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Developing of the calixarene based diamide chemical sensor chip for detection of aromatic hydrocarbons' vapors

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Abstract

In the present work, a new macrocycle materials (SB77) was selected and Langmuir-Blodgett thin films of this macrocycle compounds were examined for its vapor sensing capabilities against vapor of aromatic BTX hydrocarbons (benzene, toluene, xylene) through Quartz Crystal Microbalance (QCM) technique. In accordance with this aim, the calix[4]arene LB thin films were prepared onto quartz crystal substrates. The characterization of SB77 LB thin film was performed for nine LB layers fabricated onto the quartz crystal. The frequency shifts and the mass changes for monolayer of these LB thin films were obtained as 32.35 Hz / per layer and 2206.65 ng (8.32 ng mm^{-2}), respectively. All QCM results indicated that SB77 LB thin film chemical sensors exhibits high response, a good sensitivity and selectivity for benzene vapor at saturated or different concentrations than other aromatic hydrocarbon vapors. These LB thin film sensors with SB77 calix [4]arene macrocycle materials have been potential candidates for organic vapor sensing applications with simple and low cost preparation at room temperature.

Keywords: *Calixarene based diamide, LB thin film, chemical sensor, QCM.*

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Aromatik hidrokarbonların dedekte edilmesi için kaliksaren bazlı diamid kimyasal sensor çiplerinin geliştirilmesi

Öz

Sunulan çalışmada, yeni kaliks[4]aren bazlı diamid makrosiklik malzemesi (SB77) sensör malzemesi olarak seçildi ve bu makrosiklik bileşiklerin Langmuir-Blodgett (LB) ince filmlerinin, aromatik hidrokarbon (benzen, toluen, ksilen)buharlarına karşı buhar algılama kapasiteleri Kuartz Kristal Mikrobalans (KKM) tekniği ile araştırılmıştır. Belirtilen amaç ile uyumlu olarak, kaliks[4]aren LB ince filmler kuartz kristal yüzeyler üzerinde hazırlanmıştır. SB77 LB ince filmlerin karakterizasyonu kuartz kristal yüzey üzerine üretilmiş 9 LB tabaka için gerçekleştirilmiştir. Bu LB ince filmlerin her bir tabaka için frekans değişimleri ve kütle miktarı değişimi sırasıyla 32.35 Hz / tabaka and 2206.65 ng (8.32 ng mm^{-2}) olarak elde edilmiştir. Bütün QCM sonuçları, SB77 LB ince film kimyasal sensörlerin benzer buharının doymuş ve farklı konsantrasyonlarda diğer aromatik hidrokarbon buharlarına göre yüksek tepki, iyi bir hassasiyetlik ve seçicilik sergilediğini göstermiştir.SB77 kaliks[4]aren makrosiklik malzemesi, oda sıcaklığında basit ve düşük maliyet ile hazırlanması ile organik buhar dedekte etme uygulamaları için potansiyel aday olmaya sahiptir.

Anahtar kelimeler: *Kaliksaren bazlı diamid, LB ince film, kimyasal sensör, KKM.*

1. Introduction

Benzene, toluene and xylene (BTX) which is known as aromatic hydrocarbons widely found in industrial environments are highly toxic in nature. These aromatic hydrocarbons are commonly involved in some daily use products like thinners, cleaners, lubricants, degreasers and liquid fuels [1-3]. With rapid absorption by the human system, these aromatic hydrocarbons cause severe effects such as skin dehydration, dermatitis and defeating, along with much more important and long-term risks like carcinogenicity, leukemia and lymphomas [4]. For the minimizing of volatile organic compounds (VOCs) such as BTX damages on our health it is important to detect the amount of VOCs in our daily life using VOC sensor which is highly sensitive and selective. The selection of a suitable sensor element (host molecules) is very important during improve to chemical sensor in terms of potential interactions with guest species [5].

