

## **Determination of Isotherm of Supramolecule Calix[4]arenes Monolayer using Langmuir-Blodgett Technique**

*Penentuan Isotherma bagi Ekalapisan Supramolekul Kaliks[4]arena Menggunakan Teknik Langmuir-Blodgett*

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### **Abstract**

The principle of Langmuir-Blodgett technique lies in the formation of a closely packed monolayer of amphiphilic molecules on the surface of water. By monitoring the pressure-area isotherm, the phase changes of the monolayer from gaseous to solid phases can be determined. Once it reaches the solid phase, the monolayer can be transferred onto a substrate to construct multilayer thin films by sequential deposition. The material used in this experiment is calix[4]arenes, a supramolecule, widely used as a sensor material and in biometric applications because of its nanoporous film structure. Calix[4]arenes isotherm was analyzed to get the radius of its cavity and was found that the diameter decreases with addition of spreading volume. UV-Vis result shown almost no difference in the absorbance spectra for calix[4]arenes either in thin film or in solution.

**Keywords** Langmuir-Blodgett, Calix[4]arenes, surface pressure-area isotherm, UV-Vis

### **Abstrak**

Prinsip teknik Langmuir-Blodgett merupakan tunjang kepada pembentukan ekalapisan padat bagi molekul amfifilik pada permukaan air. Dengan memantau isoterma tekanan-luas permukaan, perubahan fasa ekalapisan dari gas ke pepejal boleh ditentukan. Ekalapisan tersebut dipindahkan ke atas substrat untuk pembentukan saput tipis berbilang lapis melalui penempatan berjujukan apabila ia mencapai fasa pepejal. Bahan yang digunakan dalam eksperimen ini ialah kaliks[4]arena, iaitu sejenis supramolekul yang digunakan secara meluas sebagai bahan penderia dan aplikasi biomimetik kerana struktur saputnya yang berliang nano. Isotherma kaliks[4]arena dianalisis untuk mendapatkan jejari rongga dan didapati diameternya berkurangan dengan penambahan isipadu sebaran larutan. Keputusan UV-Vis menunjukkan hampir tiada perbezaan spektrum penyerapan kaliks[4]arena sama ada dalam bentuk saput tipis mahupun larutan.

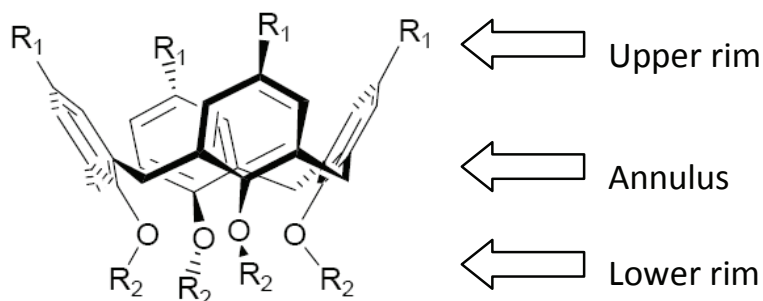
**Kata Kunci** Langmuir-Blodgett, kaliks[4]arena, isoterma tekanan-luas permukaan, UV-Vis

### **Introduction**

Calixarenes is the third generation of supramolecules, after cyclodextrins and crown ethers. It is a type of cyclooligomers, where phenolic subunits are bridged by methylene spacers

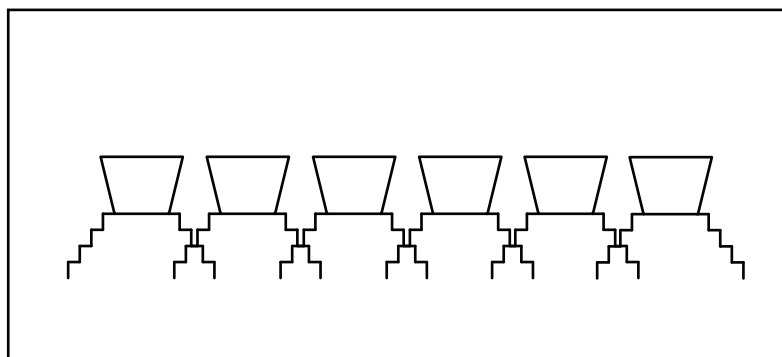
forming a ring with a defined hydrophobic upper rim, hydrophilic lower rim and a central annulus (see Figure 1). Upper and/or lower rims can be functionally modified to prepare various derivatives with differing selectivities for various guest ions and small molecules (Faridah, 2010). It has been extensively studied for Host-Guest chemistry and frequently used as nanowires (Hong *et al.*, 2001), chiral supramolecular assemblies (Orr, Barbour & Atwood, 1999), self organized nanostructures (Prins *et al.*, 2000) or artificial enzymes (Chen *et al.*, 2006) due to their unique cavity-shaped architecture and pre-organized binding sites (Gutsche, 2008). Calixarenes also form a unique nanoporous film due to empty spaces between calixarenes and its neighbors and between hydrocarbon chains. Apparently, this is the property that makes calixarenes serve well as sensors (Coquière *et al.*, 2006 & Ji *et al.*, 2006) material and in biomimetic applications.

