

## ***In Situ* Weighing of Water-deposited Langmuir–Blodgett Films on a Piezoelectric Quartz Plate**

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Monolayers of cadmium stearate were deposited on a piezoelectric crystal plate by the Langmuir–Blodgett (LB) technique, and it was found from frequency changes of the crystal that the LB films were deposited on the crystal with water which gradually evaporated through the layers of the films when exposed to air.

Interest in Langmuir–Blodgett (LB) films is widespread and formation of ordered thin films by transferring lipid monolayers from a water surface is well known. The characterization of LB multilayer films has been widely studied in the dry state by various methods such as Fourier transform i.r. spectroscopy, X-ray diffraction, ellipsometry, and X-ray photoelectron spectroscopy;<sup>1</sup> however, the *in situ* evaluation of LB films during the dipping process has not been fully explored.

In this communication we report that water is incorporated when LB films are deposited, which can be directly observed by using a piezoelectric crystal plate as a dipping substrate, and that the molecular orientation in the monolayers influences both the amount of water incorporated and its evaporation rate from the layers. Piezoelectric crystals are known to provide very sensitive mass measuring devices because of resonance frequency changes upon the deposition of a given mass on the crystal electrode.<sup>2</sup>

A benzene solution (0.81 mg ml<sup>-1</sup>) of highly purified stearic acid (Nippon Yushi Co., Tokyo) was spread on Milli-Q water (Millipore Corporation) containing 0.1 mM CdCl<sub>2</sub> (aqueous phase, pH 6.5) in a Teflon-coated trough with a microprocessor-controlled Teflon barrier (San-Esu Keisoku Co, Fukuoka, Japan). The  $\pi$ -A isotherm curve of cadmium stearate was consistent with those in the literature.<sup>3</sup> A piezoelectric crystal plate (8 × 8 mm, 9 MHz At-cut quartz on which 24 mm<sup>2</sup> of Ag

electrode had been deposited) was used as a relatively hydrophilic substrate surface (contact angle against water 60°). The crystal was lowered and raised through the monolayer on a water surface, depositing two layers on each side of the crystal with each successive cycle. The frequency of the crystal was measured each time the crystal was raised out of the water phase (using an Iwatsu universal frequency counter, SL 7201, connected to a microcomputer). Calibration showed that a frequency change of 1 Hz corresponded to a mass of  $1.27 \times 10^{-9}$  g deposited on the crystal electrode. The apparatus is illustrated in Figure 1.

Typical time courses of the frequency change of the crystal in air are shown in Figure 2. The crystal was lowered at point A and lifted out of the monolayer-covered subphase (surface pressure 20 mN m<sup>-1</sup>) at point B four times, then lowered (point A') and lifted out of the aqueous phase without deposition of a monolayer (point B') at a rate of 100 mm min<sup>-1</sup>. The frequency of the crystal gradually increased with time and reached a constant value after 15 min in air, each time the crystal was lifted through the monolayer-covered subphase. The increased mass on the crystal with each cycle ( $M_{LB}$ ) was calculated, from the decrease of the frequency of  $183 \pm 3$  Hz from points A to C, to be  $(2.32 \pm 0.03) \times 10^{-7}$  g. This value was consistent with the theoretical mass of four dry monolayers of cadmium stearate ( $2.25 \times 10^{-7}$  g) calculated

from the surface area per molecule in the monolayer ( $0.237 \text{ nm}^2$  from a  $\pi$ -A curve). The increase of the frequency between points B and C in Figure 2 (the decrease of the mass) can be explained by evaporation of water from interlayers of the LB films. The amount of incorporated water ( $M_w$ ) and its evaporation speed ( $v_w$ ) were calculated from the frequency change and the initial slope of the curves between points B and C, respectively, and those values are shown in Table 1 (Run 1), together with the mass of the four dry deposited monolayers ( $M_{LB}$ ) and the transfer ratio.

When a crystal with eight monolayers on each side was lowered at point A' and lifted out of the aqueous solution with no monolayer on its surface, the frequency reverted to almost the starting value after the slow evaporation of a small amount of water (points B' to C' in Figure 2; run 2, Table 1). This shows that the LB film is not removed from the crystal plate by dipping in water. The evaporated water ( $0.30 \times 10^{-7} \text{ g}$ ) was

probably incorporated by swelling of the LB film. It represented only one seventh of the amount incorporated when the crystal was dipped in a monolayer-covered water surface ( $2.09 \times 10^{-7} \text{ g}$ ). This shows that most of the water in LB films is from the water surface with the monolayer.

When monolayers were deposited on the crystal at a low surface pressure (5 or  $10 \text{ mN m}^{-1}$ ), both the amount of lifted water and its evaporation speed were increased, but the mass of deposited LB film was less than that lifted at the high surface pressure of  $20 \text{ mN m}^{-1}$  (runs 3 and 4, Table 1). Thus, a relatively large amount of water is lifted with disordered monolayers and this incorporated water evaporates easily through the disordered monolayers. When the monolayer was lifted at slower speeds (runs 5 and 6) the evaporation rate of incorporated water decreased, suggesting that a better-oriented monolayer was deposited on the substrate compared to that deposited at the higher speed ( $100 \text{ mm min}^{-1}$ ). When monolayers were deposited before complete evaporation of water from the preceding layers, the transfer ratios decreased and much water was lifted with the disordered monolayers.