The use of macrocycle molecules in the field of sensing applications has several advantages because of cyclization structural organization and their unique cavity-size for host-guest interaction, binding affinity and selectivity [6, 7]. Some important macrocycle molecules used for sensing applications can be given as cyclodextrins, porphyrins, crown ethers and calix[n]arenes. Among these macrocycle molecules, calix[n]arenes are preferred as sensor chip element in the presented study. These macrocycle calix[n]arene molecules have been generally worked for various sensing applications for host-guest [8, 9], hydrogen bonding [10], dipole-dipole [11], π-π interaction [12, 13] mechanisms.
In this research, a new chiral calix[4]arene macrocycle material was selected as a chemical sensor element. The calix[4]arene based diamide chemical sensor was

prepared by using LB thin film technique. QCM technique was preferred to investigate the characterization of SB77 calix[4]arene LB thin film and its sensing properties against to pollutant BTX aromatic hydrocarbon vapors. All experimental results demonstrated that the SB77 monolayers were uniformly picked up at the air-water interface and these very uniform arrangements were transferred onto the quartz crystal to be formed as LB layers. SB77 materials displayed a reproducible and fast response to benzene vapor and so presented promising outputs in the detection of pollutant aromatic hydrocarbon vapors.

2. Experimental details

2.1 The procedure of SB77 LB thin film preparation

The 3D chemical structure of SB77 molecule was presented in Figure 1. The synthesis process of this material is detailed and reported in previous study by Bozkurt et al. [14]. In this study, 1.75 mg mL^{-1} concentration of SB77 and chloroform solution was smoothly spread on cleaned pure water to search the behavior of SB77 molecules floating on the water surface which were achieved via LB trough (Model 622-NIMA). A temperature control unit and the microbalance sensor were fixed to this trough in order to control the temperature of pure water and surface pressure, respectively. The Y type (the selected deposition type) SB77 LB thin films were prepared with fixed value of surface pressure at 26 mN m^{-1}, and all measurements were fixed at room temperature.

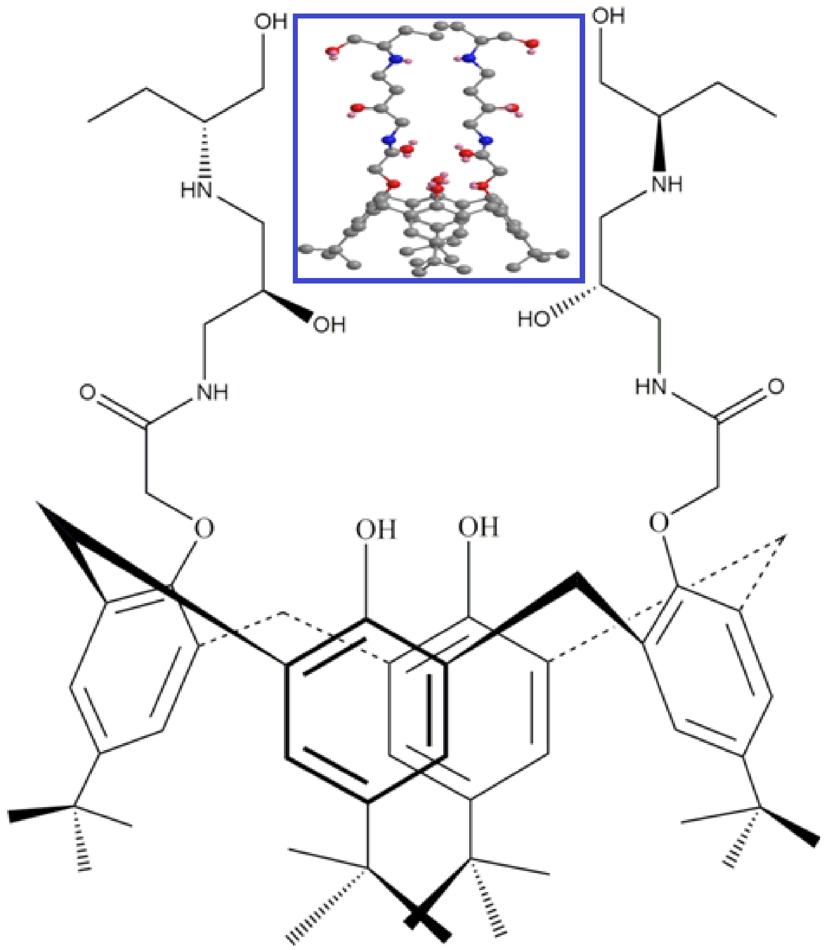

Figure 1. The chemical structure of SB77 materials. Inset: Ball-and-stick model representation of SB77 structure.

