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Research Article

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Calix[4]arene-based Langmuir-Blodgett (LB) Thin Film for Volatile Organic Compounds Detection

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Abstract: In this study, the sensing ability of the calix[4]arene-based Langmuir-Blodgett (LB) thin films were investigated by using Surface Plasmon Resonance (SPR) technique. Dichloromethane, acetone and benzene vapors were selected as a harmful Volatile Organic Compounds (VOCs) to examine the kinetic responses of the calix[4]arene-based LB thin films against to these organic vapors at room temperature. Two calix[4]arene-based chemical sensors were prepared at different thickness values (4 and 8 LB thin film layers) to examine the effect on sensitivity of chemical sensor. The calix[4]arene-based chemical sensor prepared with 4 LB layers was found to be higher sensitive than prepared with 8 LB layers with fast response and recovery times. All kinetic measurements represented that the calix[4]arene molecule used in this study is a promising material for the development of chemical sensor devices at the room temperature with sensitivities between 0.66 and 1.41 percent response ppm^{-1}.

Keywords: Volatile Organic Compounds, Calix[4]arene, Optical sensor, Langmuir-Blodgett thin film

Uçucu Organik Bileşiklerin Dedeksiyonu için Kaliks[4]aren Tabanlı Langmuir-Blodgett (LB) İnce Filmler

Öz: Bu çalışmada, Yüzey Plazmon Rezonans (YPR) tekniği kullanılarak kaliks[4]aren tabanlı Langmuir-Blodgett (LB) ince filmlerin hassasiyet yetenekleri araştırıldı. Kaliks[4]aren tabanlı Langmuir-Blodgett (LB) ince filmlerin zararlı Uçucu Organik Bileşikler (UOB)olarak seçilen diklorometan, aseton ve benzene buharlarına karşı kinetik tepkisi oda sıcaklığında incelendi. Kalınlığın kimyasal sensörün hassasiyeti üzerinde etkisini incelemek için iki kaliks[4]aren tabanlı kimyasal sensör farklı kalınlık değerlerinde (4 ve 8 LB ince film tabakaları) hazırlandı. 4 tabaka LB ince film kaplanarak hazırlanan kaliks[4]aren tabanlı kimyasal sensörün hızlı tepki ve kendini yenileme süresi ile 8 tabaka LB ince film kaplanarak hazırlanan kaliks[4]aren tabanlı kimyasal sensörden daha fazla hassasiyet göstermiştir. Bütün kinetik ölçümler, bu çalışmada kullanılan kaliks[4]aren molekülü 0.66 and 1.41 %. ppm^{-1} hassasiyet değer aralığı ile oda sıcaklığında kimyasal sensör cihazlarının geliştirilmesi için umut verici bir malzeme olabileceğini göstermiştir.

Anahtar Kelimeler: Uçucu Organik Bileşikler, Kaliks[4]aren, Optiksel sensör, Langmuir-Blodgett ince film

1. Introduction

Calix[n]arenes are extensively utilized in detecting anions, cations and even neutral molecules. These macrocycles have further advantages in applications as efficient selective chemical sensors thanks to its incorporation of chemical groups and binding capabilities that respond to analytes complexation. Therefore these macrocycle molecules have been extensively studied hydrogen bonding (Sekiya et al., 2014), dipole-dipole (Capan et al., 2019), π-π interaction (Hinestroza et al., 2019; Ozbek et al., 2011) mechanisms and sensing applications for host-guest (Kim et al., 2012; Halay et al., 2019). In our previous studies, calix[4]arene-based materials prepared as LB thin film sensing elements were studied for optical and mass detection sensitivities using SPR and QCM techniques (Acikbas et al., 2017; Halay et al., 2019; Halay et al., 2020). These researches showed that they have high sensitivity and selectivity responses toward particular chemical classes of VOC molecules. In addition, macrocycle calix[4]resorcinarene molecule is suitable for the fabrication of a chemical sensing element with a precise controlled film thickness using the LB thin film deposition technique onto a solid substrate. The multilayer LB film arrangement for a chemical sensing element has a hydrophilic group on its external face and a hydrophobic group on the internal side (Kursunlu et al., 2019; Acikbas et al., 2020a; Büyükkabasakal et al., 2019). The active site, the hydrophilic surface of the calix[4]arene molecule in the open form, interacts with vapor molecules due to strong hydrogen bonds (Ozmen et al., 2014a). At the same time, the cavity of the calix[4]arene can provide an advantage for the binding of organic guest molecular species and the sensitivity and selectivity of calix[4]arene (Ozmen et al., 2014b).

