Turkish Journal of Physics

http://journals.tubitak.gov.tr/physics/

Research Article

Turk J Phys
(2017) 41: 65 – 71

doi:10.3906/fiz-1606-12

A quartz crystal microbalance study of the adsorption of benzene and acetone vapors onto coumarin-substituted manganese phthalocyanine film

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Received: 22.06.2016 • **Accepted/Published Online:** 22.09.2016 • **Final Version:** 02.03.2017

Abstract: A novel coumarin-substituted manganese phthalocyanine (**5**) was successfully synthesized and used as sensing element for benzene and acetone vapor detection. The effects of water vapor on the benzene and acetone vapor-sensing properties and adsorption isotherms on thin film of **5** were also studied. Our preliminary results indicated that the presence of humidity modifies the baseline frequency but not the sensitivity of the sensor toward benzene and acetone vapors. Two isotherm models, Langmuir and Jovanovic isotherms, were selected to describe the adsorption process. Linear regression analysis, which is the most basic and commonly used predictive analysis method, was used to estimate the suitability of the selected isotherm models. The Jovanovic model was found to be adequate for describing benzene and acetone adsorption onto compound **5**.

Key words: VOC sensing, adsorption isotherm, frequency shifts, phthalocyanine

1. Introduction

Phthalocyanines (Pcs) have triggered wide research interest in recent years due to their unique physical and chemical properties. On the basis of their thermal and chemical stabilities and high absorption spectra in the visible region, Pcs have been used as dyes in dye-sensitized solar cells [1] and gas sensors for emissions such as NO, NO_2, SO_2, and volatile organic compound vapors [2–5]. The gas-sensing application of Pc is based on the change in the material resistance when exposed to different atmospheres; hence the adsorption and diffusion behaviors of guest molecules in Pcs are important in terms of sensing performance. Of the various volatile organic compounds, benzene and acetone are very common in our daily life as cleaning agents and starting material in making other chemicals such as rubbers and detergents. Benzene is also a well-known human carcinogen. Studies in both people and lab animals show that benzene evaporates quickly and causes cancer. According to WHO guidelines for indoor air quality [6], the permitted concentration limit of benzene is 16 μg m^{-3} and such concentration can be found in living areas. Therefore, a considerable number of works have been focused on the development of organic-based sensors for the detection of benzene and acetone vapors. In this respect, quartz crystal microbalance-based sensors suffer many advantages over chemoresistive and optical sensors such as high sensitivity, short response and recovery times, portability, and simple instrumentation [7,8]. Responses of the quartz crystal microbalance (QCM) sensors vary in direct proportion to the extent of vapor sorption, which is typically rapid, reversible, and a linear function of vapor concentration [9]. Therefore, QCM sensors coated with a sensing layer have a number of useful attributes for the analysis of volatile organic compounds.

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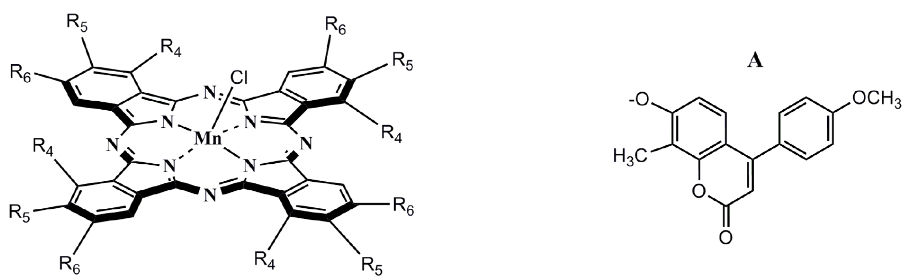
The present work focused on applications of manganese (III) phthalocyanines bearing 7-oxy-4-(4-methoxyphenyl)-8-methylcoumarin functionalized QCM sensor for sensing of benzene and acetone vapors. The effect of increasing concentration of solvent vapors on the resonance frequency of QCM was studied. This study also highlighted the isotherm of benzene and acetone adsorption and the influence of humidity on it. The adsorption isotherms evaluated include Langmuir and Jovanovic isotherm models.

