

On the layer structures in acid- and amine-substituted calixarene Langmuir–Blodgett films



C.M. McCartney^a, N. Cowlam^a, F. Davis^{b,*}, T. Richardson^{a,2}, A. Desert^c,
A. Gibaud^c, C.J.M. Stirling^d

^a Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, UK

^b Cranfield Health, Cranfield University, Cranfield MK43 0AL, UK

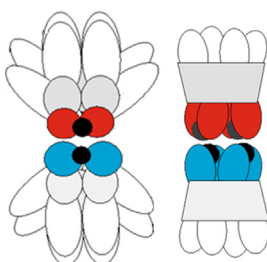
^c Laboratoire P.E.C. Rayons-X, Faculté des Sciences, Université du Maine, 72085 Le Mans Cedex 9, France

^d Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

HIGHLIGHTS

- X-ray reflectometry measurements made on LB films of calixarenes.
- Total film thickness and the bilayer spacing were obtained from reflectivity profiles.
- The “pinched loop” molecular conformation found for calix[8]arenes.
- The classical bowl and chain configuration found for calix[4]arenes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 March 2013

Received in revised form 30 May 2013

Accepted 5 June 2013

Available online 14 June 2013

Keywords:

X-ray reflectometry

Calixarene

LB film

Pinched loop

ABSTRACT

X-ray reflectometry measurements have been made on Langmuir–Blodgett (LB) films of an amine-substituted tertiary octyl calix[8]arene and of alternating layers of acid and amine-substituted tertiary octyl calix[8]arene as well on LB films of alternating layers acid/amine-substituted tertiary butyl calix[4]arenes. The total film thickness and the bilayer spacing were obtained for each sample from its reflectivity profile $R(Q)$ vs. Q . Simulations of the reflectivity profiles were made with a programme based on Parratt's recursive relations, using models of their multilayer structures. The “pinched loop” molecular conformation which, rather surprisingly, describes the layer structure in an acid substituted tert-octyl calix[8]arene, also describes the structures in the amine-substituted and the alternate layer acid/amine-substituted calix[8]arenes, with the exception that the amine head-groups are larger and their interpenetration is prevented. In contrast, the smaller calix bowl in the acid/amine-substituted calix[4]arene molecules defines their conformation more rigidly. The layer structure of the alternate layer acid/amine-substituted calix[4]arene sample is therefore well described by the repetition of the classical bowl and chain configuration.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The general characteristics of the calix[4]resorcinarenes and the calixarenes [1] have been described in our previous papers on the layer structures in a calix[4]resorcinarene film [2,3] and in a Langmuir–Blodgett (LB) film of an acid-substituted tertiary octyl calix[8]arene [4]. These compounds are of interest in host-guest chemistry and also as pyroelectric materials [5,6] for use in thermal detectors and thermal imaging devices. LB films can

* Corresponding author. Tel.: +44 1234 758332; fax: +44 1234 758300.

E-mail address: f.davis@cranfield.ac.uk (F. Davis).

¹ Current address.

² Deceased.

be fabricated by the repetition of non-centrosymmetric molecular bilayers, which usually have a low permittivity and a low dielectric loss tangent. The classical fatty acid/fatty amine systems have often been studied in the past, but functionalised calixarenes can also be incorporated into alternate layer LB films. They exhibit a high density of acid/amine pairs and a high melting point for the completed film. Pyroelectric coefficients of up to $15 \mu\text{Cm}^{-2} \text{K}^{-1}$ with figures of merit of $F_D = 75 \mu\text{Cm}^{-2} \text{K}^{-1}$ have been reported for calixarene based films [7], which are amongst the highest values of any LB films.

Calixarenes have been widely studied and shown to bind a broad range of inorganic and organic guests, however many of the studies on the specific complexation properties of calixarenes have only taken place in solution. For such materials to be of use in sensors there must be a transduction step which converts the binding event into a measurable signal. This will usually require the calixarene to be immobilised onto a solid surface such as an electrode, a piezoelectric quartz crystal or an optical chip. Therefore an understanding of the nature and structure of such layers is necessary.

