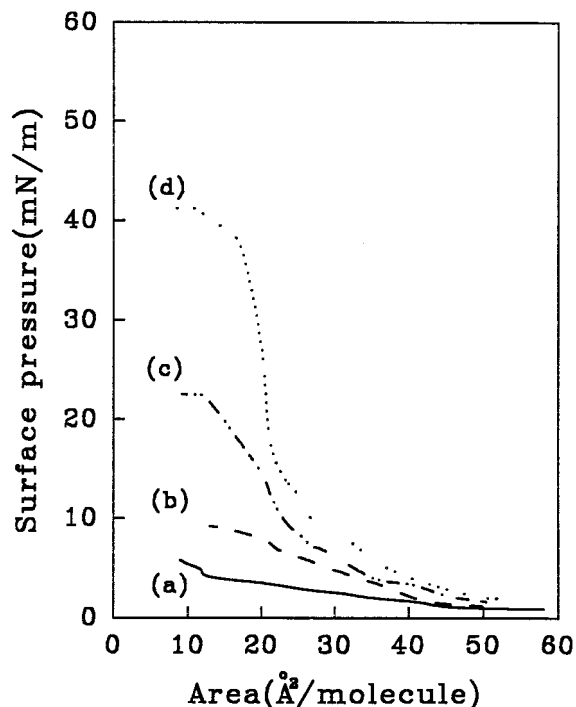
### FTIR Spectroscopic Measurements

FTIR spectra of EA8C/cadmium or barium stearate mixed LB films were recorded using a Digilab Division Bio-Rad FTS-60 spectrophotometer.

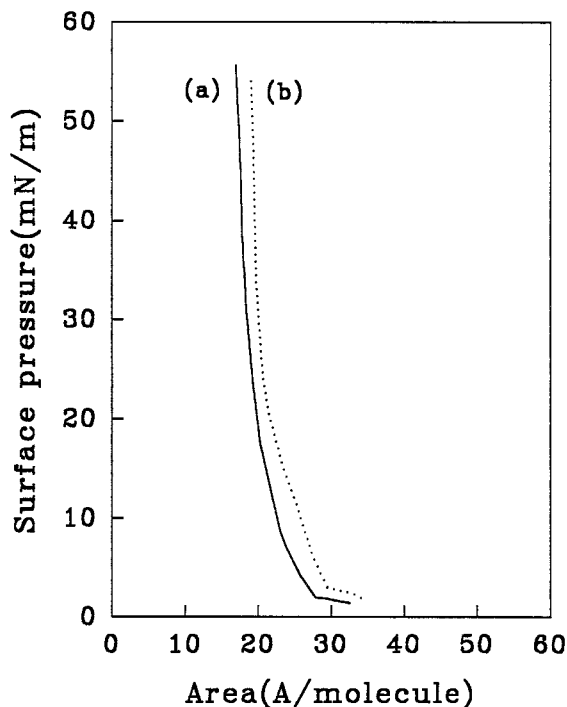
## RESULTS AND DISCUSSION

### Spreading Behaviors of EA8C/Cadmium Stearate Monolayers

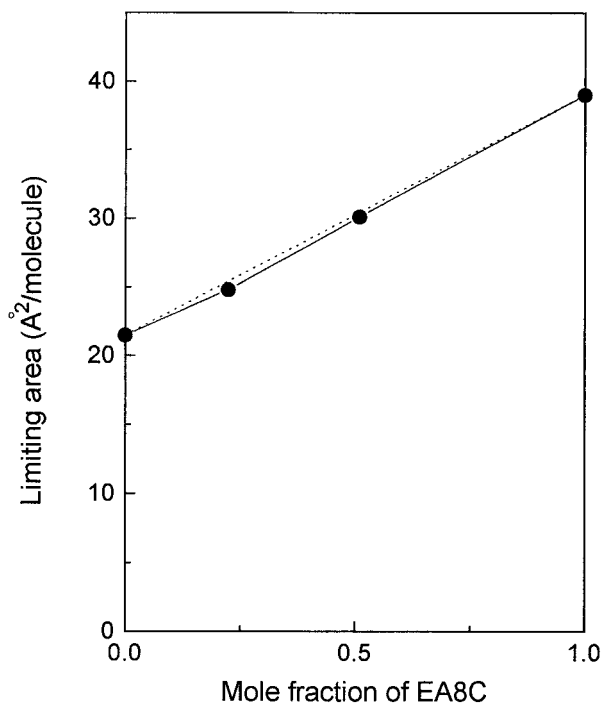
In order to find the possibility of the EA8C LB films being prepared from corresponding monolayers,  $\Pi$ -A isotherm of EA8C was obtained and shown in Figure 2(a). The isotherm exhibited that the EA8C monolayer was in a highly compressible, expanded state due to a loosely packed arrangement of the molecules. We further investigated the effects of divalent metal ions in the subphase, the  $\Pi$ -A isotherms of cadmium and barium salts of stearic acid were determined and are shown in Figure 3. Because cadmium stearate generated a more stable monolayer with less limiting area than barium stearate as shown in Figure 3, cadmium stearate was chosen as a spacer material for EA8C LB films. Thus, cadmium stearate was mixed with EA8C and the  $\Pi$ -A isotherms



