Effect of cadmium arachidate on molecular packing of zinc arachidate LB multilayers

P.K. Nayak, S.S. Talwar, S.S. Major, R.S. Srinivas

Abstract

Mixed zinc arachidate–cadmium arachidate (ZnA–CdA) LB multilayers deposited from varying subphase compositions have been characterized by FTIR and X-ray reflection (XR). The COO− symmetric stretching band of CdA and changes in CH2 scissoring band were used to monitor the CdA content and nature of molecular packing in the mixed multilayers. The XR pattern of pure ZnA multilayer with bilayer period of ∼47 Å corresponds to a rotator phase like ‘loose packing’ in a hexagonal layer cell. However, the presence of low concentrations of cadmium ion in subphase (2–5 mol%) results in biphasic multilayers with bilayer periods of ∼47 and ∼51 Å. In the cadmium concentration range of 10–25 mol%, the multilayers exhibit sharp (0 0 l) peaks in XR pattern, corresponding to a single layered structure with alkyl chains tilted by ∼23° from layer-normal. Increase in the cadmium concentration (30–50 mol%) results in biphasic multilayers with bilayer periods of ∼52 and ∼55 Å, the later corresponding to a herringbone type packing of alkyl chains, perpendicular to the layer plane. At higher concentrations of CdA, the layered structure and molecular packing resemble that of pure CdA multilayer.

Keywords: Langmuir-Blodgett; Mixed multilayers; Cadmium arachidate; Zinc arachidate; Effect of cadmium arachidate

1. Introduction

Organic multilayers deposited by the Langmuir-Blodgett (LB) technique have been the subject of intense research due to the rich variety of organized molecular layered structures they provide [1,2]. Long chain fatty acids and their divalent arachidate/stearate metal salts such as cadmium arachidate (CdA) and lead arachidate (PbA) have been the most extensively studied LB systems and their three dimensional structure and molecular packing have been investigated using a variety of techniques [3–9]. CdA molecules are known to pack in a rectangular herringbone arrangement, with alkyl chains nearly perpendicular to the layer plane [6–9], the ideal closed packed structure of long chain organic compounds [10]. In contrast, the molecular packing in zinc arachidate (ZnA) multilayers is based on a ‘rotator phase like’ loosely packed hexagonal layer cell, with alkyl chains tilted at an angle of ∼32° from the layer-normal [9,11], which is distinctly different from that reported for any other fatty acid salt multilayer. It has also been shown that the layered structure in ZnA multilayers, in fact, depends strongly on subphase pH at which the monolayers are transferred [12]. It is of interest to investigate the mixing behaviour of CdA and ZnA, which are systems similar in many respects and yet show very dissimilar organizational behaviour, both at the air water interface as well as in multilayer structures. The interest is mainly from the viewpoint of understanding nanostructured composite organic systems and is also prompted by the possibility of using these mixed multilayer systems as precursors to develop alloy semiconductor nanoclusters such as sulphides, selenides and oxides within organic matrix as well as inorganic alloy nanocrystalline filims.

In an earlier work [13], it has been reported that CdA–ZnA mixed multilayers with comparable concentrations exhibit presence of two types of structural domains with different molecular packings. In the present work, the ZnA rich mixed LB multilayers have been studied to explore the effect of CdA on the molecular packing of ZnA, which is known to exhibit a variety of polymorphs with unusual three dimensional structures [14].
Based on these studies, a complete phase diagram of the binary ZnA–CdA system indicating the three dimensional structure has been presented.

