

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

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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 (00*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.

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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 films.

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].

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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 subphase 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 of deposition parameters, more particularly the subphase pH was maintained at the above mentioned value. The multilayer depositions were carried out at a surface pressure of 30 mN/m. 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 in all the cases.

FTIR studies were carried out with a Perkin Elmer make Spectrum One instrument. X-ray reflection (XR) studies were performed with X'pert Pro diffractometer using Cu Kα radiation in the 2θ range, 4–20°. FTIR and ICP-AES techniques were also used to study the composition of the multilayers. The multilayers were characterized by FTIR and XRD techniques at room temperature. Repeated measurements over prolonged periods confirmed the stability of the multilayers. 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.

3. Results and discussion

In all the cases of mixed monolayers under the conditions mentioned above, the π–A isotherms 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 isotherms were found to be $\approx 20 \text{ \AA}^2$, for all the compositions as expected for fatty acid salts [14].

Fig. 1(a) and (b) shows the FTIR spectra in the region, 1300–3200 cm⁻¹, for the as-deposited CdA and ZnA multilayers on CaF₂ substrate, respectively. The assignment of bands based on available literature [16] is listed in Table 1. The spectra of the multilayers show intense bands at ~ 2918 and ~ 2850 cm⁻¹

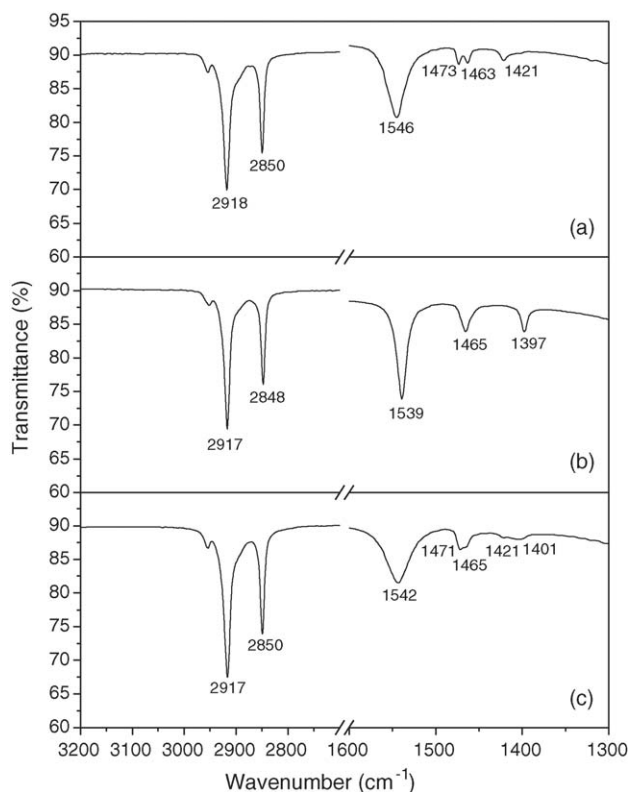


Fig. 1. FTIR spectra of (a) pure CdA, (b) pure ZnA and (c) mixed ZnA–CdA (with 40 mol% CdA in subphase) LB multilayers.

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 C=O stretching band of unionized 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 [17]. 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

Table 1
Band assignments for FTIR spectra of CdA and ZnA multilayers

Assignment	Peak positions (cm ⁻¹)	
	CdA	ZnA
Asymmetric stretching, $\nu_a(\text{CH}_2)$	2918	2917
Symmetric stretching, $\nu_s(\text{CH}_2)$	2850	2848
Asymmetric Stretching, $\nu_a(\text{COO}^-)$	1546	1539
Scissoring, $\delta(\text{CH}_2)$	1473, 1463	1465
Symmetric stretching, $\nu_s(\text{COO}^-)$	1421	1397

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