Recently, McCaffrey *et al.*<sup>4</sup> deposited calcium stearate monolayers on a quartz crystal plate by the LB technique and showed that the change in frequency was a linear function of

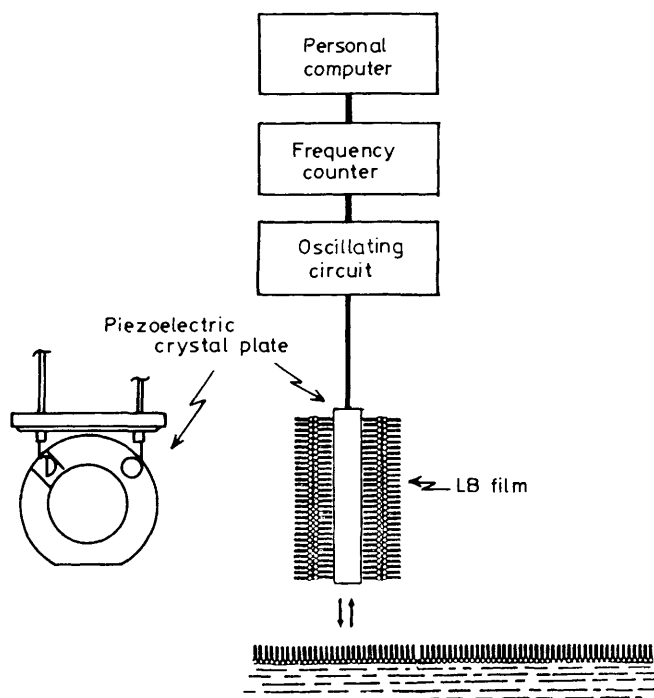


Figure 1. The piezoelectric crystal plate and frequency measuring apparatus.

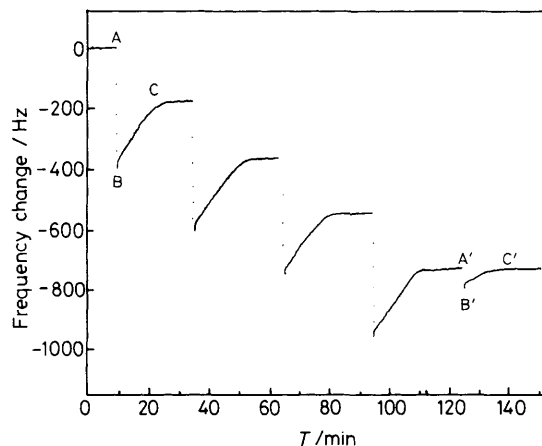


Figure 2. Frequency changes of a piezoelectric crystal plate in air. The crystal was lowered (A) and raised (B) four times through the cadmium stearate monolayer on the water surface (surface pressure:  $20 \text{ mN m}^{-1}$ ), then lowered (A') and raised (B') through the water phase with no surface monolayer, at a rate of  $100 \text{ mm min}^{-1}$ , at  $20^\circ \text{C}$ .

Table 1. Water and LB films deposited on a piezoelectric crystal plate obtained by measurement of changes of frequency of the crystal.

Run	Surface pressure / $\text{mN m}^{-1}$	Dipping speed / $\text{mm min}^{-1}$	$10^7 M_{LB}^a$ / g	Transfer ratio	$10^7 M_w^b$ / g	$10^7 v_w^c$ / $\text{g min}^{-1}$
1 <sup>d</sup>	20	100	2.32	1.03	2.09	0.157
2 <sup>c</sup>	—	100	0.07	—	0.30	0.042
3 <sup>d</sup>	10	100	1.77	0.86	3.61	0.267
4 <sup>d</sup>	5	100	1.50	0.78	3.99	0.362
5 <sup>d</sup>	20	60	2.32	1.03	2.12	0.160
6 <sup>d</sup>	20	40	2.31	1.03	2.62	0.077

<sup>a</sup>  $M_{LB}$  = dry mass of deposited LB monolayers. <sup>b</sup>  $M_w$  = mass of incorporated water. <sup>c</sup>  $v_w$  = evaporation rate of incorporated water. <sup>d</sup> The crystal was lowered and raised through the cadmium stearate monolayers on the water phase. <sup>e</sup> The crystal was lowered and lifted out of the subphase with no monolayer.

the number of layers deposited. However, the weight associated with each layer is 25% larger than the calculated mass of the LB layers, probably because they weighed the deposited LB films with the water lifted still incorporated in them.

In conclusion, we have directly observed the incorporation of water into LB films by dipping a piezoelectric quartz plate, and have correlated the amount of incorporated water and its evaporation rate with the molecular orientation of the monolayers. The water in LB films is known to have an adverse effect on electric, optical, and other properties.<sup>3b,5</sup> This technique provides a new tool for monitoring and evaluating the monolayer dipping process.

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