2. Experimental details

Mixed LB multilayers of zinc arachidate–cadmium arachidate (ZnA-CdA) were prepared by the conventional LB deposition technique using a KSV 3000 instrument in a clean room. A solution of arachidic acid (Aldrich, 99%) in HPLC grade chloroform (1 mg/ml) was spread on an aqueous subphase containing ZnCl2 and CdCl2 in varying proportions and a total concentration of 5 × 10−4 M. Deionised and ultra filtered water (Millipore) having resistivity of 18.2 MΩ cm was used to prepare the subphase. Mixed ZnA-CdA multilayers were prepared with varying cadmium concentrations in subphase. The sub-phase temperature was kept constant at 10°C and the subphase pH was maintained at 6.4 ± 0.1. The monolayer was compressed with a constant barrier speed of 3 mm/min. Though single phase, acid free CdA LB multilayers can be grown under much wider deposition parameters, ZnA LB multilayers have a much limited window for their deposition parameters such as pH to yield a single, most stable phase[12,14]. The deposition conditions of ZnA-CdA mixed multilayers were chosen within this window for their deposition parameters such as pH to yield a single, most stable phase[12,14]. The deposition conditions of ZnA-CdA mixed multilayers were chosen within this window for their deposition parameters such as pH to yield a single, most stable phase.

The deposition of ZnA–CdA multilayers was carried out with a constant barrier speed of 3 mm/min. Typically, 25 monolayers were transferred on quartz and CaF2 substrates for X-ray reflection and FTIR studies, respectively. Y-type depositions were observed with near unit transfer ratios with a constant barrier speed of 3 mm/min. Though single phase, acid free CdA LB multilayers can be grown under much wider deposition parameters, ZnA LB multilayers have a much limited window for their deposition parameters such as pH to yield a single, most stable phase[12,14]. The deposition conditions of ZnA-CdA mixed multilayers were chosen within this window for their deposition parameters such as pH to yield a single, most stable phase.

3. Results and discussion

In all the cases of mixed monolayers under the conditions mentioned above, the π–A isomers exhibited a condensed nature, without a liquid condensed region, that is indicative of complete ionization of arachidic acid [15]. The limiting mean molecular area (LMMA) obtained by extrapolating the solid region of the π–A isomers were found to be ≈20 Å², for all the compositions as expected for fatty acid salts [14].

Fig. 1(a) and (b) shows the FTIR spectra in the region, 2100–400 cm−1, for the as-deposited CdA and ZnA multilayers on CaF2 substrate, respectively. The overlapping peaks in the region of interest of FTIR spectra (as indicated below) were deconvoluted assuming Gaussian peak profiles. Chi-square minimization was used to obtain the best fit.

Table 1

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Peak positions (cm⁻¹)</th>
<th>CdA</th>
<th>ZnA</th>
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<tbody>
<tr>
<td>Asymmetric stretching, ν(CH2)</td>
<td>2918</td>
<td>2917</td>
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<tr>
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due to CH2 asymmetric and symmetric stretching vibrations of the alkyl chain of the arachidates. The shoulder at ~2952 cm⁻¹ is attributed to CH3 asymmetric stretching. The strong absorption band seen at ~1546 cm⁻¹ (in CdA) and ~1539 cm⁻¹ (in ZnA) are assigned to the asymmetric stretching vibrations of the carboxylate (COO⁻) group, consistent with the asymmetric COO⁻ stretch, normally observed for divalent fatty acid salts at ~1540 cm⁻¹ [16]. The presence of this band and the complete absence of O=C stretching band of unimerized carboxylic acid at ~1700 cm⁻¹ confirm that the as-deposited multilayers consist of arachidate salt and not a mixture of arachidic acid and salt. The bands seen at ~1421 cm⁻¹ (in CdA) and ~1397 cm⁻¹ (in ZnA) are assigned to COO⁻ symmetric stretch of respective arachidate salts [16]. There is, however, a noticeable difference in the nature of the CH2 scissoring band in the two cases. The CH2 scissoring band of the alkyl chain is known to be sensitive to the intermolecular interaction [7]. It appears as a doublet in the case of CdA multilayer indicating that the molecular packing in this case is orthorhombic subcell based close packed (herringbone

Fig. 1. FTIR spectra of (a) pure CdA, (b) pure ZnA and (c) mixed ZnA-CdA (with 40 mol% CdA in subphase) LB multilayers.

