

# Maximum withdrawal speed for Langmuir–Blodgett film deposition of arachidic acid

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## Abstract

The maximum withdrawal speed of Langmuir–Blodgett (LB) film deposition of arachidic acid (AA) was investigated. The quality of LB deposited film was determined by the transfer ratio (TR), together with measurements of surface roughness using atomic force microscopy (AFM). A Langmuir mini-trough was used to provide the surface pressure versus molecular area ( $\pi$ - $A$ ) curves and a flow visualization technique was applied to estimate the dynamic contact angles and to observe the fluid motion. The effects of hydrophobic and hydrophilic substrates, pH and the addition of four different ions, i.e.,  $K^+$ ,  $Ba^{2+}$ ,  $Cd^{2+}$ , and  $Al^{3+}$ , on the withdrawal speed were examined. The “transition point” from liquid to solid states on the  $\pi$ - $A$  curve provided a clear indication of the maximum withdrawal speed. The lower the transition point, the higher was the maximum withdrawal speed. Stable deposition was possible only if the pH of the solution was maintained in a narrow range. The observation of dynamic contact angles and fluid motion, particularly the movement of air–liquid interface, was consistent with previous findings. Owing to the “soap effect” of the divalent ions  $Ba^{2+}$  and  $Cd^{2+}$ , the maximum speed for successful LB film deposition without significant water entrainment could be extended substantially with the addition of divalent ions.

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## 1. Introduction

Langmuir–Blodgett (LB) film deposition technique has received wide attention in the past two decades owing to its potential applications for monolayer or ultrathin film production. Until now, LB technique remains only a laboratory tool with very limited industrial applications due to its slow deposition speed and lack of reliability [1,2].

The deposition speed of LB films is limited by air and water entrainments. Air entrainment would appear if the immersion speed of the substrate into the coating solution was too high. On the other hand, water entrainment would occur if the substrate was removed rapidly from the coating solution. Usually, the critical speed for air entrainment is much higher than that for water entrainment for the same material. Hence, water entrainment is considered as a major obstruction for LB film

deposition. There are two possible causes for water entrainment. One is the strong adhesion of water on the substrate due to the hydrophilic groups of the molecules that have deposited on the solid surface. The other is the gravitational and molecular forces that expel water into the sub-phase [3]. Schulman et al. [4] showed that water would be expelled within 1–2 s if there were monolayer molecules adhered to the solid. Srinivasan et al. [5] used an on-line capacitance technique to detect the entrainment of an aqueous sub-phase during LB film deposition, and found that more water was entrained on the solid substrate at high deposition speed. Zhang and Srinivasan [6] performed a hydrodynamic analysis on water entrainment by incorporating molecular forces and the Marangoni effect into the film evolution equation.

Bikerman [7] suggested that contact angle could play an important role on the deposition of LB films. Gaines [8] concluded that molecular layer deposition during the immersion to the sub-phase would be possible if the dynamic contact angle was greater than  $110^\circ$ . On the other hand, molecular layers deposition during the withdrawal from the sub-phase would also be

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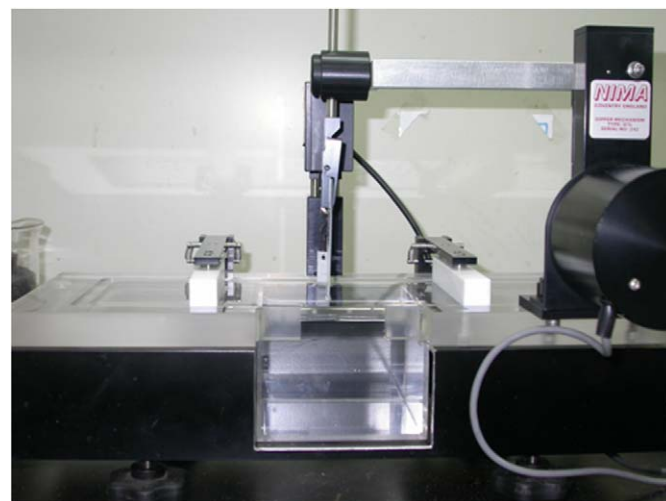
possible if the dynamic contact angle was between  $30^\circ$  and  $50^\circ$ . De Gennes [9] pointed out that the Y-type LB film deposition could take place during the substrate withdrawal if the interface was under the condition of split ejection motion. Cerro [2] provided experimental evidence on the fluid motion during the immersion of substrate and developed a relationship between contact angles and contact lines, which could be used for determination of the operating window for LB film deposition. He showed that LB film deposition was possible when the dynamic contact angle was greater than  $95^\circ$  during the immersion process, or smaller than  $95^\circ$  during the withdrawal process. It was also suggested that LB film deposition would be possible if the air–liquid interface had moved closer to the substrate.

