The Behavior of Π-A Isotherm with Increasing Amount of Calix[4]arene at Air–Water Interface

Pelakuan Isoterma Π-A dengan Penambahan Kaliks[4]arena pada Antaramuka Udara-Air

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Abstract

The surface pressure-mean molecular area (Π-A) isotherm of surfactant (Mat 7) was obtained by using Langmuir-Blodgett technique. The characterization of Mat 7 Langmuir film was carried out in terms of Π-A isotherm. The Langmuir monolayer was successfully formed by spreading the Mat 7 solution directly at air-water interface. The optimum condition such as the volume of surfactant loaded on the subphase was studied. It is observed that with increasing amount of Mat 7 on water surface, Π-A isotherm shifted towards the left. The mean surface area occupied by each Mat 7 molecule was estimated by extrapolating the linear portion of each curve (between 10 and 20 mN/m) to a surface pressure equal to zero. The UV-Visible spectra of Mat 7 in chloroform showed a significant result. The absorption peak increased as more concentrated solution was added.

Keywords   Calixarenes, Langmuir film, surface pressure

Abstrak

Tekanan permukaan keluasan min isoterma (Π-A) surfaktan (Mat 7) diperolehi menggunakan teknik Langmuir-Blodgett. Ciri saput tipis Langmuir Mat 7 dilakukan mengikut terma isoterma Π-A. Lapisan mono saput tipis Langmuir berjaya dibentuk dengan menyerakkan larutan Mat 7 secara terus ke atas antaramuka udara-air. Keadaan optimum seperti isipadu surfaktan yang digunakan pada subfasa telah dikaji. Diperolehi bahawa penambahan Mat 7 pada permukaan air telah menyebabkan isoterma Π-A teranjak ke kiri. Min luas permukaan yang diliputi oleh setiap molekul Mat 7 telah dianggarkan melalui mengekstrapolasikan bahagian linear setiap lengkung (di antara 10 dan 20 mN/m) pada tekanan permukaan bersamaan dengan sifar. Spektra UV-boleh nampak bagi Mat 7 dalam kloroform menunjukkan keputusan yang signifikan. Puncak serapan semakin meningkat dengan pertambahan kepekatan larutan.

Kata kunci   Kalixarena, saput tipis Langmuir, tekanan permukaan

INTRODUCTION

Synthesis and design of functional molecules that could serve as molecular devices for sensing of specific ion is an area of intense activity in current research (de Silva *et al*., 1997). Macrocyclic ligands are excellent choices for this purpose because of their remarkable selectivity towards various metal ions compared with some organic molecules that have been used as ionophore to design molecular sensor (Patra *et al*., 2012).

With respect to the issue being discussed, calixarenes, which are macrocyclic oligomers made up of phenol units linked by methylene bridge are found to be very attractive because of their ability to bind varieties of ions (Patra *et al*., 2012). Calixarenes are monodisperse, easily synthesized, and easily purified in large amounts. Amphiphilic calixarenes are surfactants with a host–guest recognition site (Shinkai *et al*., 1986) which are attractive for applications where a guest molecule must be stabilized, transported or protected in aqueous media. As amphiphilic calixarenes can interact with aqueous systems, they are of particular interest for biological and environmental applications such as waste water treatment, medical diagnosis, and highly sensitive and selective sensors (Asfari *et al*., 2001; Nostro *et al*., 2001).

The main aim of this work was to determine the behaviour of Π-A isotherm with increasing volume of Mat 7 solution in terms of the mean molecular surface area (A_{lim}) using Lamgmuir-Blodgett technique and its optical properties using UV-Visible.

MATERIALS AND METHODS

Chloroform (>99.8% purity) and ethanol (>99.4% purity) were purchased from Fisher Scientific, while 5,17,dinitro-11,23-ditert-butyl-25,27-diethoxycarbonylmethyleneoxy-26,28-dihydroxycalix[4]arene (Mat 7) was obtained from Institute of Technology, Tallaght, Dublin, Ireland. The molecular structure of Mat 7 is shown in Figure 1. All reagents were of analytical grade and used without further purification. Water, as a subphase, was purified with a Millipore Milli-Q system with a resistivity of 18.2 MΩ.