The nomenclature for calixarenes is straightforward and involves counting the number of repeating units in the rings. Its generic formula is Calix[n]arenes, where  $n = 2, 4, 8$ . For example, calix[4]arenes has four phenols units in the ring and a calix[6]arenes has six.

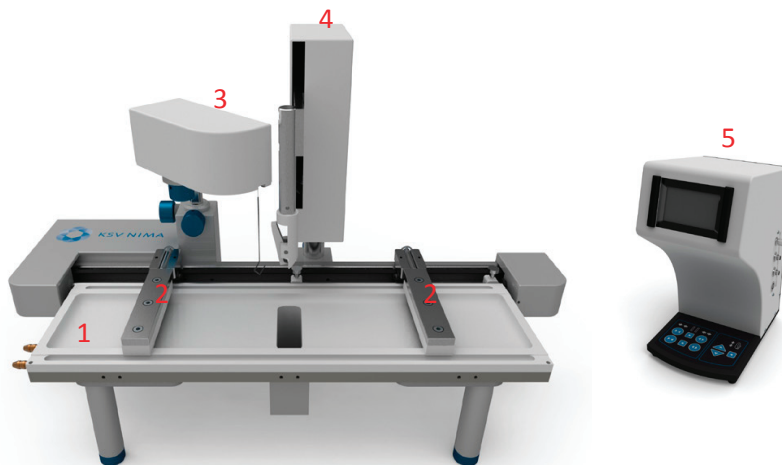


**Figure 1** Cone conformation of a typical calix[4]arenes

Once the calixarenes is spread on the surface of water, the polar head groups (lower rim) will interact with the dipole moments of the water molecules and get drawn into the water. The hydrophobic part (upper rim) on the other hand is being repelled from the water as depicted in Figure 2. Langmuir-Blodgett technique can be used to measure calixarenes' surface tension as a function of mean molecular area (Mma). Mma gives information how foreign substance alters the structure of the monolayer.