Blodgett [10,11] first investigated the influence of divalent ions on the deposition of long-chain saturated carboxylic acids. The results showed that these divalent cations dramatically increased the film stability during the deposition. It has been observed that the transfer of Langmuir film from the gas–liquid interface onto a solid substrate is dependent on the characteristics of the sub-phase, solid substrate and deposition speed [12–15]. Previous studies [16–23] have revealed that divalent ions interact with arachidic acid (AA) and stearic acid (SA) in each layer to form “di-soap,” which could enhance film stability. Petrov et al. [24] found that the LB film deposition speed of arachidic acid could be improved with the presence of cadmium ions. They suggested that the divalent cations would react with the dissociated carboxyl groups to form soaps, resulting in a decrease of surface potential and facilitation of water expulsion in the deposition process. More recently, Diaz and Cerro [25] investigated the effect of sub-phase pH and counter-ions on the LB film deposition of a fatty acid–salt system, and found that successful deposition is strongly dependent on the critical pH, which is defined as the value of pH at which half of the acid molecules are ionized.

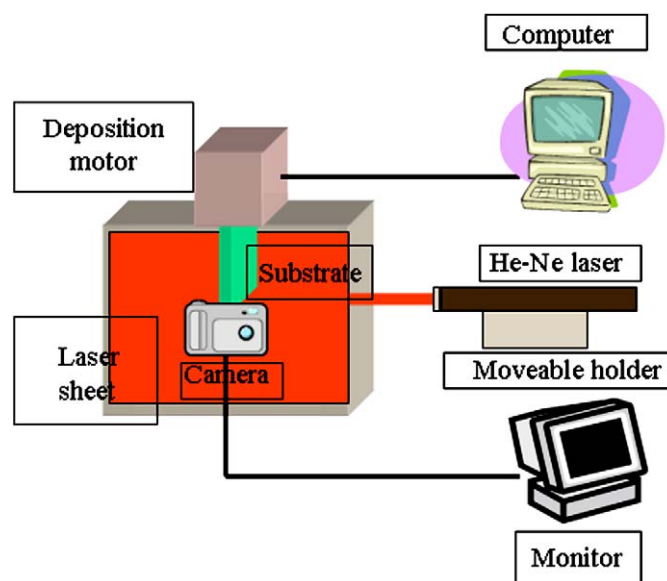
The aim of the present study is to experimentally investigate the maximum withdrawal speed for LB film deposition of arachidic acid, in the presence of different types of ions. Attempts are made to find some simple and clear indicators to estimate the maximum withdrawal speed. A flow visualization technique is also employed to provide some basic understanding on the influence of dynamic contact angles and fluid motion on the stability of LB film deposition.

## 2. Experimental

Arachidic acid (AA; 99% purity) was purchased from Sigma–Aldrich Chemical Co. without further purification for the LB film deposition experiment. The coating solution was prepared by dissolving arachidic acid in chloroform (supplied by J.T. Baker) with a concentration of 1 mg/ml. Microscopic glass slides (FEA) were chosen as substrates. Ferric stearate (Chem Service) was applied onto the glass surface to render its hydrophobicity. De-ionized water was obtained from a Milli-Q system (Millipore, Eschborn, Germany) and the resistance was controlled at  $18.2 \text{ M}\Omega \text{ cm}^{-1}$ . The sub-phase was prepared by dissolving different ions including potassium chloride (Riedel–de Haen), barium chloride (Riedel–de Haen), cadmium chloride



(a)



(b)

Fig. 1. The experimental set-up for dynamic contact angle and flow visualization. (a) Transparent Langmuir trough. (b) Flow images recording system.

(Sigma–Aldrich) and aluminum chloride (Riedel–de Haen), in de-ionized water to make up a  $5 \times 10^{-4} \text{ M}$  solution. Grounded polystyrene (PS) particles, supplied by Aldrich (Polystyrol, Bimodal) were used as tracer particles.

The experimental set-up of the Langmuir trough is shown in Fig. 1a. Pressure–area ( $\pi$ – $A$ ) isothermal curves for LB film deposition of AA were generated by a Nima 312D mini-trough (Nima Technology, UK). The mini-trough is a precision machined, computer controlled Langmuir trough with an area around  $300 \text{ cm}^2$ . It was equipped with a dipping well of area  $50 \times 20 \text{ mm}^2$  and 75 mm deep, situated at the center of the trough. Two detachable Teflon (PTFE) barriers were attached to compress the liquid surface toward the center of the trough. A Wilhelmy plate pressure sensor was used to detect the surface pressure. A 50-mm stroke dipper with a deposition speed varying from 1 to 100 mm/min was used to perform the LB film deposition.

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