**Figure 2** Surface pressure ( $\Pi$ )-area ( $A$ ) isotherms of EA8C/cadmium stearate mixed monolayers: (a) 1/0, (b) 4/1, (c) 1/1, (d) 1/4 molar ratios.

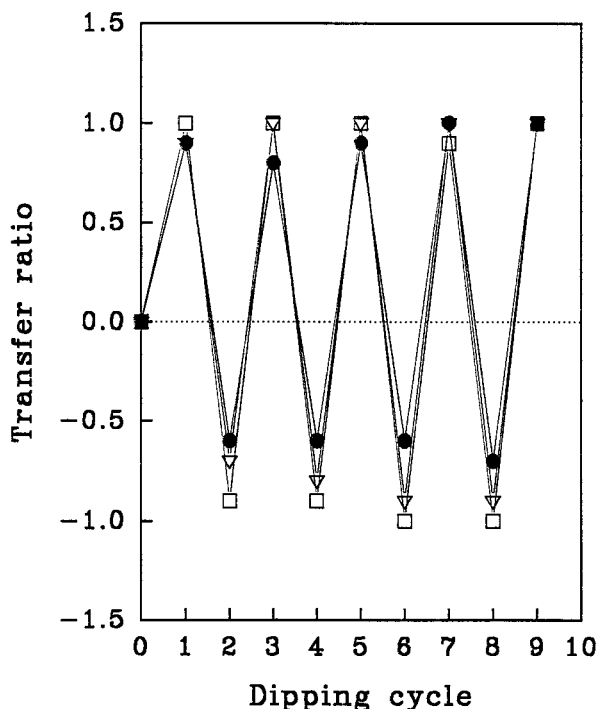


**Figure 3** Surface pressure ( $\Pi$ )-area ( $A$ ) isotherms of the stearic acid monolayers spread on the subphase containing (a)  $\text{Cd}^{2+}$ , (b)  $\text{Ba}^{2+}$ .



**Figure 4** Plots of the limiting area versus the mole fraction of EA8C for the EA8C/cadmium stearate mixed monolayers.

of EA8C/cadmium stearate mixed monolayers with molar ratios of 4/1 [Fig. 2(b)], 1/1 [Fig. 2(c)], and 1/4 [Fig. 2(d)] were determined. The EA8C/cadmium stearate mixed monolayers with the molar ratio of 4/1 and 1/1 still showed highly compressible expanded states and, thus, it was impossible to prepare uniform mixed LB films from these mixed monolayers. But the EA8C/cadmium stearate mixed monolayer with the molar ratio of 1/4 exhibited a fairly condensed state and was observed to be easily deposited to a glass substrate from a subphase. The  $\Pi$ - $A$  isotherm of this sample [Fig. 2(d)] was relatively steep and showed a collapse pressure of about 40 mN/m, being a value well above 20 mN/m required for transferring the monolayer to a solid substrate. If true random mixtures of EA8C and cadmium stearate were achieved, the limiting areas obtained by extrapolating the steepest part of  $\Pi$ - $A$  isotherm to zero surface pressure should exhibit a linear relationship with the mole fraction of EA8C as shown in Figure 4. These observations, the high collapse pressure for the 4/1 EA8C/cadmium stearate monolayer and the linear relationship between the limiting area and the mole fraction, suggested that EA8C was randomly dispersed in cadmium stearate rather than being

