

Dependence of the structure of zinc arachidate LB multilayers on subphase zinc ion concentration and pH

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Abstract

Zinc arachidate (ZnA) multilayers transferred at different subphase pH and zinc ion concentrations in subphase are studied by X-ray reflection (XR) and FTIR studies. In this range of process parameters, the multilayers showed the presence of several phases, which were often coexistent. The observed phases were characterized by bilayer periods of ~ 56 Å (α), ~ 52 Å (β), ~ 51 Å (γ) and ~ 47 Å (δ). Although these polymorphic phases were observed at all the concentrations studied, pH windows over which the phases were observed, varied with concentration of zinc ions in the subphase. At lower end of zinc concentration, multilayers with single δ -phase could be obtained in the range of pH 6.6–7.1, but under most other conditions, the multilayers were found to be bi-phasic. Similar behavior was observed in the mid-range of zinc concentrations. However, at higher zinc ion concentrations, pure δ -phase could be deposited only in a narrow pH range of 6.2–6.3. Interestingly, in the pH range of 7.4–7.6, multilayers with pure α -phase could be deposited. FTIR spectra of all the multilayers showed overlapping singlet and doublet features corresponding to CH₂ scissoring band, indicating the presence of sub-cell packing of alkyl chains with both one and two molecules per unit cells. Thermal stability studies show that the δ -phase is the most stable phase of ZnA and melts at ~ 140 °C. The α -phase melts at relatively lower temperature (~ 110 °C). However, both β and γ phases undergo a gradual phase transition to δ -phase at ~ 130 °C.

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1. Introduction

Long chain fatty acids and their divalent arachidate/stearate metal salts such as cadmium arachidate (CdA) have been the most extensively studied LB systems and their three-dimensional structure and molecular packing have been investigated using a variety of techniques [1–10]. The molecular packing in the divalent metal fatty acid salt multilayers has been reported [5] to depend on the electronegativity of the metal ion and in several cases, corresponds to the closed packed structures proposed by Kitaigorodskii [11] for long chain organic compounds. These structures are based on orthorhombic, monoclinic and triclinic subcells in which the molecular chains are tilted at specific angles determined essentially by the constraints of optimizing chain packing density in the plane perpendicular to the chains. It has however been reported [12] that zinc arachidate

(ZnA) multilayers do not follow this trend, and the molecules pack in a distorted hexagonal layer cell with chains tilted at an angle $\sim 32^\circ$ towards the nearest neighbour. It has been shown [13], that the molecular packing in ZnA multilayers exhibits strong dependence on subphase pH, not observed earlier in LB multilayers of divalent fatty acid salts. Recently, the structures of the polymeric phases of ZnA have also been studied [14].

In view of the strong and unusual dependence of the structure of ZnA multilayers on subphase conditions, a detailed study of the combined effect of subphase zinc ion concentration and pH has been under taken. This work establishes the process parameter windows in which various stable polymorphic phases of ZnA LB multilayers can be obtained. Thermal stability of the polymorphic phases of zinc arachidate multilayers is also reported.

2. Experimental details

Zinc arachidate multilayers were made by the conventional LB deposition technique using a KSV 3000 LB instrument.

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Arachidic acid (Aldrich 99%) dissolved in HPLC grade chloroform as solvent (1mg/ml) was used to spread the monolayer on Millipore ultrafiltered water subphase (resistivity = 18.2 M Ω cm). ZnCl₂ (1 \times 10⁻⁵ M, 1 \times 10⁻⁴ M and 5 \times 10⁻⁴ M) was used as the subphase. The subphase pH was adjusted to desired values by adding dil. HCl, NaHCO₃ and NaOH solution to the subphase. The layers were transferred at a constant surface pressure of 30 mN/m and at a substrate dipping speed of 3 mm/min. The monolayers were transferred on quartz and CaF₂ substrates with near unit transfer ratio.

X-ray reflection measurements were carried out using an X'pert Pro diffractometer with Cu K α radiation. FTIR studies were carried out on multilayers transferred on CaF₂ substrates, using a Perkin-Elmer Spectrum One instrument. The as-deposited ZnA multilayers were annealed in a quartz tubular furnace in the temperature range 60–160 $^{\circ}$ C (\pm 5 $^{\circ}$ C) in air at atmospheric pressure. XR and FTIR measurements of all the samples were carried out at room temperature.

3. Results and discussion

The π -A isotherms for ZnA monolayers (not shown here) at all the subphase zinc ion concentrations were studied, to ensure complete ionization of arachidic acid, as reflected by the absence of a liquid condensed region in the isotherms. It was found that for the zinc ion concentrations of 1 \times 10⁻⁵ M, the liquid condensed region was absent for a subphase pH of 6.5 or above, while for the zinc ion concentrations of 1 \times 10⁻⁴ M and 5 \times 10⁻⁴ M, it was absent above a subphase pH of 6.3. The limiting mean molecular area (LMMA) obtained by extrapolating the solid region of the π -A isotherm was found to be \approx 20 \AA^2 for all cases, as expected for fatty acid salts [15].