**Figure 2** Schematic representation of amphiphilicity of calixarenes on the surface of water

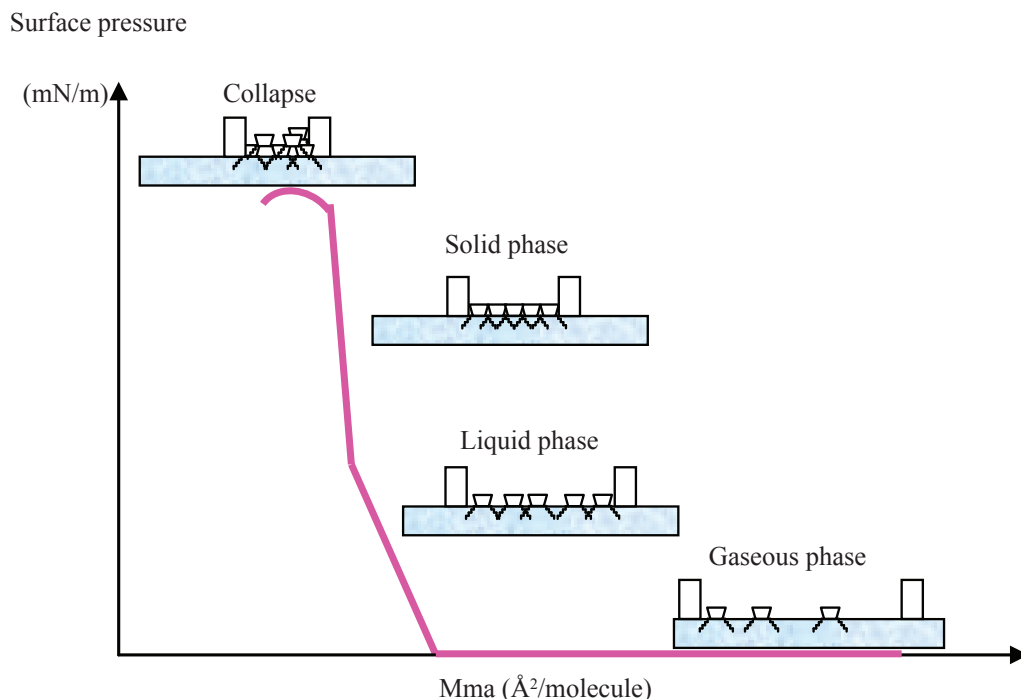


**Figure 3** Langmuir-Blodgett Apparatus; (1) Trough (2) Movable barrier (3) Pressure sensor (4) Dipping mechanism (5) Interface unit

Figure 3 shows the apparatus used in Langmuir-Blodgett technique. It comprises a hydrophobic trough, two movable barriers with controllable speed, a pressure sensor where a Wilhelmy plate or paper sensor is connected to a micro-electronic feedback system, dipping mechanism for film deposition and an interface unit to manually control the movement of barriers and dipping system. Control of the functions of the instruments is done through a RS-232C interface.

The Langmuir-Blodgett technique requires the spreading of an amphiphilic compound dissolved in an evaporating solvent such as chloroform at the air/water interface (subphase) in the Langmuir trough. The solvent is allowed to evaporate for 10 – 15 minutes prior to starting the movable barriers. Once the barriers start to move towards each other the monolayer at the interface will be correspondingly compressed. This allows for the surface pressure to be measured by determining the force due to surface tension on a suspended Wilhelmy plate partially immersed in the subphase.

At the beginning of the compression process the monolayer is deemed to be in a “gaseous phase” because the molecules are still far apart without any interaction between them. As the compression increases the molecules start to come closer together thereby exerting a repulsive force on each other. The area per molecule decreases and the surface pressure increases. At this stage the monolayer is considered to be in the “liquid phase” which is still compressible. However, when the compression reaches a critical value the monolayer turns into a “solid phase” where now the molecules are arranged in their closest possible packing. This is indicated by a sharp discontinuity in the slope of the isotherm graph. When the surface pressure continues to increase with decreasing surface area a “collapse” phenomena occurs due to mechanical instability at very high surface pressures. At this stage the molecules are forced out of the interfacial film resulting in disordered multilayers. This event can be discerned from the surface pressure-mean molecular area isotherm graph as shown in Figure 4. The isotherm graph allows us to determine the optimum pressure for LB deposition.



**Figure 4** An example of a surface pressure-area isotherm.

## Materials and Method

In this experiment we use calix[4]arenes (Figure 5), courtesy of Prof. Tim Richardson, University of Sheffield, United Kingdom. Chloroform obtained from Mallinckrodt was used as the solvent to prepare a solution of concentration 0.2 mg/mL.

Langmuir-Blodgett technique employed to study the calixarenes monolayer at the air/water interface is based on a trough where the area of the monolayer can be modulated. We used KSV 2002 System 2 (Helsinki, Finland) of dimensions 150 (w) × 530 (l) × 10 (h) (mm) which is coated with a highly hydrophobic and inert material - polytetrafluorethylene (PTFE). The trough is cleaned using chloroform and then filled with ultra-pure water (Milli-Q system, resistivity 18.2 MΩ at 25°C) as the subphase. Monolayer was formed by spreading 50 – 250 μL of calix[4]arenes in chloroform (0.2 mg/mL) using Hamilton syringe, and the chloroform was allowed to evaporate for 10 – 15 minutes before starting the measurement. The film area is compressed with two barriers on each side of the trough. During compression, the barrier speed was set at 12 mm/min.

LB film was then deposited onto a quartz slide (25 × 25 mm) based on isotherm plotted. The quartz was cleaned and treated with 1,1,1,3,3,3 – Hexamethyldisilazane (HMDS) overnight to make it hydrophobic. The spreading volume chosen was 250 μL. The film was fabricated by vertical dipping method with a dipping speed of 5 mm/s. Ten minutes delay was allowed between dips for each upstroke to ensure the film is dry. Thirty layers of film were deposited onto the quartz.

Optical absorption measurements were made with a Jasco V-500 spectrophotometer. The UV-Vis spectrum of thin film is compared with calix[4]arenes in solution.