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type) with two molecules per unit cell, the characteristic packing of CdA multilayers [9]. In contrast, the ZnA multilayer shows a peak at \(\sim 1465\) cm\(^{-1}\), that indicates an intralayer molecular packing with one molecule per unit cell, attributed to the ‘rotator phase’ like hexagonal layer cell based loose packing observed in ZnA multilayers [9]. Fig. 1(c) shows the FTIR spectrum for a mixed ZnA–CdA multilayer with 40 mol% CdA, as a typical case. The FTIR spectra of all the mixed multilayers showed characteristic CH\(_2\) symmetric and asymmetric stretch as above but the bands associated with the COO\(^{-}\) group showed the effect of the presence of CdA and ZnA molecules within the multilayers. In particular, as seen in Fig. 1(c), the asymmetric COO\(^{-}\) stretch appears at \(\sim 1452\) cm\(^{-1}\), in between the corresponding values seen for pure CdA and pure ZnA multilayers. Further, the symmetric COO\(^{-}\) stretch appears at \(\sim 1421\) and \(\sim 1401\) cm\(^{-1}\). The above observations on the carboxylate group bands were seen in varying degrees in all the mixed arachidate LB multilayers. Most interestingly, the CH\(_2\) scissoring band shows a noticeable change in its shape indicating the presence of an overlapping doublet and singlet. It may be mentioned that none of the mixed multilayers showed \(\pi\)\(\pi\)O stretching band of unionized carboxylic acid at \(\sim 1700\) cm\(^{-1}\), confirming that all the mixed multilayers consist of arachidate salt and not a mixture of arachidic acid and salt. This observation is in tune with the nature of the \(\pi\)-\(A\) isotherms as mentioned earlier.

The changes observed in the characteristic COO\(^{-}\) group bands and the CH\(_2\) scissoring band of ZnA with the addition of CdA are discussed below. A continuous shift was observed in the asymmetric stretch of COO\(^{-}\) from \(\sim 1539\) cm\(^{-1}\) (ZnA) to \(\sim 1546\) cm\(^{-1}\) (CdA) over the composition range studied. However, there was no significant change in the shape of the band, except for small differences in the peak width. In comparison, the symmetric stretch of COO\(^{-}\) for pure ZnA and pure CdA showed marked differences. While pure ZnA showed a nearly symmetric peak at \(\sim 1397\) cm\(^{-1}\) along with a weak shoulder at \(\sim 1408\) cm\(^{-1}\), pure CdA showed a strong peak at \(\sim 1421\) cm\(^{-1}\) along with several shoulders. In view of the large difference in the nature and position of these peaks for ZnA and CdA, these were analyzed to assess the incorporation of CdA and ZnA in mixed multilayers. Fig. 2 shows the experimental and deconvoluted spectra for the symmetric stretch of COO\(^{-}\) observed in the range of 1380–1430 cm\(^{-1}\) for the pure and mixed multilayers. The bands obtained in the case of mixed multilayers with 2 and 5 mol% CdA, show an enhancement in the shoulder at \(\sim 1408\) cm\(^{-1}\), which is attributed to the incorporation of CdA in the mixed multilayers. Further, with increase in CdA content, the peak at \(\sim 1421\) cm\(^{-1}\) along with two shoulders at \(\sim 1413\) and \(\sim 1406\) cm\(^{-1}\), attributed to CdA, becomes prominent and the peak \(\sim 1400\) cm\(^{-1}\) decreases. These observations clearly show the incorporation of both CdA and ZnA in all the mixed multilayers.