2.2 QCM technique

QCM measurement technique was preferred to examine both the preparation of the SB77 LB film layers and search the chemical vapor sensing properties of the SB77 calix[4]arene based diamide sensor chip with subjected to the pollutant aromatic hydrocarbon vapors. An oscillating circuit (a home-made designed) and quartz crystals (oscillation frequency of 3.5 MHz) were employed for the controlling of SB77 LB thin films' homogeneity and all kinetic measurements. QCM measurement technique, which was developed by our group, is presented in Figure 2. The performance of SB77 LB thin film sensor was fixed by using microliter syringe. In addition, a special vapor cell was developed to offer a suitable media for interactions between sensor molecule and vapor molecule. The SB77 sensor chip was subjected to pollutant vapors for 120 seconds, and then this chip was subjected to dry air for recovery process, periodically. The change in resonance frequency of QCM sensor was recorded as a function of time in the course of the interaction between the molecules of SB77 sensor and pollutant vapor. This performance, which is known as host-guest interaction, was took place with the pollutant aromatic hydrocarbon vapor entered into the special designed vapor cell at saturated or different concentration (the volume varied between 1 and 5 μL).

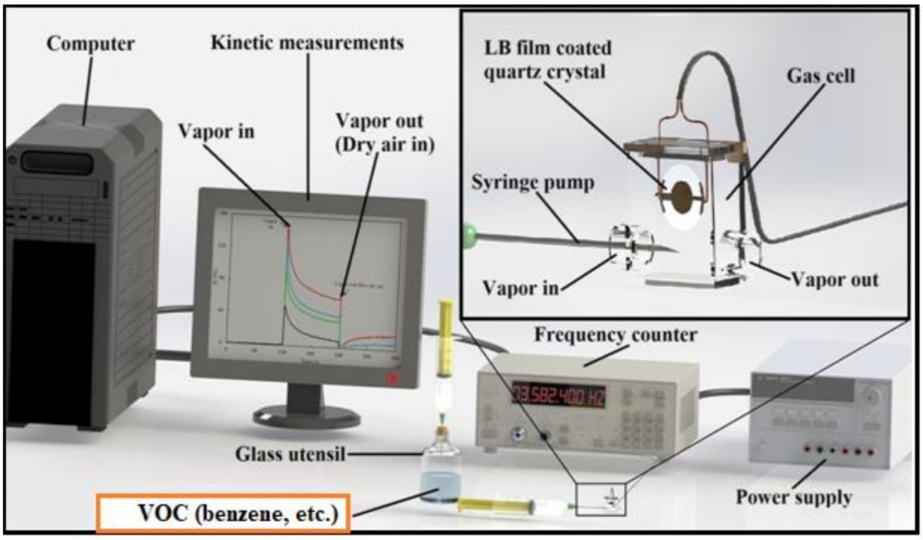

Figure 2. VOCs sensing measurement technique (A home-made QCM).

3. Results and discussion

3.1 The process of SB77 LB thin film fabrication and characterization

SB77 LB thin films were prepared onto quartz crystal substrates using LB deposition process of Y-type. The surface pressure (26 mN m^{-1}) fixed stable by utilizing the movable barrier (under the certain deposition conditions) to obtain the deposition graph of SB77 monolayer film from surface to solid substrate up to four layers (Figure 3). This graph displays that the each layer was successfully transferred by considering and calculating of the transfer ratio for deposited layers [15, 16]. It can be estimated that SB 77 is a preferable macrocyclic materials for the fabrication of organized LB thin films from the high value (calculated as ≥ 91%) of transfer ratio. In this presented work, the SB77 LB films were prepared in a symmetrical mode which is known as Y-type. The molecules were successfully arranged both tail-to-tail and a head-to-head forms onto suitable substrates (given in Figure 4).