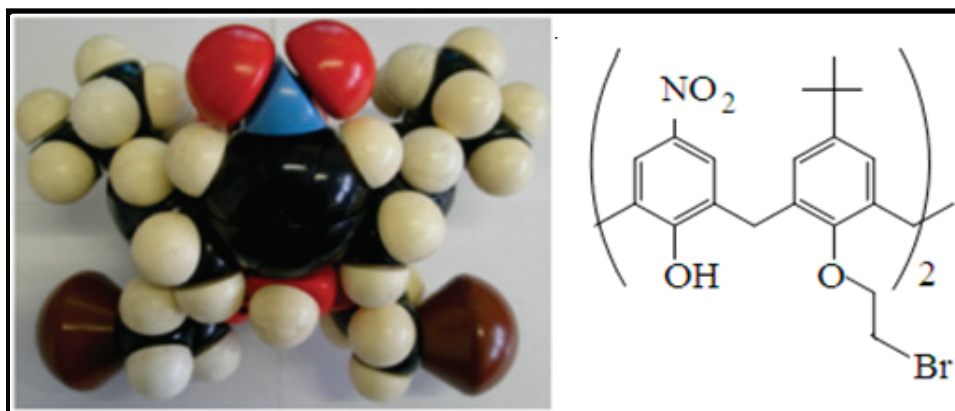


Figure 5 CPK model and chemical structure of calix[4]arenes

## Results and Discussion

Calix[4]arene is yellow in color, owing to Nitrogen atoms at the upper rim whilst Bromine at the lower rim intensify the color. The molecular weight calculated from its chemical structure is 814.608. Space filling model or CPK model (Figure 5) is used to visualize the effective shape and relative dimensions of the molecule. The model is a powerful tool in estimating orientation of the molecules at air/water interface. We found that orientation for calix[4]arenes is parallel.

Figure 6 shows the curves surface pressure against mean molecular area at various spreading volume. Generally, all solutions enter “solid phase” when the surface pressure reach 15 mN/m. This is the steepest part of the graph. By extrapolating this part to 0 mN/m, the mean molecular area (Mma) can be deduced. Assuming the area occupied by a calix[4]arene is a circle, we can get the radius, hence a cross section of the calix[4]arenes as tabulated in Table 1. The isotherm graph also shows that the Mma of the calix[4]arene decreases as the spreading volume increases due to intermolecular packing.

Table 1 Limiting area and radius of calix[4]arenes

Volume ( $\mu\text{L}$ )	Mma ( $\text{\AA}^2/\text{molecule}$ )	Radius (nm)
50	135.98	0.658
100	104.743	0.577
150	90.702	0.537
200	89.538	0.534
250	84.545	0.519

Conjugated system in calix[4]arenes causes chromophores that can be observed using UV-Vis Spectrometer. Strong absorption around 330 nm can be observed in Figure 7 owing to  $\text{NO}_2$  upper rim group connected to phenolic hydroxyl group (Rouis *et al.*, 2007). Another peak at 285 nm is probably due to the presence of the Br atom at the lower rim.

LB thin film deposited onto the quartz substrate was 30 layers, equal to 30 – 35 nm. This film is compared with calix[4]arene in solution. As shown in Figure 7, there is only slight absorbance difference between spectra of film and solution. This shows the material

is stable because it still has the same fingerprints. The strongest peak for thin film is at 327 nm. This result is consistent with A. Rouis *et al.*'s (2007) report. The group has evaluated azo-calix[4]arenes in solution and in spin coated thin film of 200 nm.