The pure ZnA multilayer shows a broad and nearly symmetric scissoring band which is dominated by a peak at \(\sim 1465\) cm\(^{-1}\). In contrast, it is noticed from Fig. 3(b) that the presence of even 2 mol% CdA in the mixed multilayers diminishes the \(\sim 1466\) cm\(^{-1}\) peak and simultaneously the doublet \(\sim 1470\) and \(\sim 1462\) cm\(^{-1}\) becomes more prominent, with a stronger higher frequency component \(\sim 1470\) cm\(^{-1}\). Similar features are observed till the case of mixed multilayers with 20 mol% CdA. In the case of mixed multilayers with 20–30 mol% CdA, the lower frequency component of CH\(_2\) scissoring doublet becomes stronger. Subsequently, for 50 mol% CdA or more (not shown here), the scissoring band doublet dominates and resembles the features associated with pure CdA multilayer.

Fig. 4 shows the corresponding XR patterns of these multilayers showing third and higher order Bragg reflections. The average bilayer periods for CdA and ZnA were found to be \(\sim 55\) Å (herein after called \(\alpha\)-phase) and \(\sim 47\) Å (herein after called \(\delta\)-phase), respectively, as reported earlier [9]. A shoulder begins to appear in XR pattern of mixed multilayers with
2 mol% of CdA, which clearly develops into a separate set of Bragg peaks for the multilayer with 5 mol% of CdA. This new set of peaks correspond to a layered structure with a bilayer period of \( \sim 51 \text{ Å} \) (herein after called \( \beta \)-phase). The reduced bilayer period of \( \sim 51 \text{ Å} \) indicates that the molecules are tilted by \( \sim 23^\circ \) from the layer-normal. Interestingly, the mixed multilayers with 10–25 mol% of CdA show a single layered structure (\( \beta \)-phase) with the bilayer period \( \sim 51 \text{ Å} \). Multilayers with 30–50 mol% CdA shows the presence of peaks with two different bilayer periods, one corresponding to the \( \alpha \)-phase and the other to the \( \beta \)-phase with a bilayer period of \( \sim 52 \text{ Å} \). However, the mixed multilayers with 60 mol% or more CdA showed the presence of a single \( \alpha \)-phase similar to the pure CdA. These results are summarized in Fig. 5, which shows the approximate phase fields along the composition axis. In this figure, the observed bilayer periods are plotted as a function of the composition of the mixed LB multilayer. The boundaries of phase fields are clearly seen in this phase diagram.
4. Conclusions

Based on the XR and FTIR studies, the following inferences can be drawn. Mixed multilayers with 2–5 mol% of CdA show two types of layered structures and molecular packings. The fingerprint of the herringbone type packing starts appearing even at low concentration of CdA. The differences in the intensities of the high and low frequencies of the CH\textsubscript{2} scissoring doublet, characteristic of the herringbone packing is attributed to the tilting of molecular chains [18], which is supported by the appearance of a set of Bragg peaks which are attributed to \( \beta \)-phase. However, the presence of a peak at \( \sim 1465 \) cm\(^{-1}\) show the continued presence of molecular domains with ‘rotator’ like ‘loose’ packing. Interestingly, the mixed multilayers with 10–25 mol% of CdA show a single \( \beta \)-phase in terms of layered structure. However, the FTIR results suggest that the presence of two types of intralayer molecular packings within the same layered structure cannot be completely ruled out. The dominating presence of layered structure corresponding to a single \( \beta \)-phase is attributed to the influence of CdA molecules on the molecular packing of ZnA rich mixed multilayers, which results in the reduction of tilt angle to \( \sim 23^\circ \), as compared to \( \sim 32^\circ \) in pure ZnA multilayer. In the concentration range of 30–50 mol% of CdA, multilayers clearly consist of both \( \alpha \)- and \( \beta \)-phases. These results show that while a large concentration of ZnA (\( \geq 50 \) mol%) in the mixed multilayers has little effect on the three dimensional structure of the multilayers, CdA molecules, even at very low concentrations have a strong influence on the three dimensional structure of mixed multilayers.

Acknowledgment

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References