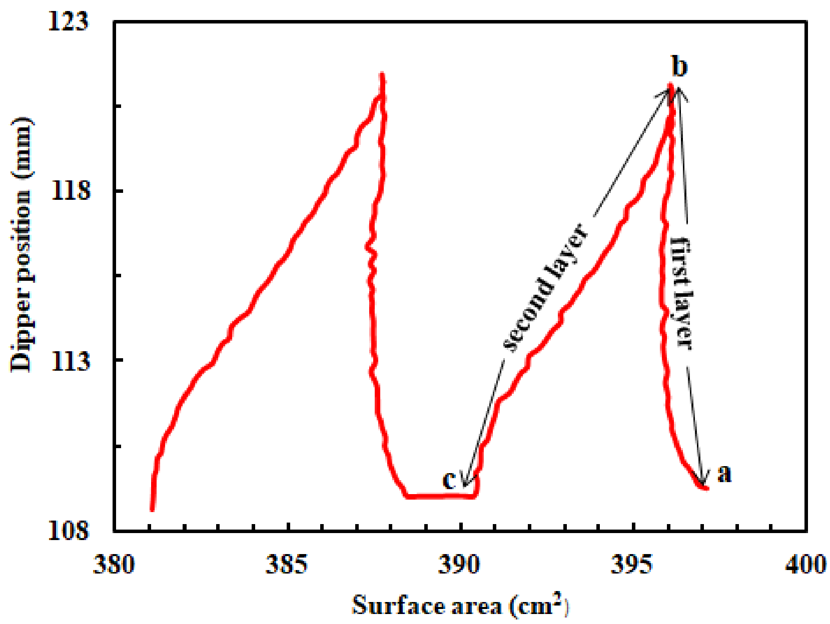

Figure 3. Transfer graph of SB 77 on quartz crystal.

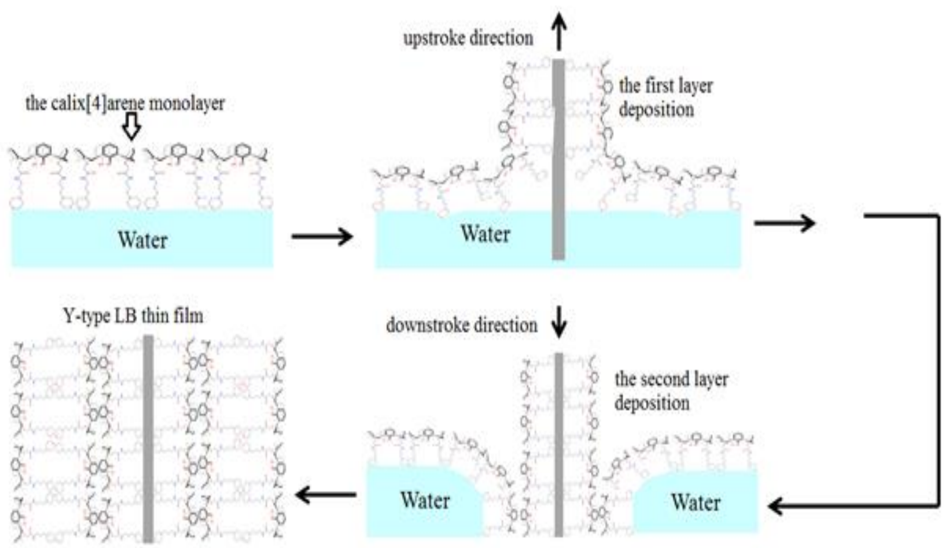

Figure 4. The process of Y-type LB film deposition for SB77 calix[4]arene.

The preparation of the SB77 LB films (for nine layers) onto quartz crystal substrate is presented in Figure 5. The resonance frequency change of quartz crystal can be illuminated in terms of the SB77 LB layer mass shift. A linear relationship was observed from the Figure 5 and it can be explained that nearly equal mass was transferred on the quartz crystal for per layer in the course of SB77 thin film fabrication. From the curve of the plot given in Figure 5 the frequency change for per bilayer of SB77 LB thin films was obtained as 32.35 Hz. Also, by using equation of Sauerbrey [17], the deposited mass on the quartz crystal was determined as 2206.65 ng (8.32 ng mm^{-2}) for monolayer.

