The NO$_2$ gas sensing properties of calixarene/porphyrin mixed LB films

T.H. Richardson [a,*], R.A. Brook [a], F. Davis [b], C.A. Hunter [c]

[a] Department of Physics and Astronomy, University of Sheffield, Hicks Building, Hounsfield Road, Sheffield S3 7RH, UK
[b] Institute of Bioscience and Technology, Cranfield University at Silsoe, Cranfield Centre for Analytical Science Silsoe, Cranfield MK45 4DT, UK
[c] Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, UK

Abstract

The NO$_2$ gas-sensing properties of calix[8]arene/porphyrin LB films over the concentration range 0.13–4.6 ppm have been investigated. A fast (t_{50}) response time of ∼10–15 s has been measured and the system has been shown to recover after gentle heating to around 70–90 °C. The kinetics of the adsorption process have revealed that 85–90% of the observed optical absorbance change occurs very quickly but that the final 10–15% change occurs with a much longer time constant. The former has been assigned to a fast, surface adsorption process and the latter can be thought of a slow, diffusion of analyte gas molecules through the bulk of the LB film. The concentration dependence of the sensing response follows simple Langmuir kinetics and indicates that these two-component materials may be attractive candidates for sensing NO$_2$ in the sub 1 ppm concentration range. Pre-exposure of the mixed films to toluene vapour, prior to measuring the NO$_2$ optical response, results in increasing the response time considerably. This is thought to occur as a result of blocking the calixarene cavities owing to their affinity for toluene.

1. Introduction

1.1. Background

All gas and vapour sensors rely on achieving a physical or chemical property change which is related in some way to the concentration of the analyte being investigated. Most commercially available gas detectors operate either by electrical conductivity modifications induced by the analyte such as tin oxide based sensors [1] or electrochemical sensors [2]. These often require high operating temperatures and are therefore power hungry and are sometimes susceptible to electrical interference. On the other hand, sensors reliant on changes in the optical properties of the active sensing material, generally operate at room temperature and remain relatively immune to interference effects.

In this work, the gas-sensitive optical properties of a porphyrin compound have been explored. Porphyrins [3] are highly conjugated macrocycles which are less electrically conducting than their phthalocyanine relations [4] but they possess highly distinctive UV–vis absorption spectra as a result of their electronic structure. Binding of various gas analytes to the porphyrin ring has been shown to induce dramatic changes in the optical absorption spectra both experimentally [5] and by computational modelling [6]. Research on LB films of porphyrins [7–9] has revealed that the chemical substitutions made to the porphin ring are important in determining their gas-sensitivity. Less positively, porphyrin molecules are prone to aggregate into three-dimensional clusters hindering access for an analyte molecule to molecular binding sites. Furthermore, often pure porphyrin LB films are not very uniform as a result of unsatisfactory reproducibility in Langmuir layer transfer from sample to sample. Therefore, a method of improving the homogeneity of the porphyrin film coupled to a means of enhancing the porosity of the sensing layer is required.

Calix[n]arenes are known to be excellent Langmuir film—forming materials [10,11]. They are cyclic "basket" shaped molecules containing phenolic monomers joined cyclically to enclose a cavity, the size of which depends on the number of monomers in the calix ring. In the case of the calix[8]arene carboxylic acid used in this work, each molecule possesses eight highly polar carboxylic acid moieties which serve to anchor

* Corresponding author. Tel.: +44 114 2224280; fax: +44 114 2223555.
  E-mail address: t.richardson@sheffield.ac.uk (T.H. Richardson).

the molecule to the water surface and thus to facilitate a very well defined molecular orientation. This view is not entirely correct since the presence of geometric isomers [12] means that there are actually several possible forms of each calix[8]arene molecule but nevertheless they spread efficiently on the water surface and can be transferred as LB films easily. Furthermore, calix[n]arenes are capable of binding certain ions or small molecules within their cavities (calixes) [13] and for exhibiting high porosity to other species [14]. These properties are ideal characteristics for a host material into which a gas-sensitive molecule such as EHO can be embedded in order to produce a highly porous and uniform thin film.