In this study, an amphiphilic calix[4]arene-based organic materials was used to produce a selective and sensitive sensor element for a detection of VOCs. Benzene, acetone and dichloromethane vapors were used for optical sensor applications. SPR kinetic results showed that the sensitivity of calix[4]arene-based 4 LB thin layers to VOCs higher than calix[4]arene-based 8 LB thin layers except acetone vapor. These kinetic results revealed that calix[4]arene-based optical sensor displays a stable and reversible response to all VOCs and sensitive response to dichloromethane vapor than other VOCs.

2. Materials and Methods

2.1. Sensor Materials

Ball-and-stick model representation of calix[4]arene-based molecule structure was represented in Fig. 1. Bozkurt et al., 2012, report the detailed information about the synthesis process of this material in previous study. In our work, 1.75 mg mL^{-1} concentration of calix[4]arene-based material in chloroform.This solution was used for two process. Firstly, the behavior of calix[4]arene-based molecules floating on the water surface were investigated via isotherm graph. Using this graph, a suitable surface pressure for LB thin film fabrication was determined as 26 mN m^{-1}. Second process was carried out for the production of Y-type LB thin film at the room temperature using same concentration of the chloroform solution.

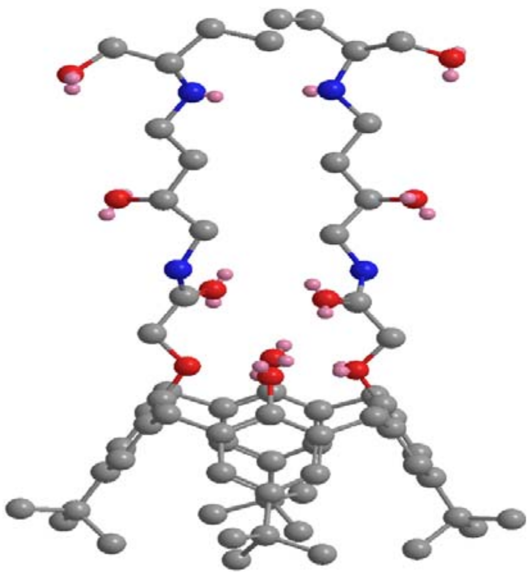

Figure 1. 3D representation of calix[4]arene-based molecule structure

2.2. Surface Plasmon Resonance (SPR) Spectrometer System

BIOSUPLAR 6Model SPR Spectrometer was utilized to perform all SPR measurements. As a light source, a laser diode at a wavelength of 632.8 nm was used for these measurements. A glass prism of reflective index 1.62 was installed to holder to take measurements in air environment, and 50 nm gold layer coated glass slides were used for all SPR measurements. All SPR kinetic measurements were performed by exposure dry air and VOCs for periodically 2 minutes. Fig. 2 represents the SPR kinetic measurement system as a symbolic representation.

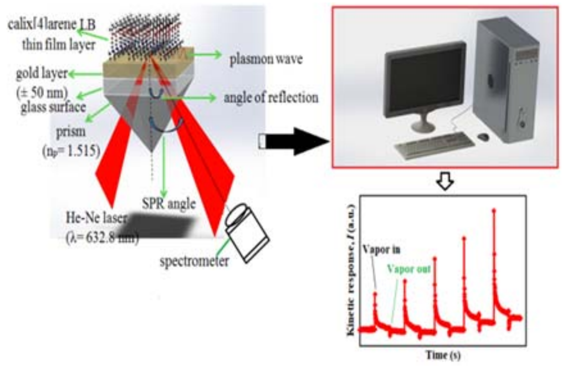

Figure 2. A a symbolic representation of the SPR kinetic measurement system.

3. Results and Discussion

SPR Spectrometer is employed to prove an interaction between the 4 layers or 8 layers calix[4]arene -based chemical sensors and VOCs by recording the photodetector responses (Figs. 3a-8a). Dichloromethane, acetone and benzene vapors, which are well known as harmful VOCs, were allowed to insert the media of vapor cell for two minutes, in order of fresh air-VOCs- fresh air - VOCs -…- fresh air, periodically. In general, the mechanism of host-guest interaction can be considered by four steps, i.e., adsorption, diffusion, and desorption. The optical responses of calix[4]arene -based chemical sensors to all VOCs abruptly increased with several seconds. This step is known as an *adsorption process*. Then an exponential decrease was viewed because of the *diffusion process*. This rapid change can be resulted from a change of thickness and refractive index of calix[4]arene. Another reason is originated from the surface effect between calix[4]arene-based LB film surface and VOCs molecules. All vapor measurement studies were carried out using SPR technique in the kinetic mode. The calix[4]arene-based chemical sensors coated 4 LB thin layers and 8 LB thin layers were exposed to three different VOCs at different concentration. From the Figs. 3a-8a, the high response values were observed for dichloromethane among used VOCs. All SPR kinetic results revealed that the calix[4]arene-based chemical sensor displayed good the repeatability and renewability properties to all vapors.