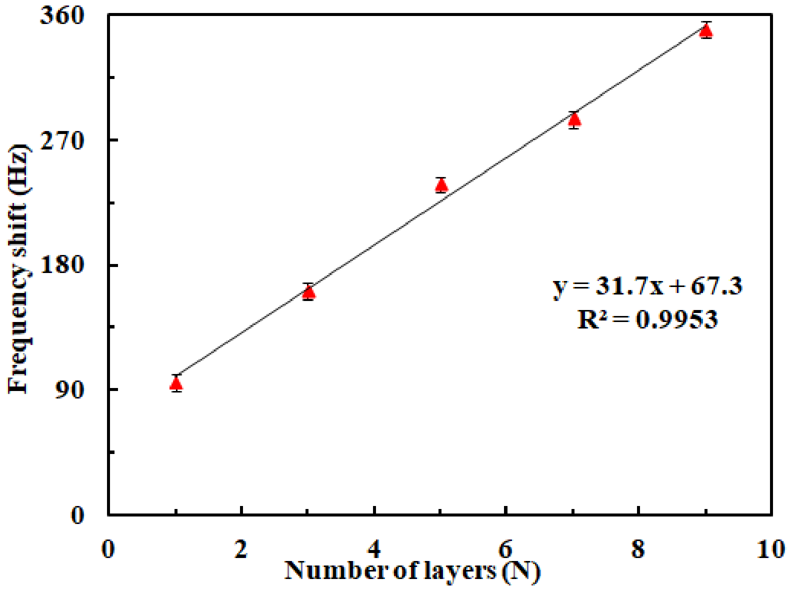

Figure 5. The mass shift of SB77 calix[4]arene based diamide LB film on the quartz crystal.

3.2 Chemical sensing properties of SB77LB thin film

The kinetic response of the QCM chemical sensor is measured, after depositing the SB77 LB films on the quartz crystal. The response-time figure for SB77 films under exposure of benzene, toluene, and *m*-xylene vapors are presented in Figure 6. It can be generally mentioned that chemical sensor measurements were performed in three steps (adsorption, diffusion, and desorption). Before the adsorption process started, SB77 LB film chemical sensor had exposed to fresh air for 120 s. Whenever the first interaction occurs between SB77 chemical sensor and the harmful vapor, the response of SB77 chemical sensor increases (Δf decreases) rapidly due to the surface adsorption effect (between ~120. s and 125. s). When the harmful organic vapor molecules are moved into the SB77 thin film, the response decreases gradually because of bulk diffusion effect. This interaction between host-guest molecules is called a dynamic process. In this process, adsorption and desorption occurs simultaneously. Then, the kinetic response of SB77 chemical sensor reaches the fixed value and it can be explained that the amount of the adsorbed and the desorbed molecules is approximately equal. At 240 s, the fresh air is moved to the surface of SB77 chemical sensor to observe whether the response value of chemical sensor returns to the initial value or not.

