Swelling behaviour of calixarene film exposed to various organic vapours by surface plasmon resonance technique

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ABSTRACT

Calixarene molecules can be deposited using the Langmuir–Blodgett (LB) film technique as an active layer which can be utilised in the field of volatile organic vapour sensing applications. The sensing responses of the films against benzene, ethyl benzene, toluene and m-xylene were measured by the surface plasmon resonance (SPR) method. Fast and reversible adsorption of organic vapours could be observed. The changes in reflectivity implied the swelling behaviour of calixarene film during adsorption and can be explained by the capture of organic vapour molecules. Fick’s law for early-time diffusion was adopted to quantify real time SPR data for the swelling processes. It was observed that diffusion coefficients \( D \) for swelling obeyed the \( \text{t}^{1/2} \) law and could be correlated with the various organic vapours used.

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1. Introduction

In the recent years, calix[\( n \)]arenes and their derivatives have been extensively studied for their possible application within sensors and electronic devices. This is because these materials can be highly selective molecular receptors for various metal ions and organic compounds, allowing for their use in various separation and analysis applications [1,2]. The host–guest interaction is often a dynamic process where adsorption and desorption of vapour molecules will occur when a sensing element is exposed to vapours. It is widely known that when a gas molecule is adsorbed onto the surface of an organic material, the physicochemical properties such as the structural, electrical or optical properties of this sensing material can change. It is a very important issue to understand the interaction mechanism between sensing element and organic vapours for the design and synthesis of new molecules to detect and identify organic vapours at low concentration. The major difficulty in gas identification is the fabrication of stable sensors with a high sensitivity and selectivity towards the substance to be detected. Several measurement techniques such as surface plasmon resonance (SPR), UV–vis and quartz crystal microbalance (QCM) are used to detect and monitor various gases because of their wide range of potential applications. An example is environmental monitoring, such as detecting the presence and concentration of toxic or otherwise dangerous gases that are released through spillage or leakage [3]. Another broad application area is quality control and industrial monitoring, particularly in such industries as food processing, perfumes, beverages and other chemical products [4,5]. Monitoring and determining the constituents of a sample gas typically involve collecting samples and analysing them in a gas chromatograph–mass spectrometer (GC–MS) of significant size and cost [6]. Although GC–MS systems work very well, many applications need sensor systems that are smaller, more portable, cheaper and even disposable [7].

SPR is a total internal reflection system utilising a thin metal film on top of a high-index dielectric surface. SPR is a method that combines optical and electrochemical phenomena at a metal surface and is a powerful technique to measure molecular interactions in real time in a label free environment. In this approach a laser beam is focused onto the back of a metal film, usually gold of thickness about 40 nm. When the gold is of this critical thickness [10], at certain angles of incidence of the laser with the gold film, energy is adsorbed and used to create surface plasmons which can propagate along the metal surface. This means that the reflected light intensity at this angle can drop dramatically, often to almost zero. However the plasmons are not strictly located at the surface but rather the intensity of its electromagnetic field exponentially decays from the metal surface into the adjacent medium. The resonance of surface polarons at the metal–dielectric interface is extremely sensitive to the dielectric constant and thickness of the medium adjacent to the metal film [8–10]. Using a flow-injection type electrochemical SPR sensing system, adsorption and desorption of water-soluble polymers on gold surfaces have been observed [11]. It has been found that lightly crosslinked molecularly imprinted polymer particles
can serve as the basis of a sensitive and selective membrane for the detection of organic contaminants such as pharmaceuticals in aquatic environments [12].

In the present work, Langmuir–Blodgett (LB) thin films formed from calix[4]amine were studied to determine the swelling process during adsorption of vapour molecules. Calix[4]amine derivative has been chosen for this study since this material is an excellent material to organize as a monolayer on the water surface and to prepare Langmuir–Blodgett (LB) thin film with a highly ordered structure and controlled thickness. Using a SPR measurement system during which organic vapours are introduced into a gas cell, variations in the intensity of reflected light were monitored in real time during swelling of the film. The organic vapour uptake causes an increase in the transparency of polymeric film that explains the changes in reflected light intensity during swelling. Fick’s second law for diffusion [13] was employed to determine the diffusion coefficients for the swelling processes.

