Detection of Phase Transition of Thin Langmuir–Blodgett Film based on an Electrical Capacitance Measurement

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Langmuir–Blodgett films (10 layers) of a double-chain ammonium amphiphile complexed with poly-(styrenesulphonate) on a pair of platinum electrodes have been found to show phase transition in aqueous electrolyte solution, which was successfully detected electrochemically by measuring electrical capacitance under applied alternating current.

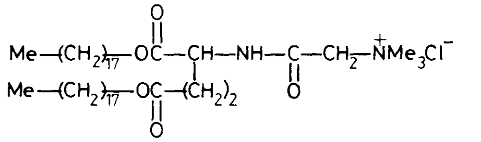
Growing attention has been focused on synthetic bilayer membranes[1] because they possess fundamental physicochemical properties similar to those of biological membranes. Deposition of these ordered films onto solid substrates and surface fabrication of well-ordered molecular assemblies using the Langmuir–Blodgett (LB) technique is also of current interest.[2]

One of the most fundamental characteristics of bilayers is that they exhibit a phase transition between the crystalline and liquid crystalline states.[3] However, despite intense studies, there has been no report of phase transition phenomena in LB films, because they are formed, in general, from non-bilayer-forming amphiphiles. Recently we found that the electric impedance parameters of multi-bilayer cast films on solid electrodes show a drastic change due to the bilayer phase transition.[4] We have now investigated, by a.c. impedance measurements, the occurrence of phase transitions on thin LB film-modified electrodes by using a polyion-complexed lipid.

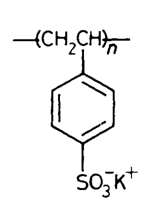
An 80 µl portion of a benzene/ethanol (8:2 volume) solution of a cationic amphiphile, $2C_{18}GluC_2N^+$ (ref. 4a) (1.3×10^{-3} M) was spread on a subphase (Milli-Q water, 20 ± 0.2 °C) containing 10^{-4} unitmole/dm^3 potassium poly-(styrenesulphonate) (PSS^-) in a Teflon-coated Langmuir trough.[2] Anionic PSS^- was used for the sake of the polyion complex formation at the air–water interface. It has already been shown that this type of lipid is water-insoluble but can retain fundamental bilayer characteristics.[5] A surface pressure–area (π–A) curve measurement and the preparation of LB films on electrodes were performed with a microprocessor-controlled film balance and a film lift (San-Esu Keisoku FSD-20,23 Japan).

Figure 1 shows the π–A curve of $2C_{18}GluC_2N^+$ at a compression rate of 0.4 mm sec^{-1}. Condensed monolayer is formed at a surface pressure of up to 40 mNm^{-1} on PSS^- solution. Platinum plates (10 × 10 × 0.5 mm) washed with aqua regia, water, and chloroform were used as a solid substrate, and $2C_{18}GluC_2N^+PSS^-$ monolayers were transferred under a constant surface pressure of 30 mNm^{-1} at 20 ± 0.2 °C. Although the deposition ratio varied from 0.6 to 1.6, the film could be transferred by Y-type (bilayer type) deposition in each successive cycle.

A pair of equivalent electrodes modified with LB films (10 layers) in this manner were immersed in 10^{-2} M aqueous KCl solution, and a.c. electrical measurements were conducted with an impedance analyser (YHP, Model 4192A) assuming a parallel combination of resistor and capacitor. A schematic illustration of the LB film and a typical measurement set-up are shown in Figure 2. The electrical capacitance of the pair of bare Pt electrodes was, at *ca.* 10 µF (at 100 Hz), much larger than that of the modified electrodes, and the values were



$2C_{18}GluC_2N^+Cl^-$



PSS^-K^+

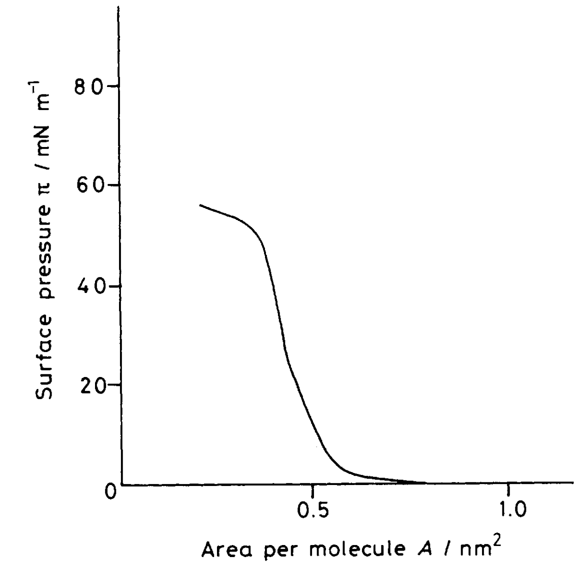


Figure 1. Surface pressure–area (π–A) isotherm of $2C_{18}GluC_2N^+Br^-$ on a potassium poly(styrenesulphonate) solution at 20 °C.