The change of the reflected light intensity during the kinetic interaction is stated by ΔI is given by $\Delta I = I - I_o$ where I and I_o indicate the reflected light intensity values at the beginning of the adsorption process (exposed thin film) and the unexposed thin film (the air media), respectively. Response value of optical sensor is presented by Duran and Capan (2020):

$$Response\ (R) = \frac{\Delta I}{I_o} x100$$

In the SPR kinetic studies, calix[4]arene-based chemical sensors subject to VOCs for 120 seconds followed by fresh air injection for another 120 seconds. The kinetic studies were performed with five cycles of VOCs injection in which the exposed VOCs was applied with a syringe consisting between 20 % and 100 % saturated amounts of VOCs molecules in the following cycles.

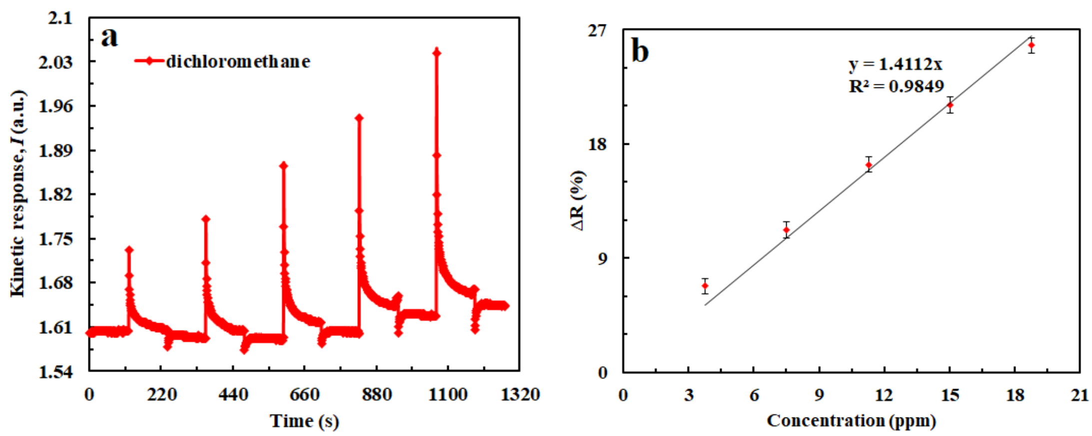

Figure 3. a) The kinetic response of optical LB thin film with 4 layers for dichloromethane vapors at different concentrations **b)** The determination of the sensitivity value against to dichloromethane vapor.

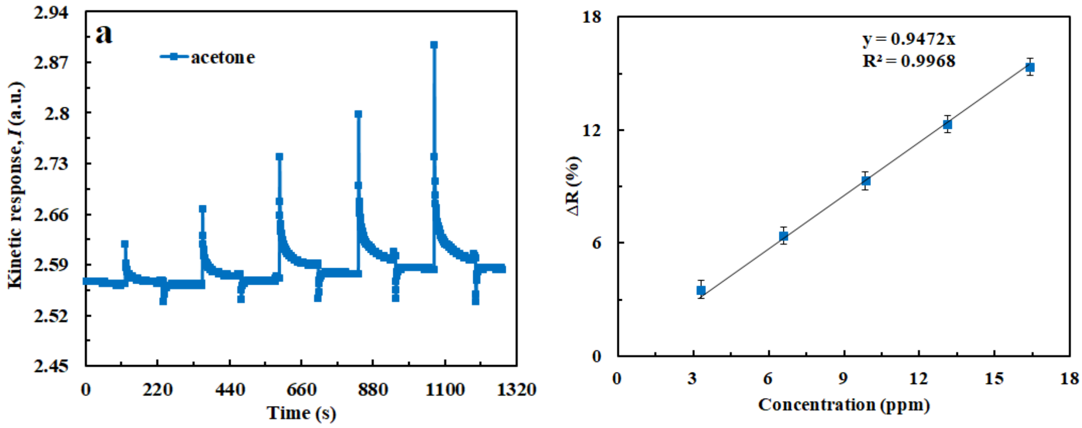

Figure 4. a) The kinetic response of optical LB thin film with 4 layers for acetone vapors at different concentrations **b)** The determination of the sensitivity value against to acetone vapor.