2. Experimental preparation

The chemical structure and molecular model showing the predicted cross-sectional area and thickness of the material used in this work is shown in Fig. 1. Ultrasonically cleaned microsolv glass slides coated with 40 nm thick gold films were used as substrates. Gold was thermally evaporated with a rate of $1 \text{nm s}^{-1}$ under vacuum of $10^{-1} \text{Pa}$ and the thickness of the gold film was estimated to be 40 nm using the conventional quartz crystal microbalance method. Chloroform was used as a solvent with a solution concentration of 0.5 mg ml$^{-1}$. This solution was spread onto the water surface using a microlitre syringe and approximately 15 min were allowed for the chloroform to evaporate. Monolayers at the water surface were sequentially transferred onto a gold substrate by the LB film deposition procedure. A surface pressure of 22.5 mN m$^{-1}$ was selected for the LB film deposition process. Y-type Langmuir–Blodgett (LB) films were prepared with a transfer ratio of ~0.95 which is a good agreement with the transfer ratio (0.9–1.0) obtained for similar calix materials [14,15].

A Kretschmann type optical set-up system was employed for SPR measurements [16]. Prism and sample were mounted on a $\theta$–$2 \theta$ rotation platform driven by a stepping motor (with a resolution of 0.01°) and controlled by a microprocessor. A p-polarised monochromatic ($\lambda = 633 \text{nm}$) He–Ne laser light source was used to excite surface plasmons. An optical contact between these samples and a semi-cylindrical prism (of refractive index $n_p = 1.515$) was made using an index matching liquid (ethylsalicylate from Aldrich). The shift in the position of SPR resonance was employed to measure the deposition of calix[4]amine LB film layer onto the gold substrate. Variations in the intensity of reflected light were observed for calix[4]amine LB films of four different thicknesses. The SPR curves are shifted to larger angles when the number of layers is increased. The inset in Fig. 2 gives the shift of SPR minima versus number of monolayers in LB films. A linear relationship is observed and it suggests that an equal mass per unit area is deposited onto the gold–coated glass substrate during the transfer of LB film layers. Similar results were found for tetraphosphorylated calix[4]resorcinarene LB films studied by a SPR measurement system [17].

A special polytetrafluoroethylene (PTFE) gas cell, sealed via rubber O-rings, was constructed to study adsorption properties of calix[4]amine LB film on exposures to benzene, toluene, ethyl benzene and $x$-ylene vapours. Kinetic measurements were made in which a fixed angle $\theta^*$ was chosen near the minimum on the left side of the SPR curve. The reflection intensity at this angle was measured as a function of time when the sample was exposed to an organic vapour for at least 2 min and was then allowed to recover after injection of dry air. Variations in the intensity of reflected light indicate that organic vapour uptake causes an increase in the transparency of calix[4]amine LB film during swelling. Fick’s second law for diffusion [13] was employed to determine the diffusion coefficients for the swelling processes.

3. Results and discussions

The deposition process of calix[4]amine LB film was studied by SPR technique. The shift of SPR curves must be related with the deposited layer number onto the gold substrate due to increasing of the film thickness. The relationship between SPR shift $\Delta \theta_0$ and film thickness $d$ can be given by [18]:

$$
\Delta \theta_0 = \frac{(2 \pi / \lambda)(|\epsilon_m| |\epsilon_i|)^{1/2} d}{n_p \cos \theta (|\epsilon_m| - |\epsilon_i|)^2 |\epsilon|}(e - \epsilon_i)
$$

(1)

where $\lambda$ is the wavelength of the beam used for the excitation of surface plasmon, $\epsilon$ is the complex dielectric constant of the thin
layer, \( \varepsilon_m \) is the modulus of the complex dielectric constant of gold film, \( \varepsilon_l \) is the dielectric constant of the medium in contact with the thin layer and \( n_p \) is the refractive index of the prism, respectively.

Fig. 2 shows a set of experimental SPR curves showing the variation of reflected intensity as a function of internal angle for bare gold and the overlayers of calix[4]amine LB films of four different thicknesses. The SPR curves are shifted to larger angles when the number of layers is increased. The inset in Fig. 2 gives the shift of SPR minima versus number of monolayers in LB films. The angle of incidence is set to a particular angle, i.e. near the minimum on the left side of the SPR curve. The reflection intensity at this angle as the vapour is adsorbed was measured as a function of time and was then allowed to recover after injection of dry air.

Fig. 3 displays the photodetector response as a function of time when the sample was periodically exposed to several organic vapours (benzene, ethyl benzene, toluene and \( m \)-xylene vapours) for 2 min, followed by injection of dry air for a further 2 min period.