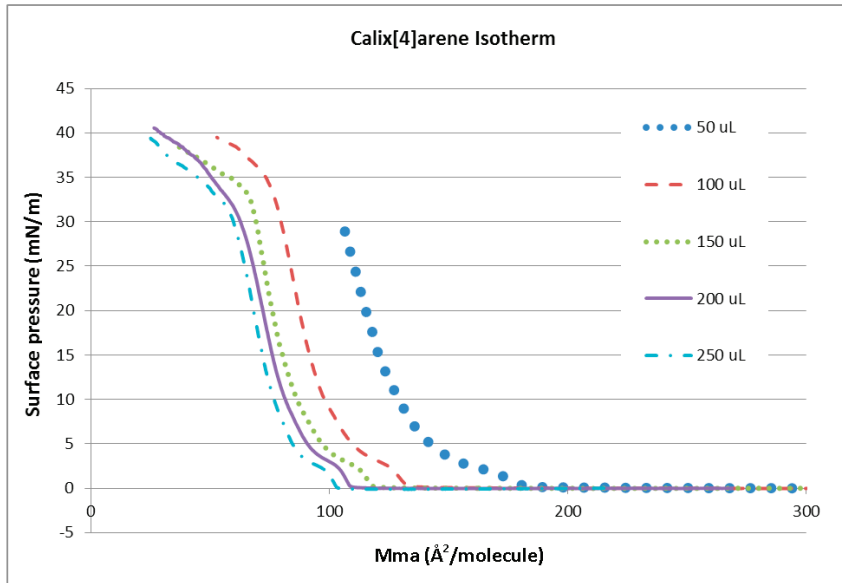


Figure 6 Isotherm for calix[4]arenes

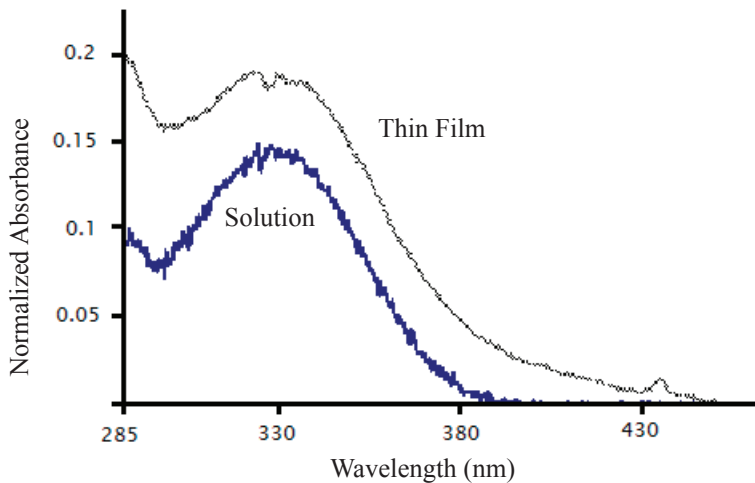


Figure 7 UV-Vis Spectra for Calix[4]arenes in solution and in thin film

## Conclusion

Langmuir-Blodgett deposition technique was used to study the isotherm of organic material of calix[4]arenes. The real-time pressure-area isotherm plotted by the computer clearly shown the phase changes of the molecules. The isotherm graph also shown that the Mma of the calix[4]arene decreases as the spreading volume increases due to intermolecular

packing. UV-Vis results for thin film of calix[4]arenes shown strong absorbance peak at 327 nm which was due to the NO<sub>2</sub> upper rim group. Slight absorbance spectrum difference between calix[4]arenes in thin film and in solution confirmed the material stability.

## Reference

- Chen, L., Zhang, J., Zhao, W., He, X. & Liu, Y. (2006). Double-armed calix[4]arene amide derivatives as ionophores for lead ion-selective electrodes, *Journal of Electroanalytical Chemistry*, 589 (1), 106 – 111.
- Coquière, D., Marrot, J. & Reinaud, O. (2006). Encapsulation of a (H<sub>3</sub>O<sub>2</sub>)- unit in the aromatic core of a calix[6]arene closed by two Zn(II) ions at the small and large rims, *Chemical Communication*, 37, 3924 – 3926.
- Faridah L. S., (2010) *Sensing Interaction within Nanoscale Calixarene and Polysiloxane Langmuir Blodgett Film*, PhD Thesis, University of Sheffield.
- Gutsche, D.C. (2008). *Calixarenes: An Introduction*. Royal Society of Chemistry, Cambridge, UK.
- Hong, B. H., Bae, S. C., Lee, C. W., Jeong, S. & Kim, K. S. (2001) Ultrathin Single Crystalline Silver Nanowire Arrays Formed in an Ambient Solution Phase, *Science*, 294 (5541), 348–351.
- Ji, H., Yang, Y., Xu, X. & Brown, G. (2006). A Calixarene Based Fluorescent Sr<sup>2+</sup> and Ca<sup>2+</sup> probe, *Organic & Biomolecular Chemistry*, 4, 770 – 772.
- Orr, G. W., Barbour, L. J. & Atwood, J. L. (1999) Controlling Molecular Self-Organization: Formation of Nanometer-Scale Spheres and Tubules, *Science*, 285 (5430), 1049–1052.
- Prins, L. J., De Jong, F., Timmerman, P. & Reinhoudt, D. N. (2000) An enantiomerically pure hydrogen-bonded assembly, *Nature*, 408: 181 – 184.
- Rouis A., Dridi, C., Bonnamour, I. D., Davenas, J. & Ouada, H.B. (2007) Transport mechanism and trap distribution in ITO/azo-calix[4]arene derivative/Al diode structure, *Physica B* 399, (2), 109 – 115.