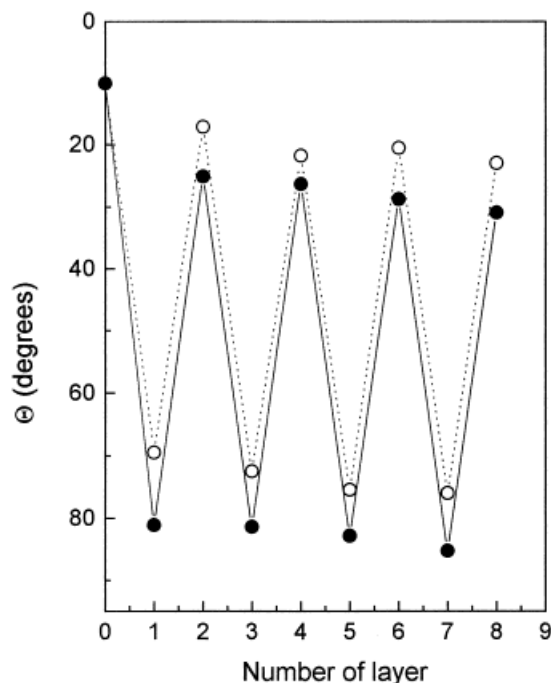


**Figure 5** Transfer ratio curves of the EA8C/cadmium stearate mixed monolayers as a function of molar ratio: (a) 0/1 ( $\square$ ), (b) 1/1 ( $\bullet$ ), (c) 1/4 ( $\nabla$ ) molar ratios.

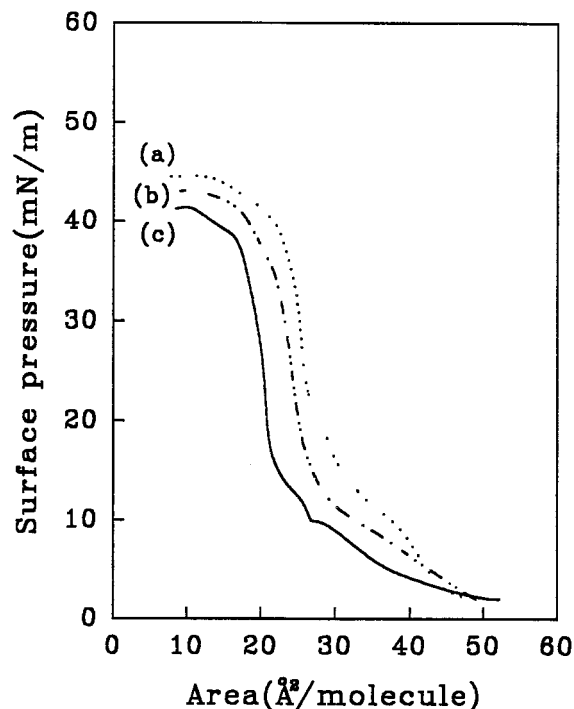
clustered in an individual island of EA8C and cadmium stearate.<sup>9</sup>

To investigate the effects of the spacer, cadmium stearate, on the preparation of EA8C/cadmium stearate mixed LB films, the average transfer ratio for 8 strokes of the monolayers is shown in Figure 5. This result indicated that the consistent transfer to a solid substrate was achieved by incorporating cadmium stearate to the EA8C monolayer. Especially the transfer ratio of EA8C/cadmium stearate mixed monolayer with the molar ratio of 1/4 was almost the same as that of the cadmium stearate monolayer. Surface polarity of the LB films was estimated from the contact angle ( $\theta$ ) measurements with the water drop, and the results are shown in Figure 6. Surface polarity of the LB films changed alternately from hydrophilic to hydrophobic nature with successively increasing the number of layers. Hydrophobicity of surfaces of EA8C/cadmium stearate mixed LB films appeared at odd numbered layers and the intensity of hydrophobicity increased with increasing the number of film layers. The surface of mixed LB films was more hydrophobic than that of cadmium stearate LB films. These results should be due to the "Y-type" nature of the LB films having a highly ordered structure.