1.2. Adsorption and adsorption kinetics

There are many theories of adsorption of molecules onto surfaces [15] one of the simplest being Langmuir adsorption theory. This theory predicts how the fractional surface coverage of a surface by adsorbate molecules depends on the concentration of the adsorbate, the temperature and the mean lifetime of the adsorbed molecule interacting with the surface (often referred to as "sticking time"). In the context of the optical absorbance measurements performed here, the coverage corresponds to the change in the optical absorbance of the Soret band of the porphyrin, ΔAbs, and the Langmuir adsorption isotherm can be written as:

$$\Delta Abs = \frac{[NO_2]\Psi}{1 + \Psi} \qquad (1)$$

where $[NO_2]$ represents the concentration of the analyte in this study, nitrogen dioxide gas, and Ψ is given by

$$\Psi = \frac{\tau_0}{n_0 \sqrt{2\pi m k T}} \qquad (2)$$

in which τ_0 is the adsorption lifetime, n_0 is the number of available binding sites and T is the temperature.

The expression (1) can be linearised to obtain

$$\frac{[NO_2]}{\Delta Abs} = [NO_2] + \frac{1}{\Psi} \qquad (3)$$

suggesting that a plot of $[NO_2]/\Delta Abs$ versus $[NO_2]$ would yield a linear relationship if Langmuir adsorption were obeyed.

Furthermore, in all sensing systems the sensing signal takes a finite time to evolve as the analyte adsorbs and binds to the active sensing molecules. These kinetics can be modelled by following one of several different theories [15] but the Elovich theory [16] is particularly insightful in this work.

According to the Langmuir adsorption model, each binding site on a sensing molecule can capture only one analyte molecule and adsorption ceases when all these sites are occupied. Therefore, the rate at which binding occurs is expected to decrease as the degree of surface coverage increases. The Elovich approach states that the rate of gas adsorption onto a surface decays exponentially as the amount of gas adsorbed increases. This leads to an expression for the dependence of the surface coverage on time which can be written in terms of ΔAbs for our

purposes here:

$$\Delta Abs = \frac{1}{\delta} \ln(t) + k \qquad (4)$$

where δ and k are constants and t is time, valid for $t > 0$. Thus, we can anticipate that a plot of ΔAbs versus $\ln(t)$ may reveal information about the nature of the adsorption process in that a linear relationship between ΔAbs and t would indicate a single, simple adsorption mechanism.

2. Experimental

2.1. Materials

The materials used in this work are shown in Fig. 1. The synthesis of the porphyrin, 5,10,15,20-tetrakis(3,4-bis[ethylhexyloxy]phenyl)-21H,23H-porphine (EHO), has been described previously [8]. EHO is a bright purple powder which is dissolved in chloroform (HPLC grade) to yield a bright green/brown solution. The calixarene is substituted with eight –CH_2CO_2H groups on the lower edge of the calix bowl and eight –C(CH_3)_3 groups on the upper edge, rendering the molecule strongly amphiphilic. It is a white powder which dissolves in chloroform to yield a colourless solution. Its synthesis has been detailed in the literature [10].

2.2. Langmuir and LB film preparation

EHO is not a classic Langmuir monolayer-forming material such as stearic acid but the four 3,4-bis(ethylhexyloxyphenyl) groups attached to the tetraphenyl porphyrin are predominantly hydrophobic and encourage some degree of alignment on the water surface. However, LB films of pure EHO are non-uniform and it is difficult to obtain reproducible quality layers from sample to sample. It is well-known that mixing functional materials with passive matrix materials such as fatty acids improves film quality as a result of the amphiphilicity of the carrier material. In this case, a calixarene has been used as the host material owing to its excellent film-forming capability as described in other work [11].

A 0.1 mg/ml solution of EHO was mixed with a 0.1 mg/ml solution of the calixarene to form a calixarene (62%)/EHO (38%) mixed solution (molar ratio). This was spread drop wise using a Hamilton micro syringe onto the cleaned surface of a Joyce-Loebl Mini Trough. Surface pressure–area isotherms showed a gently rising surface pressure with no abrupt phase transitions and revealed that deposition surface pressures in the range 15–25 mN/m would be ideal. LB deposition was thus carried out at 25 mN/m at a linear withdrawal and insertion speed of 30 mm/min onto silanized glass plates (pH 6.2, 20 °C). The resulting LB samples were stored in a dry, dark environment until the gas measurements were performed.

2.3. Gas testing methodology

A custom gas-testing apparatus, a schematic diagram of which is shown in Fig. 2, was used to assess the gas sensing