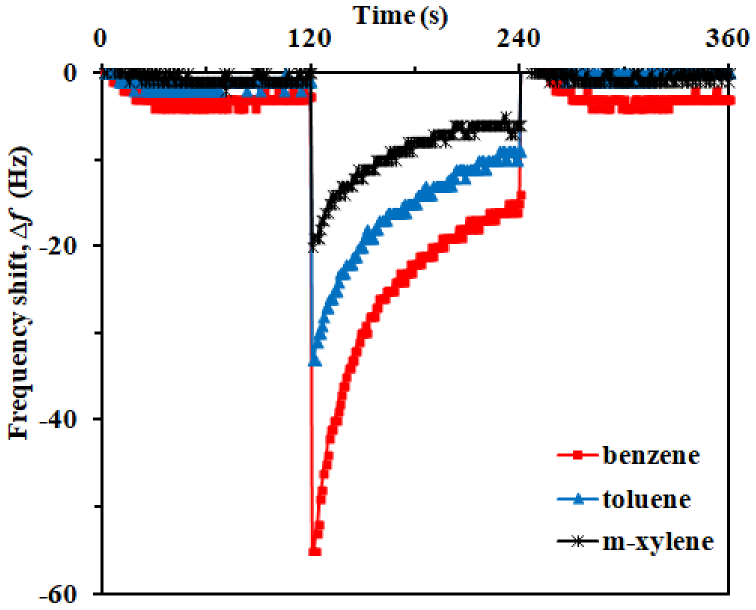

Figure 6. The frequency shift of SB77 calix[4]arene based diamide sensor against aromatic hydrocarbon vapors.

Figures 7-9 present the kinetic response of the SB77 chemical sensor chip for benzene, toluene and m-xylene with the described values as 20 %, 40 %, 60 %, 80 %, and 100 % at different concentrations of BTX vapors. These organic vapors at different concentrations were subjected to the SB77 chemical sensor for 2 minutes during exposure. When the concentration of the percentage increased, the resonance frequency change of SB77 chemical sensor increased proportionately. Accordingly, the large, fast and reversible responses were observed to BTX vapors utilized in QCM kinetic measurements.

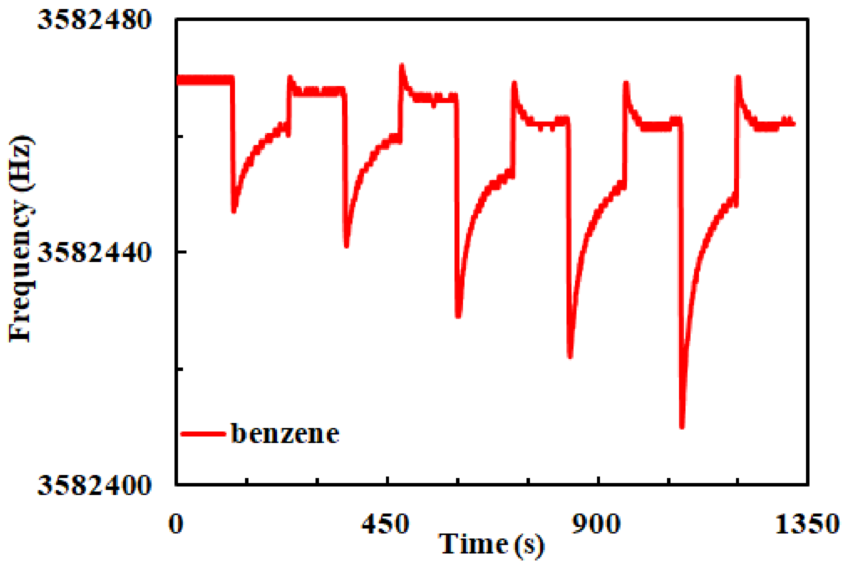

Figure 7. The frequency shift of SB77 calix[4]arene based diamide sensor for benzene vapor.

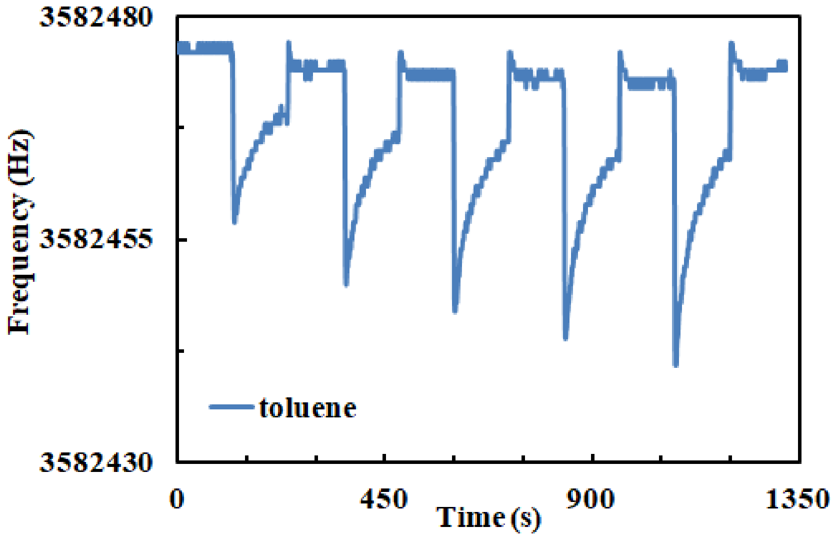

Figure 8. The frequency shift of SB77 calix[4]arene based diamide sensor for toluene vapor.