The Mat 7 samples were dissolved in chloroform with concentrations of 0.05, 0.10, 0.15 and 0.20 mg/ml. Surface pressure–area (Π–A) isotherms were measured on a KSV 2000 Langmuir–Blodgett system (KSV Instruments Ltd., Finland). Filter papers were used
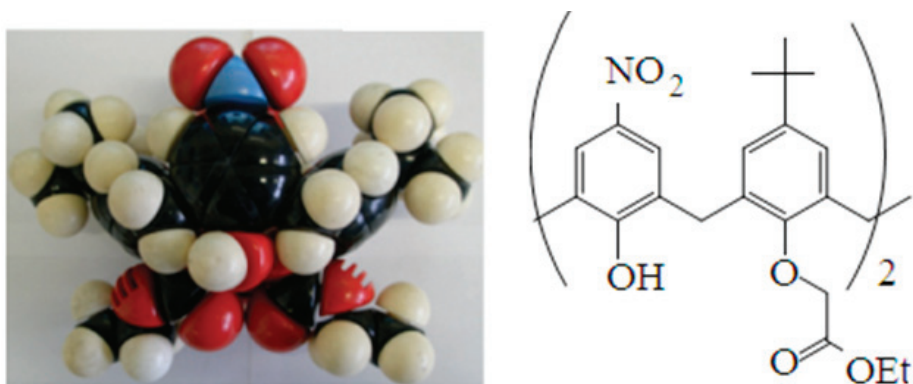

Figure 1   Molecular structure of Mat 7

as Wilhelmy plates to measure the surface pressure (Π). The chloroform solution of a given sample (0.20mg/ml) was spread onto water subphase with varying volumes. After evaporation of the chloroform for 10 to 15 min, the monolayer film was compressed at a speed of 12 mm/min. An accuracy of 0.1 mN/m was the characteristic for the measurements. All experiments were performed at a subphase temperature of 23°C and kept constant within ±2°C. The Π–A isotherms were measured several times to ensure the measurements were reproducible.

UV–Vis spectra were determined on a JASCO V-570 UV/VIS spectrophotometer using quartz cells with 1 cm optical path length.

RESULTS AND DISCUSSION

Surface pressure-area (Π-A) isotherms

Figure 2 shows Π-A isotherms of Mat 7 at different volumes of spreading on subphase of deionized water. Initially, the value of surface pressure was nearly zero, then increased linearly, after which it increased sharply at lower mean molecular area before collapsing. The collapse pressure was 27 mN/m. At higher pressure the monolayer was of poor quality.
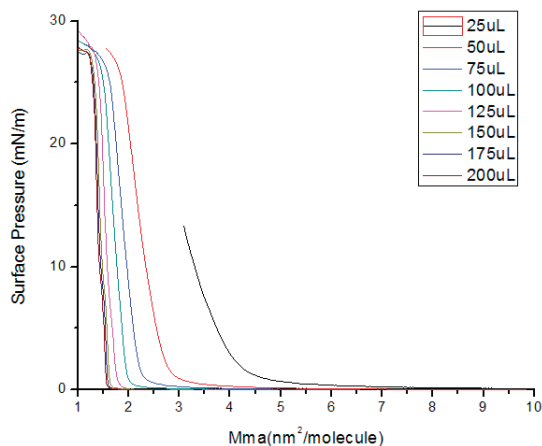

Figure 2   Variation of pressure-area isotherm of Mat 7 at different
spreading volume (Mean molecule area/Mm a)

The monolayers were very rigid, collapsing rapidly and appeared of irregular. From the isotherms, the mean molecular surface area (A_{lim}) occupied by each Mat 7 molecule was estimated by extrapolating the linear portion of each curve (between 10 and 20 mN/m) to a surface pressure equal to zero. Such extrapolations were routinely used to estimate the surface area per molecule in films that were condensed. These extrapolations yielded A_{lim} as listed in Table 1.

Table 1 Mean molecular surface area (A_{lim}) of Mat 7

Volume (uL)	A_{lim} from experiment (nm^2)	Orientation
25	-	-
50	2.6	‖
75	2.2	‖
100	1.9	‖
125	1.7	‖
150	1.6	‖
175	1.5	‖
200	1.5	‖

The effect of increasing loading of Mat 7 was studied as shown in the isotherms graph (Figure 2). With increasing volume spread of Mat 7 solution against concentration of 0.2 mg/ml, the Π-A curve shifted towards the left. When 25 uL was spread on the subphase, the isotherm was not fully complete because too little surfactant on the water surface could not form a monolayer film. As the volume of Mat 7 increased, the mean surface area decreased until it reachesed a certain value. This value is close to that expected for a calix[4]arene molecule with the same substituents lying flat on the water surface (about 1.6 nm^2) in Supian (2010). Mat 7 possesses a parallel (‖) orientation of the plane of the calixarene ring with respect to the plane of the water surface.