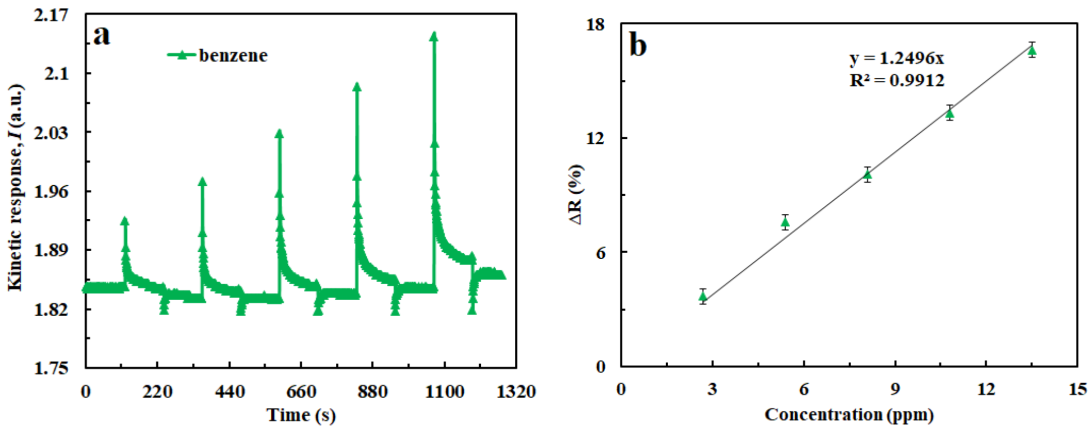

Figure 5. a) The kinetic response of optical LB thin film with 4 layers for benzene vapors at different concentrations **b)** The determination of the sensitivity value against to benzene vapor.

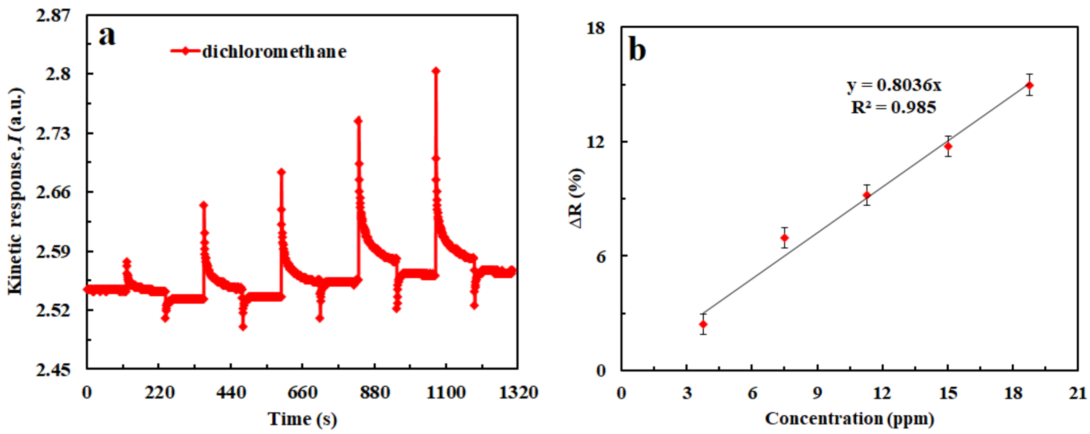

Figure 6. a) The kinetic response of optical LB thin film with 8 layers for dichloromethane vapors at different concentrations **b)** The determination of the sensitivity value against to dichloromethane vapor.