The initial response of calix[4]amine LB film in the SPR system for all vapours increased sharply over the first 3 s. The response of the calix[4]amine LB film to benzene vapour is the largest with the fastest recovery time (8 s). The responses of LB film to benzene and ethyl benzene vapours are reversible when the gas cell is flushed with dry air. The results indicate that the LB films investigated in this work show a response to all vapours but are more selective towards benzene and ethyl benzene. Exposure to these vapours were found to have a larger effect on the optical parameters of this film than toluene and \( m \)-xylene and showed that the film thickness increased as a result of film swelling. Previous workers [19,20] showed that amphiphilic calix[4]resorcinarene (C-4-RA) thin films could be prepared by spin coating and used to detect benzene, toluene, ethyl benzene, and \( m \)-xylene (BTEX). These films produced a fast and reversible response which was associated with changes in the refractive index of the sensing layer due to the host–guest interaction between the C-4-RA molecules and the vapour molecules [19,20]. Adsorption of organic vapours by C-4-RA LB films was also studied in situ using quartz crystal microbalance, ellipsometry and surface plasmon resonance techniques. The results were interpreted in terms of capillary condensation of organic vapours in the nanoporous matrix of calixarene LB films accompanied by film swelling due to changes of the thickness and refractive index of the LB films caused by adsorption [21].

What is of interest is that the films used in this study displayed higher sensitivity to benzene relative to the other vapours than was found for films of C-4-RA [19]. LB films of an azobenzene derived resorcinarene when exposed to organic vapours showed similar sensitivity towards benzene and toluene and lower sensitivity for \( m \)-xylene [21].

Fick’s second law of diffusion states that the rate of change in concentration with time, is proportional to the rate at which the concentration gradient changes with distance in a given direction. As this law of diffusion is adopted to a plane sheet and solved for a constant diffusivity, \( D \) the following equation is obtained for concentration changes in time [13]:

\[
\frac{C}{C_0} = \frac{x}{n_0} + 2 \sum_{n=1}^{\infty} \frac{\cos n \pi}{n} \frac{\sin \frac{n \pi x}{a_0}}{n \pi} \exp\left(-\frac{D n^2 \pi^2}{a_0^2} t\right) \tag{2}
\]

where \( a_0 \) is the thickness of the slab, \( D \) is the diffusion coefficient, and \( C_0 \) and \( C \) are the concentration of the diffusant at time zero and \( t \), respectively. \( x \) corresponds to the distance at which \( C \) is measured. In order to replace the concentration terms with the amount of diffusant, one has to use the following equation.

\[
M = \int_V \rho(x, y, z, t) \, dV \tag{3}
\]

When Eq. (3) is considered for a plane volume element and substituted in Eq. (2), the following solution is obtained [13]:

\[
\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2} \exp\left(-\frac{(2n + 1)^2 D \pi^2}{a_0^2} t\right) \tag{4}
\]

where \( M_t \) and \( M_\infty \) represent the amount of diffusant entering the plane sheet at time \( t \) and infinity, respectively. This equation can be reduced to a simplified form which is still 99% accurate:

\[
\frac{M_t}{M_\infty} = 4 \sqrt{\frac{D}{\pi a_0^2}} t^{1/2} \tag{5}
\]

which is called the early-time equation and this square root relation can be used to interpret the swelling data [22].

In order to quantify the kinetic data given in Fig. 3, it is necessary to extract the LB film parameters due to swelling for two cycles. Fig. 4 shows the normalized photodetector response (intensity...
Table 1
Physical properties of organic vapours.

<table>
<thead>
<tr>
<th>Organic vapours</th>
<th>Molar volume (cm$^3$ mol$^{-1}$)</th>
<th>Solubility parameter (MPa)$^{1/2}$</th>
<th>Viscosity (cSt)</th>
<th>$D$ (cm$^2$ s$^{-1}$) $\times 10^{-15}$ (first cycle)</th>
<th>$D$ (cm$^2$ s$^{-1}$) $\times 10^{-15}$ (second cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>86.36</td>
<td>18.8</td>
<td>0.744</td>
<td>1.50</td>
<td>0.85</td>
</tr>
<tr>
<td>Xylene</td>
<td>122.00</td>
<td>18.2</td>
<td>0.930</td>
<td>1.20</td>
<td>1.05</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>123.10</td>
<td>18.0</td>
<td>0.669</td>
<td>0.13</td>
<td>0.93</td>
</tr>
<tr>
<td>Toluene</td>
<td>107.00</td>
<td>18.3</td>
<td>0.680</td>
<td>0.02</td>
<td>0.07</td>
</tr>
</tbody>
</table>