The X-ray reflection patterns of ZnA multilayers transferred onto quartz substrates from the subphase containing 1 \times 10⁻⁵ M ZnCl₂ at different subphase pH values are shown in Fig. 1. The bilayer period was determined from the peak positions using the Bragg equation modified for refraction effect [16]. The corresponding alkyl chain tilt angles were calculated using a value of 27.5 \AA for the typical length of an arachidate molecule [2]. The XR patterns (Fig. 1(a)) for multilayers deposited at a subphase pH \sim 6.5 exhibit a single layered structure with a bilayer period of \sim 47 \AA (hereafter called δ -phase) corresponding to alkyl chain tilt angle of \sim 32 $^{\circ}$ from the layer normal. Monophasic ZnA multilayers consisting of δ -phase were obtained upto a subphase pH

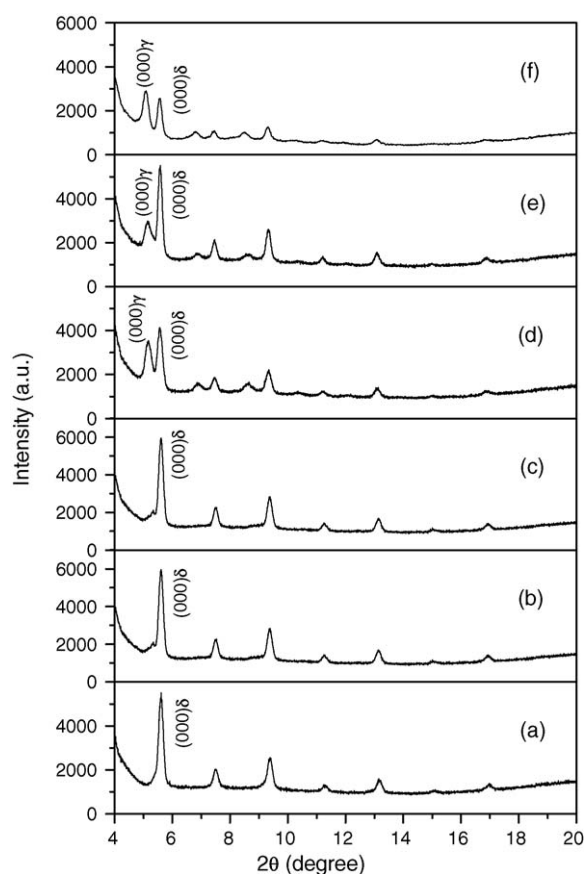


Fig. 1. XR reflection patterns of ZnA multilayers deposited from 1 \times 10⁻⁵ M zinc ion in subphase at pH of (a) 6.5, (b) 6.7, (c) 7.0, (d) 7.2, (e) 7.5 and (f) 7.7.

of 7.0 (Fig. 1(b and c)). Further increase in subphase pH causes formation of biphasic layered structures with bilayer periods of \sim 47 \AA (δ -phase) and \sim 51 \AA (hereafter called γ -phase), as seen in Fig. 1(d–f). It may be mentioned that the γ -phase consists of alkyl chains tilted by \sim 23 $^{\circ}$ from the layer normal, which is close to the value of \sim 27 $^{\circ}$, proposed by Kitaigorodskii [11] for orthorhombic subcell packing [R (\pm 1, 0)]. A summary of these results is given in Table 1.

Fig. 2 shows the X-ray reflection patterns of ZnA multilayers transferred onto quartz substrates from the subphase containing 1 \times 10⁻⁴ M ZnCl₂ in subphase at different pH. The XR patterns (Fig. 2(a and b)) for multilayers deposited in the pH range 6.3–6.5 exhibit a single layered structure consisting of δ -phase. In the pH range, 6.7–7.0, the multilayers show formation

Table 1
Bilayer period (in \AA) of multilayers transferred under different subphase conditions

Subphase pH	Subphase zinc ion concentration		
	1 \times 10 ⁻⁵ M	1 \times 10 ⁻⁴ M	5 \times 10 ⁻⁴ M
6.3	–	\sim 47 (δ)	\sim 47 (δ)
6.5	\sim 47 (δ)	\sim 47 (δ)	\sim 47 (δ) and \sim 51 (γ)
6.7	\sim 47 (δ)	\sim 47 (δ) and 51 (γ)	\sim 47 (δ) and \sim 51 (γ)
7.0	\sim 47 (δ)	\sim 47 (δ) and \sim 51 (γ)	\sim 47 (δ) and \sim 52 (β)
7.2	\sim 47 (δ) and \sim 51 (γ)	\sim 47 (δ) and \sim 56 (α)	\sim 47 (δ) and \sim 56 (α)
7.5	\sim 47 (δ) and \sim 51 (γ)	\sim 47 (δ) and \sim 52 (β)	\sim 56 (α)
7.7	\sim 47 (δ) and \sim 51 (γ)	\sim 47 (δ) and \sim 52 (β)	\sim 47 (δ) and \sim 56 (α)

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