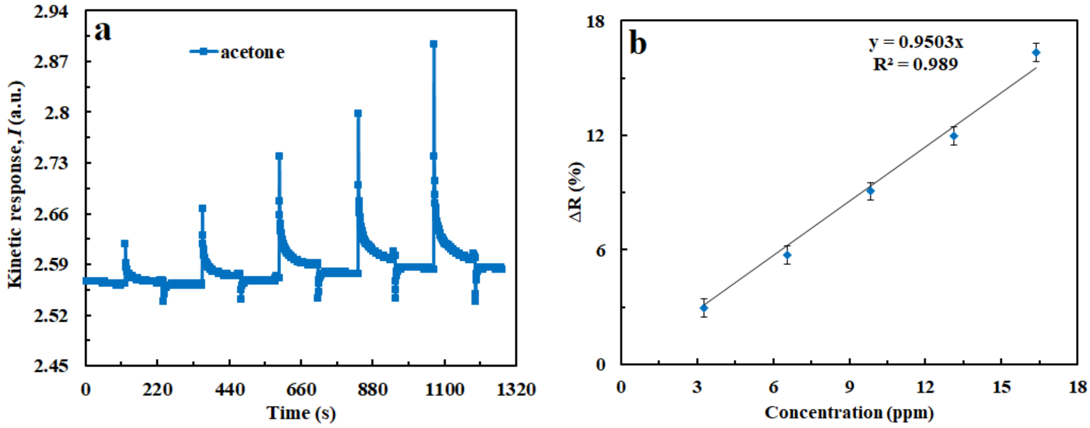

Figure 7. a) The kinetic response of optical LB thin film with 8 layers for acetone vapors at different concentrations **b)** The determination of the sensitivity value against to acetone vapor.

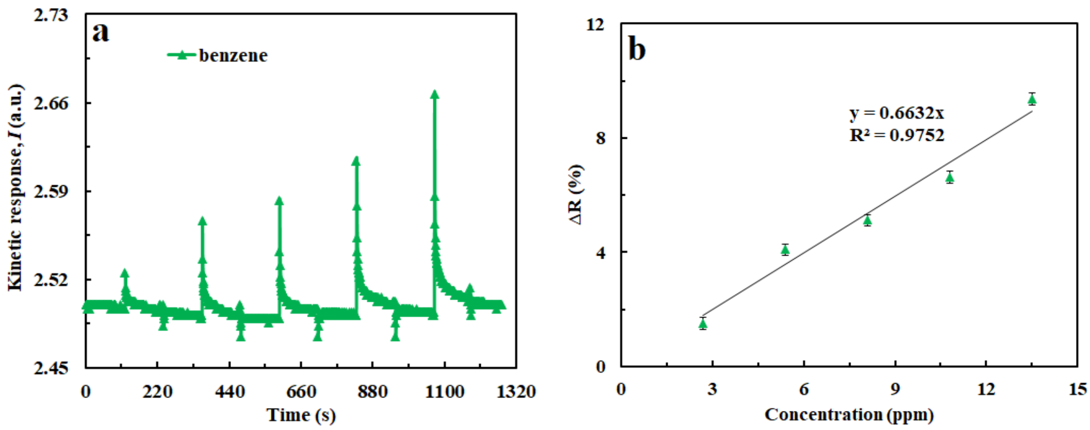

Figure 8. a) The kinetic response of optical LB thin film with 8 layers for benzene vapors at different concentrations **b)** The determination of the sensitivity value against to benzene vapor.

The calibration curves are given in Figs. 3b-5b and Figs. 6b-8b for the 4 LB layers calix[4]arene-based chemical sensor and for 8 LB thin layers calix[4]arene-based chemical sensor, respectively, subject to dichloromethane, acetone and benzene vapors. A linear dependence is observed between the response % and the different concentration of the VOCs for six different interactions. Using this linear relationship (from the slope of the curves), sensitivity values can be calculated. Table 1 presents the sensitivity values ensured from the calibration curves.

Table 1. Sensitivity values of calix[4]arene-based LB thin films.

	VOCs	Sensitivity *(% ppm^{-1})*
4 layers Calix[4]arene-based LB thin film	Dichloromethane	1.4112
	Acetone	0.9503
	Benzene	1.2496
8 layers Calix[4]arene-based LB thin film	Dichloromethane	0.8036
	Acetone	0.9472
	Benzene	0.6632

The sensitivity values given in Table 1 reveals that calix[4]arene-based LB thin films are more sensitive to dichloromethane vapour (Acikbas et al., 2020b; Kursunlu et al., 2017; Kursunlu et al., 2020). Since the dichloromethane molecule has a low molar volume (64.10 cm^3 mol^{-1}) and high dipole moment (1.60 D), it penetrates easily within the calix[4]arene-based LB thin films. The similar effect of the high dipole moment on the host-guest interaction was reported in previous works (Duran and Capan, 2020; Acikbas et al., 2015).

4. Conclusion

SPR kinetic results of calix[4]arene-based chemical sensors prepared by coating 4 LB thin film layers and 8 LB thin film layers were found very interesting for acetone vapor. The sensitivity values for two different chemical sensors against to acetone were approximately determined as same value (see Table 1). The thickness of calix[4]arene-based LB thin film chemical sensor not affected to these results obtained for acetone vapor. VOCs sensing measurements showed that the interaction of the thinner film with the gas molecules is higher. These results can be explained that the optical sensor prepared with 8 LB thin film layers is not optimum thickness of calix[4]arene-based LB thin film. From all SPR kinetic results, calix[4]arene based material can be developed as a sensing material at room temperature optical sensing devices.

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