There has been a number of works reported where the interaction of various guests with calixarene monolayers and multilayers has been studied. For example, monolayers of a calix[4]arene and a Schiff base modified calix[4]arene on various subphases were studied and showed the Schiff base calixarene demonstrated a much stronger interaction with dissolved Li^+ and Cu^{2+} ions [8]. Other workers studied the interaction of a calix[7]arene monolayer with various metal ions in the subphase and showed that incorporation of certain ions led to a more uniform LB film structure [9]. LB films of *p*-allyl calix[4]arene could be deposited onto glassy carbon electrodes which then had a much higher sensitivity for mercury

ions than unmodified carbon [10]. Thiocalixarene LB films have also been shown to greatly improve sensitivity for mercury at glassy carbon electrodes [11] using absorptive stripping voltammetry and in other work demonstrated simultaneous determination of lead and cadmium [12] as well as developing a selective electrochemical sensor for silver ions using LB films of calixarenes [13]. Incorporation of sodium ions in the subphase has also been shown to affect the properties of calixarene monolayers and also the gas permeability of LB bilayers deposited on a permeable substrate [14].

Calixarene LB films have also been shown to interact with organic guests, for example LB films of phosphorylated calix[4]arenes could be deposited on piezoelectric quartz crystals and shown to reversibly form complexes with volatile compounds such as acetone and chloroform [15]. LB films of the similar calix[4]resorcinarene have also been shown to detect organic vapours using quartz crystal microbalance [16] or surface plasmon resonance [17].

We previously reported [4] the construction of LB films of an acid substituted calix[8]arene and determination of its layer structure. Our findings led us to conclude that the calix[8]arene existed in the LB film in the unusual “pinched loop” state rather than a cone or pleated loop conformation. Despite the rather unusual molecular conformation of the “pinched loop” state, it alone described the layer structure in an acid substituted tert-octyl calix[8]arene sample [4]. We were keen therefore, to establish whether it could be applied to other substituted calixarenes as well as investigating structures made from calix[4]arenes.

The general schemes of calix[8]arene and of calix[4]arene samples measured in the present work are shown in Fig. 1, and they

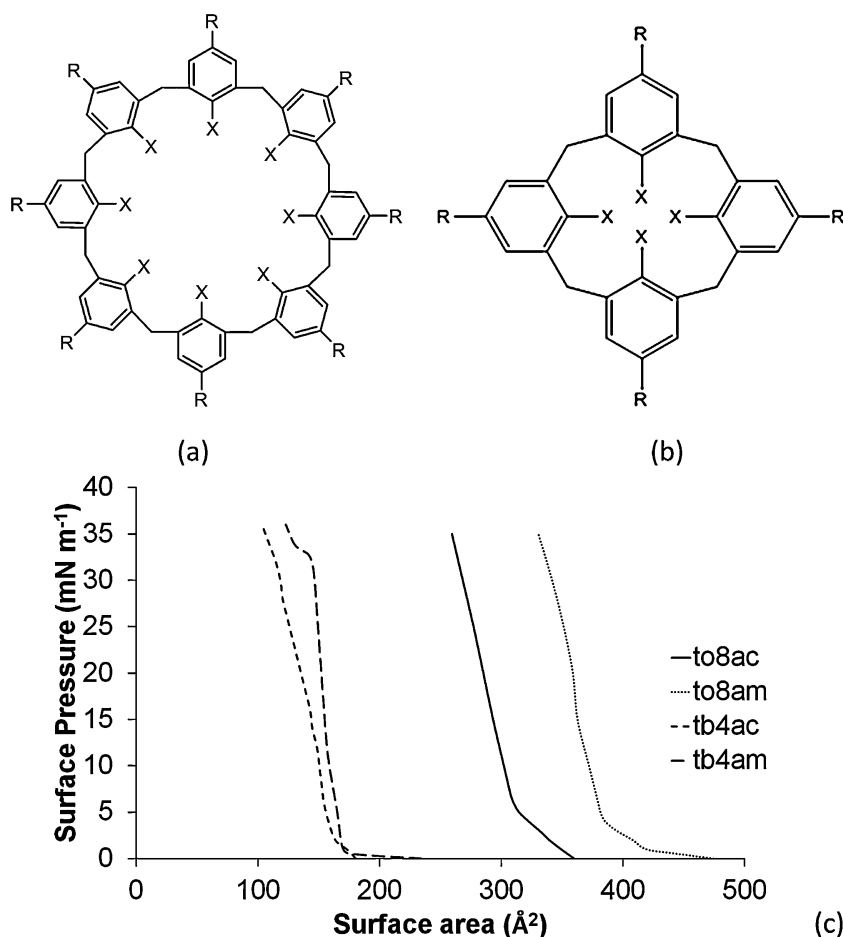


Fig. 1. The general schemes of the (a) calix[8]arenes and (b) the calix[4]arenes are given and the R- and X- substitutions of the examples studied are specified in Table 1; (c) isotherms of the calixarenes.

Download English Version:

<https://daneshyari.com/en/article/593323>

Download Persian Version:

<https://daneshyari.com/article/593323>

[Daneshyari.com](https://daneshyari.com)