UV-Visible spectra

The UV–Vis spectra of the Mat 7 are shown in Figure 3. All of these samples had strong absorption bands in the range of 250–350 nm. Mat 7 had two strong absorption peaks at 274 and 280 nm. All the strong absorptions were assigned to π-π* and n-π* transition due to the presence of chromophores at the upper rim of Mat 7 (Pavia *et al*., 2001).
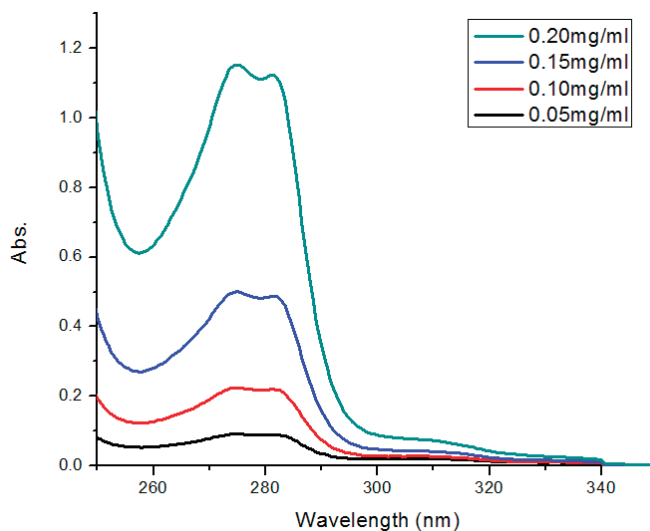

Figure 3 UV-Visible spectra

The Beer-Lambert law (or Beer's law) is the linear relationship between absorbance and concentration of an absorbing compound (Tissue, 1996). Based on the data of Figure 3, an absorbance versus concentration graph is plotted (Figure 4) which obeys the law.

$$\text{Abs.}_{max} = \varepsilon \, c \, l \tag{1}$$

where Abs._{max} is the absorbance of the sample, ε is the absorption coefficient or the molar absorptivity of the absorber, c is the concentration of absorbing species in the material and l is the distance that the light travels through the material (the path length = 1 cm).
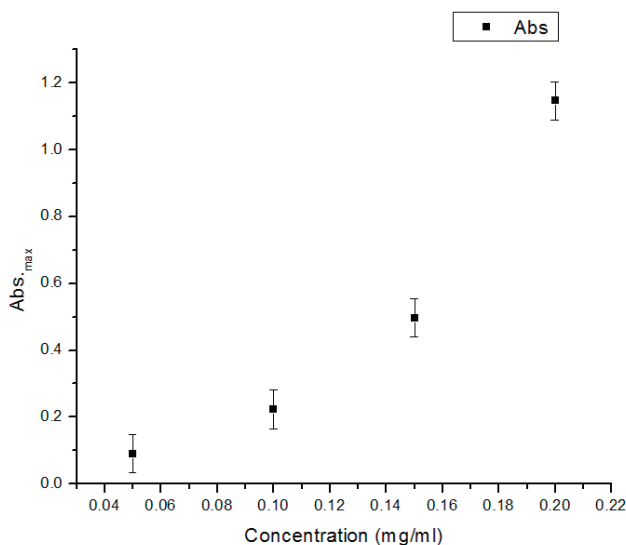

Figure 4   Graph of Abs._{max} vs concentration

CONCLUSION

In the present work, Mat 7 Langmuir monolayer was formed successfully by spreading the solution at air-water interface. The optimum condition, such as the volume spread on the subphase was studied. It was observed that the Π-A isotherms shifted to the left with increased volume spread and the optimum volume was 150 uL at 0.2mg/ml. It was deduced that the size of each Mat 7 molecule which was 1.6 nm^2. UV-Vis results explained that Mat 7 had two strong absorption peaks at 274 and 280 nm due to π-π* and n-π* transitions.

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