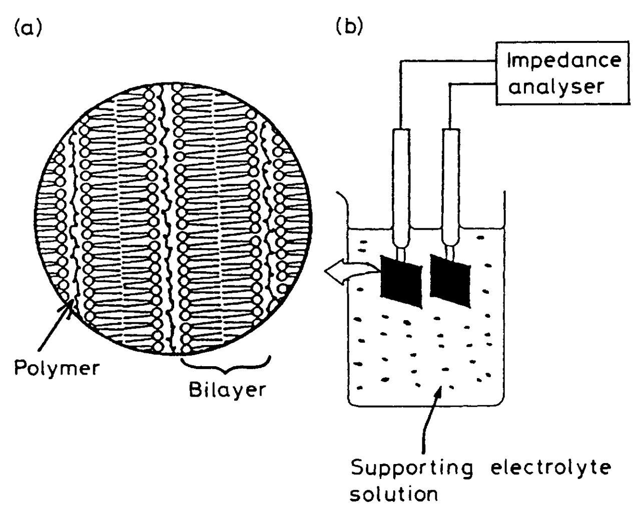


Figure 2. (a) Schematic illustration of LB film on Pt plate electrode and (b) a typical measurement set-up.

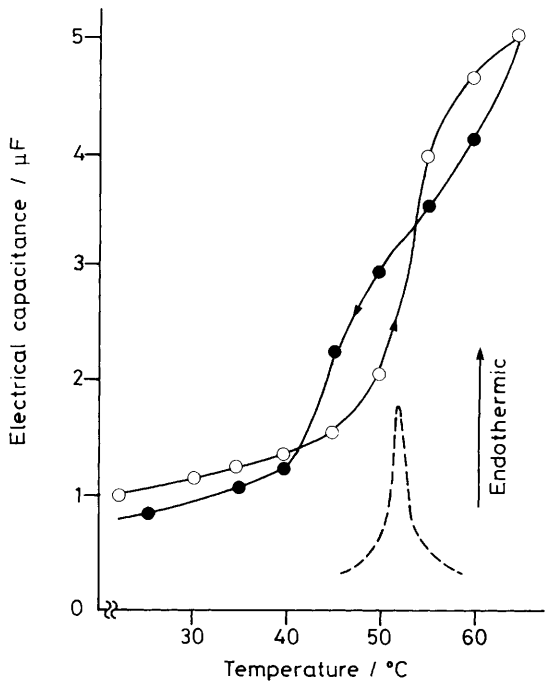


Figure 3. Temperature dependence of the electrical capacitance of Pt electrodes (10 × 10 × 0.5 mm) modified with $2C_{18}GluC_2N^+PSS^-$ polyion-complexed LB films (10 layers) in 10^{-2} M KCl at 100 Hz; applied voltage 50 mV. ○, Heating; ●, cooling. Dotted line shows a DSC thermogram of $2C_{18}GluC_2N^+PSS^-$ cast films in 10^{-2} M KCl.

almost constant within the measured temperature range (25—65 °C).

Figure 3 illustrates the strong temperature dependence of the electrical capacitance of the LB film-modified electrodes. A marked enhancement of capacitance near 50—55 °C is clearly associated with a change in membrane fluidity of the $2C_{18}GluC_2N^+PSS^-$ films on the Pt electrodes, because the phase transition temperature (T_c) of the lipid film determined by differential scanning calorimetry (DSC) (Shimazu DSC-50) is 52 °C (transition region 47—57 °C) as shown by a dotted line in Figure 3 [the lipid films (0.87 mg) were prepared in a DSC sample vessel and the DSC measurement was conducted in the presence of 20 µl aqueous KCl (10 mM) solution].

The steep change in capacitance apparently is not attributable to exfoliation of parts of the monolayers from the deposited LB films on the electrode, because the capacitance values during the cooling process are rather low compared to those during the heating cycle at temperatures below the phase transition. Hysteresis observed in Figure 3 may be ascribed to changes in membrane orientation. The results clearly demonstrate that the ultra-thin LB films on the electrode possess fundamental molecular bilayer characteristics (membrane fluidity).

This finding should be important for developing thin LB films with biomembrane-mimicing properties and also in practical applications such as the construction of molecular signal transduction devices based on highly ordered films.

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