of reflected light) against swelling time, $t_s$ where the consolidation process involves setting the starting time to $t = 0$ for each swelling event for various organic vapours. As seen in Fig. 4, the reflected light intensity, $I_{rf}$ decreased as the time of vapour exposure is increased. It is also seen that changes in $I_{rf}$ against the time of vapour exposure decreased more quickly for benzene than for toluene organic vapours. These observations can be explained that as the organic vapours penetrate into film, transparency of the film increases, which results in the decrease of intensity of light reflected from the film. These results can be related to the amounts of diffusant entering the film $M_t$; that is, $I_{rf}$ should be inversely proportional to $M_t$ [22,23]. Eq. (5) now can be written as:

$$\left( \frac{I_{rf}(t)}{I_{rf}(\infty)} \right)^{-1} = 4 \sqrt{\frac{D}{\pi a_0}} t^{1/2} \tag{6}$$

where $I_{rf}(t)$ and $I_{rf}(\infty)$ are intensities of reflected light at any time, $t$ and saturation point in $I_{rf}$, respectively. The normalized $I_{rf}$ intensities $\{I_{rf}(\infty)/I_{rf}(t)\}$ are plotted in Fig. 5 for the square root of swelling time according to Eq. (6). The slopes of the linear relations in Fig. 5 produce the diffusion coefficients, $D$ for the swelling of calix[4]amine LB film and those values are given in Table 1. It can be seen that diffusion coefficient, $D$ is strongly dependent on the organic vapours used in the cell.

4. Conclusions

In conclusion, we introduced a model to analyse the swelling behaviour of calix[4]amine LB film after exposure to various organic vapours. It is shown that the penetration of organic vapours into calix[4]amine LB film is rapid enough and diffusion coefficients...
are dependent on the organic vapours used. This behaviour can be related in terms of solubility parameters, molar volume and viscosity parameter of swelling agents. In both cycles, diffusion coefficients for benzene are faster than other organic vapours since benzene has lowest molar volume and relatively high viscosity parameter which indicates that benzene molecules are more mobile than the other organic molecules and penetrate easily into the calix[4]amine LB film. On the other hand, m-xylene has a larger viscosity parameter and also a larger molar volume which means these molecules are slow to penetrate into the calix[4]amine LB film, indicating lower diffusion coefficients than benzene. Toluene also has larger molar volume and viscosity parameters which explain its lower diffusion coefficients than the other vapours. Further work will determine whether the kinetic or thermodynamic parameters of the adsorption of swelling agents are responsible for the performance during sensor applications.

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References


Biographies

Matem Erdoğan graduated from Cumhuriyet University, Sivas-TURKEY in 1990 and received his MSc degree at Illinois Institute of Technology, Chicago-US in 1996 and his PhD degree at Istanbul Technical University, Istanbul-Turkey in 2003. He joined Physics Department, Balikesir University in 2004. He is deeply involved in swelling, drying, shrinking, aging and slow release processes in polymeric gels by using steady-state and time resolved fluorescence spectrofluorometric techniques. He is also working on the modelling of diffusion process in polymeric thin films during gas sensor application.

Rifat Çapan received MSc degree at Hacettepe University Physics Engineering Department in 1991, Ankara-Turkey and his PhD at the University of Sheffield (UK) in 1998. He established first Langmuir–Blodgett Thin Film Research Group in Turkey. He had a PhD scholarship from Turkish High Education Council between 1993 and 1998 and had Oversea's Research Student Award (UK) from 1995 to 1998. His main interests are pyroelectric heat sensor, gas sensor for environment applications, the electrical and optical properties of organic thin film materials. Dr. Çapan was appointed as assistant professor between 1999 and 2016 and associate professor from 2002 to 2007 at University of Balikesir in Turkey. He became a deputy of head of physics department in 2001 and was the head of physics department between 2003 and 2006. He has been working as a professor and the head of Department at the University of Balikesir since 2007. He is a member of American Chemical Society.

Frank Davis graduated from Lancaster University (UK) in 1987 and obtained his PhD at the same institution in 1991. Following postdoctoral experience at Manchester and Sheffield Universities, he then spent 4 years within the battery research group at Gillette UKRDL, Reading. He joined Cranfield Health, Cranfield University (UK) in August 2002. He has a wide experience of the synthesis of calixarene type materials and novel amphiphilic and surfactant molecules. Much of his research is focused towards the incorporation of novel sensing moieties within ultra-thin films and their use to detect a wide variety of species including organic solvents and carcinogens, as well as biological species such as ascorbate. Dr. Davis is the author of more than 80 published papers and 6 patents. He is a member of the Royal Society of Chemistry and a Chartered Chemist.