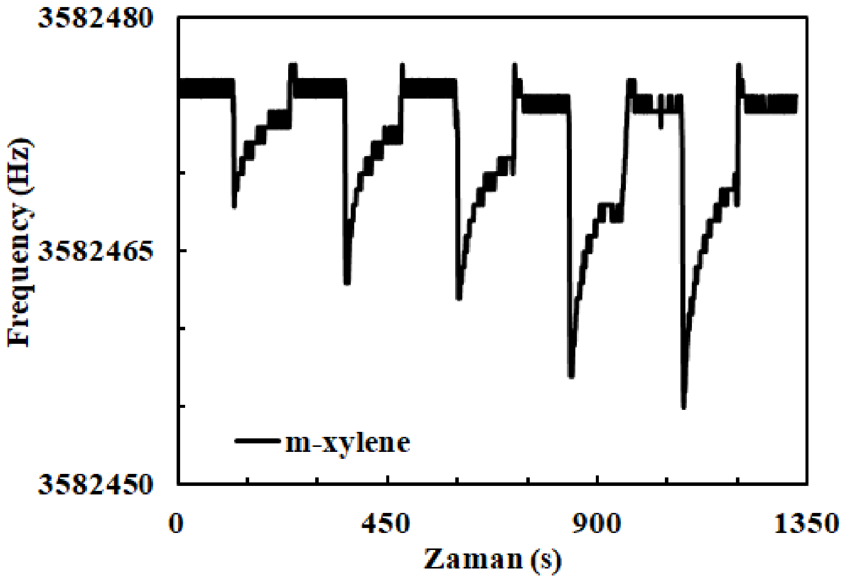

Figure 9. The frequency shift of SB77 calix[4]arene based diamide sensor for m-xylene vapor.

The changes in the kinetic response (Δf) were obtained to increase in turn benzene > toluene > *m*-xylene for the SB77 chemical sensor. This obtained ranking can be interpreted in terms of the vapor pressure and molar volume of BTX vapors [18]. The values of molar volume are known as *m*-xylene (122.00 $cm^3\ mol^{-1}$) > toluene (107.10 $cm^3\ mol^{-1}$) > benzene (86.36 $cm^3\ mol^{-1}$). While the other organic vapor molecules can difficultly penetrate into SB77 thin film, benzene molecules can easily diffusion into the same film because of its low molar volume. The effect of vapor pressure at room temperature supported to the kinetic response of SB77 QCM sensor chip against to BTX. The values of the vapor pressures are ordered as benzene (9.95 kPa) > toluene (2.91 kPa) > *m*-xylene (0.80 kPa). As a result, benzene molecules, due to its low molar volume and high vapor pressure, can easily infiltrate into SB77 calix[4]arene based diamide nano films when compared with the guest molecules of other aromatic hydrocarbon vapors.

3. Conclusions

This presented work illuminated that SB77 calix[4]arane materials could be easily deposited onto quartz crystal substrates, thus preparing an chemical sensing element. Linear relationships obtained from the figure of the mass shift indicated that SB77 LB films could be homogeneously prepared for using as sensor chip. Vapor sensing properties of SB77 sensor chip against three pollutant vapors (benzene, toluene, and m-xylene) were examined with the QCM technique. The results of these measurements demonstrated that the kinetic responses in terms of Δf were found to increase in the order benzene > toluene > *m*-xylene for the SB77 chemical sensors. Consequently, SB77 calix[4]arene based diamide can be developed as a potential sensor chip for improving of chemical sensing devices.

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