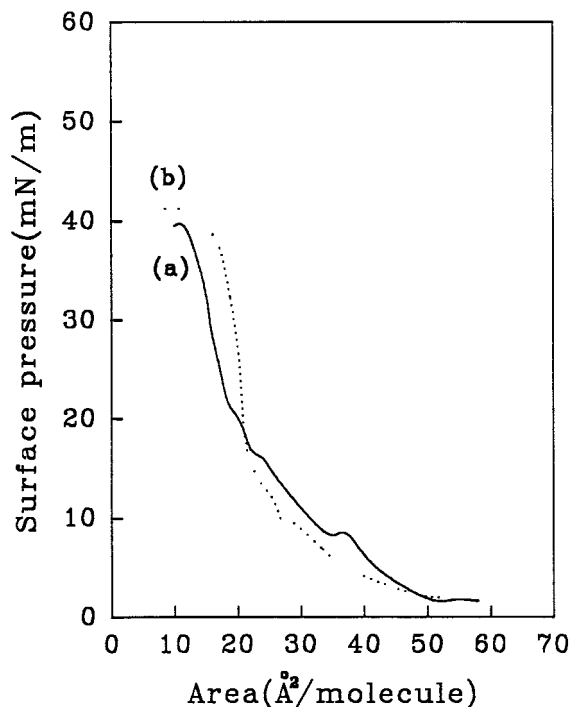
The effects of subphase pH on monolayer behaviors were investigated. Variation of subphase pH produced different ratios of salt (stearate ions) to free acid, and cations present in the subphase were adsorbed or bound to the floating monolayer. The relative amounts of  $-\text{COO}^-$  and  $-\text{COOH}$  groups in deposited layers affected the stability of the monolayers. Figures 7 and 8 exhibit the  $\Pi$ -A isotherm and the transfer ratio of the EA8C/cadmium stearate mixed monolayer as a function of the pH values of the subphase, respectively. Figure 7 confirmed that the maximum compressed surface pressure and the limiting area were somewhat influenced by the subphase pH. As shown in Figure 7, the smallest limiting area was obtained at pH 6 as a result of the highest molecular compression. Figure 8 suggested that the monolayer was transferred uniformly to a substrate on in-stroke and out-stroke at pH 6. In the case of pH 9, the transfer ratio is fairly less than one on, especially in-stroke. The observed low values of transfer ratios in the case of pH 9 are due to the increased hydrophilicity of the monolayers resulting from ionization of stearic acid, which in turn, increases the interaction between the monolayers and the water subphase. These observations clearly showed that the subphase pH value of 6 was most appropriate for the formation of



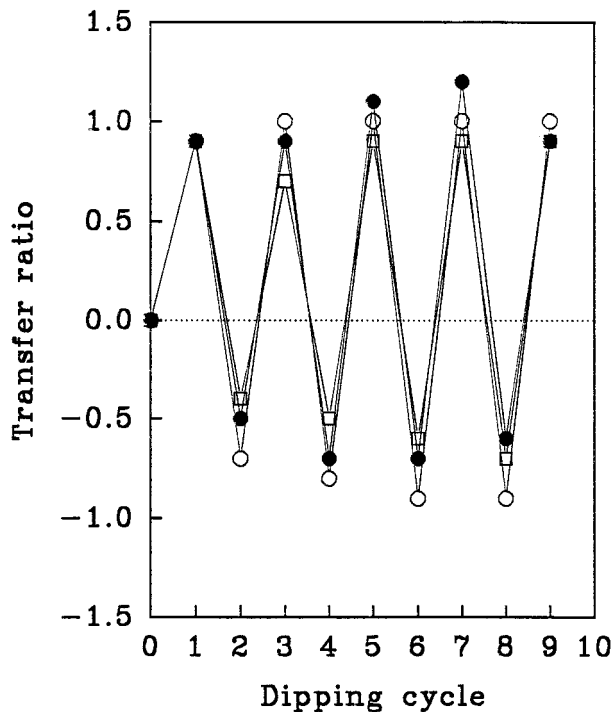
**Figure 6** Wettability of the surface of LB films prepared from cadmium stearate ( $\circ$ ) and EA8C/cadmium stearate ( $\bullet$ ) mixed monolayers.



**Figure 7** Surface pressure ( $\Pi$ )-area ( $A$ ) isotherms of the EA8C/cadmium stearate mixed monolayers as a function of pH: (a) pH 9, (b) pH 3, (c) pH 6.



**Figure 9** The effects of doping on the surface pressure ( $\Pi$ )-area ( $A$ ) isotherms of the EA8C/cadmium stearate mixed monolayers with molar ratio of 1/4: (a) doped by  $I_2$  dissolved in the water subphase, (b) undoped.



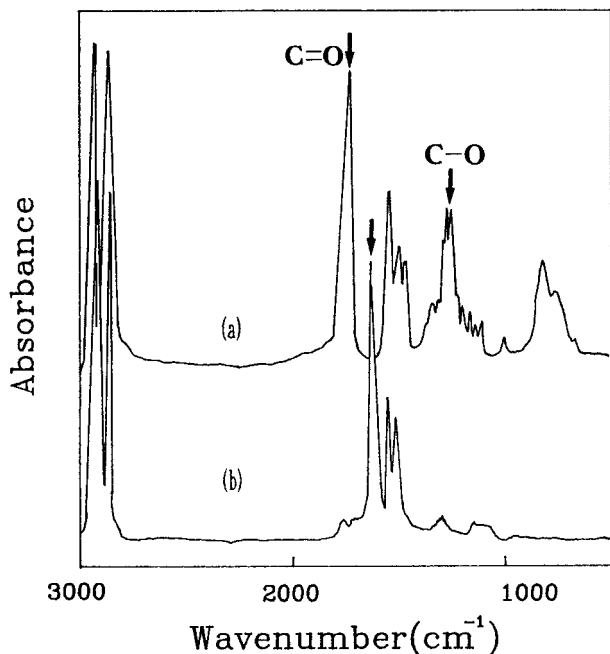
**Figure 8** Transfer ratio curves of the EA8C/cadmium stearate mixed LB films as a function of subphase pH: (a) pH 3 (●), (b) pH 6 (○), (c) pH 9 (□).

highly compressed films and for their uniform transformation to the substrate.

The effects of iodine on the  $\Pi$ - $A$  isotherms were investigated to see if highly conductive, ultrathin EA8C/cadmium stearate mixed LB films could be successfully prepared from EA8C/cadmium stearate/iodine mixed monolayers spread on water. As shown in Figure 9, the spreading behavior of the EA8C/cadmium stearate/iodine mixed monolayer was very similar to that of the EA8C/cadmium stearate mixed monolayer, which could be easily transferred to the solid supporting plate.

#### FTIR Spectroscopic Studies of LB Films

FTIR spectroscopy was utilized to obtain qualitative information on the formation of cadmium stearate and on the chemical composition of EA8C/cadmium stearate mixed LB films as a function of the aqueous subphase pH. Figure 10 shows typical FTIR spectra obtained from stearic acid powder and a cadmium stearate LB film. The bands centered at 2925 and 2865  $\text{cm}^{-1}$  are due to methylene groups. And the vibrational frequencies at 1710 and 1200  $\text{cm}^{-1}$  are characteristic



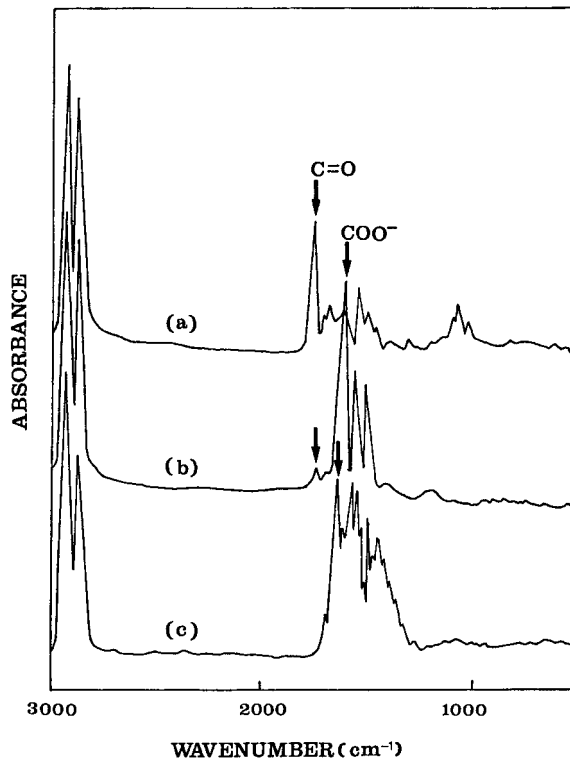
**Figure 10** FTIR spectra of (a) stearic acid powder (KBr), (b) cadmium stearate LB film.

peaks for hydrogen bonded carboxylic acid and are due to C=O and C—O stretches, respectively. The band centered at  $1580\text{ cm}^{-1}$  corresponds to asymmetric C=O stretch of carboxylate anion ( $\text{COO}^-$ ). The big frequency shift of the carbonyl group from  $1710$  to  $1580\text{ cm}^{-1}$  suggested that the acid protons of stearic acid monolayer, spread on water subphase containing cadmium cation, were displaced by cadmium cation to form cadmium stearate. FT-IR spectra of cadmium stearate LB films obtained at the three different pH values of the water subphase are shown in Figure 11. As expected, significant effects of the pH of the water subphase were noted. The cadmium stearate LB film prepared at subphase pH value of 3 shows a strong band at  $1700\text{ cm}^{-1}$  due to a carboxylic acid C=O group and a very weak band at  $1520\text{ cm}^{-1}$  due to asymmetric C=O stretch of carboxylate anion ( $\text{COO}^-$ ). These observations are quite natural because most of the carboxylic acid groups of stearic acid exist as acid form under the acidic condition. When the pH increases up to 6, the band intensity at  $1700\text{ cm}^{-1}$  significantly reduced, and a very intense band at  $1520\text{ cm}^{-1}$  appeared. With further increasing the pH of the water subphase up to 9,  $1700\text{ cm}^{-1}$  due to the carbonyl group of stearic acid completely disappeared and a very strong peak at  $1520\text{ cm}^{-1}$  was detected once again, suggesting that most of

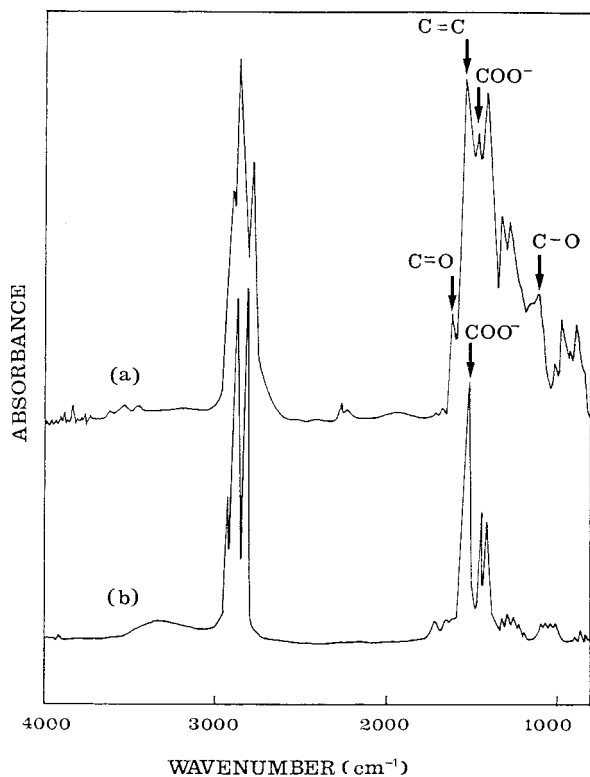
the acidic protons of stearic acid were displaced by cadmium cation at pH 6 and all of them were displaced by cadmium cation at pH 9. FTIR spectrum of the EA8C/cadmium stearate mixed LB film prepared at pH 6 together with that of the cadmium stearate film are shown in Figure 12. In Figure 12(a), the bands at  $1720$ ,  $1600$ , and  $1200\text{ cm}^{-1}$ , due to the ester carbonyl group, the C=C double bond, and the ester C—O bond, respectively, confirm the incorporation of EA8C in the LB film. The carboxylate carbonyl stretching vibration at  $1520\text{ cm}^{-1}$  also confirms the incorporation of cadmium stearate in the LB film.

## CONCLUSIONS

This work demonstrates that incorporation of cadmium stearate was observed to be important to the formation of EA8C/cadmium stearate mixed monolayers in the highly condensed and easily transferable states. The effects of subphase pH and chemical compositions of EA8C/cadmium stearate on the spreading behaviors of the EA8C/cadmium stearate monolayers were investigated.



**Figure 11** FTIR spectra of cadmium stearate LB films as a function of subphase pH: (a) pH 3, (b) pH 6, (c) pH 9.



**Figure 12** FTIR spectra of LB films prepared from (a) the EA8C/cadmium stearate mixed monolayer and (b) cadmium stearate monolayer.

The incorporation of the EA8C in the mixed LB films was confirmed by FTIR spectroscopy. The EA8C/cadmium stearate mixed monolayers with

molar ratio of 1/4 exhibited the condensed and randomly dispersed states at a subphase pH value of 6 with a collapse pressure of about 40 mN/m being well above the value of 20 mN/m required for transferring them to a solid substrate.

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