2. Experimental

2.1. Sensitive layer deposition

The sample under investigation was spray-deposited coumarin-substituted manganese phthalocyanine (Pc) thin film. The synthesis details of this novel 1 (4), 8 (11), 15 (18), 22 (25)-tetra (4-(4-methoxyphenyl)-8-methylcoumarin-7-yloxy) manganese (III) phthalocyanine (**5**), shown in Figure 1, were reported elsewhere [10]. In order to study the interaction of benzene and acetone vapors with this layer, thin film of compound **5** was formed on a QCM by spraying of 3×10^{-3} M chloroform solution of **5.** Before the spray deposition of the Pc solution, the quartz crystals were cleaned in piranha solution (3:6 mixture of 30% H_2O_2 and H_2SO_4) at room temperature for 4 min.



	R4	R5	R6
5	A	H	H

Figure 1. Structural formula for 1 (4), 8 (11), 15 (18), 22 (25)-tetra (4-(4-methoxyphenyl)-8-methylcoumarin-7-yloxy) manganese (III) phthalocyanine.

2.2. Benzene and acetone sensing measurements

Liquid benzene and acetone was purchased from Sigma Aldrich in analytical reagent grade and used as received. Bubblers were used to generate gaseous benzene and acetone from liquids, with nitrogen flowing inside the bubbler. Benzene and acetone were then diluted with a secondary nitrogen flow. The benzene- and acetone-sensing properties of the coating material were tested in a cylindrical chamber of Teflon, 8 cm long and 4 cm in diameter, through which a gas could be passed. Before the exposure to analyte vapors, the sensor was purged with reference gas (N_2) until a stable baseline was established. After the **5**-based sensor in the chamber was stable, it was exposed to eight different concentrations of the benzene and acetone vapor. In order to see the influence of relative humidity (RH) on the adsorption isotherm and sensitivity of the sensor, response/recovery characteristics of the sensor were measured in different RH conditions. The desired level of humidity was created by bubbling the nitrogen gas through deionized water. The humidity-sensing experiments were conducted at relatively low RH levels to observe the adsorption process rather than condensation. For this reason, the relative humidity was varied between 0% and 40% RH and controlled with a commercially available humidity meter during the sensing experiments. Due to the weak temperature dependence of resonance frequency, AT-cut QCM of 10 MHz fundamental frequency was used as transducer. The sensing layer, phthalocyanine in our case, was deposited onto the Au electrode surface of the QCM by spray coating. The frequency shifts due to adsorption of benzene and acetone vapors were recorded vs. time using a programmable frequency counter (Keithley Model 776). All the experimental setup was controlled using an IEEE 488 data acquisition system incorporated into a personal computer.

3. Results and discussion

3.1. QCM measurements

The working principle of the QCM gas sensors is based on a shift in the fundamental resonance frequency of the quartz crystal resonator due to the mass accumulation on its surface. As shown by Sauerbrey [11], the deposition of a homogeneous coating promotes a shift in the fundamental resonant frequency of the quartz crystal, which can be expressed by

$$\Delta m \;=\; -\,\frac{\sqrt{\rho_q\,\mu_q}}{2\,f_0^2}\,A\,\Delta f, \tag{1}$$

where A is the electrode area, f_0 is the fundamental resonance frequency (Hz), ρ_q the quartz density, and μ_q its shear modulus.

Figures 2a and 2b depict the comparative sensing performance of the **5**-coated QCM sensor towards various concentrations of benzene and acetone vapor expositions in the condition of different RH between ~5% and 40%, respectively. With each injection of benzene and acetone vapor, the adsorption of target molecules onto the sensing layer resulted in a decrease in the resonance frequency of the quartz crystals. After an adsorption time of ~30 min, a frequency shift of 12 Hz was recorded for 5% benzene vapor in dry atmosphere. As can be seen from the Figure 2, the frequency shift increases with the analytes' concentration. Figure 2 also shows that the presence of humidity, acting as interference gas, modifies the baseline frequency but not the sensitivity of the film toward benzene and acetone vapors. In order to get an idea of the influence of the RH level on sensor performance, the benzene and acetone sensitivities were calculated from the concentration dependent response/recovery characteristics of the sensor.

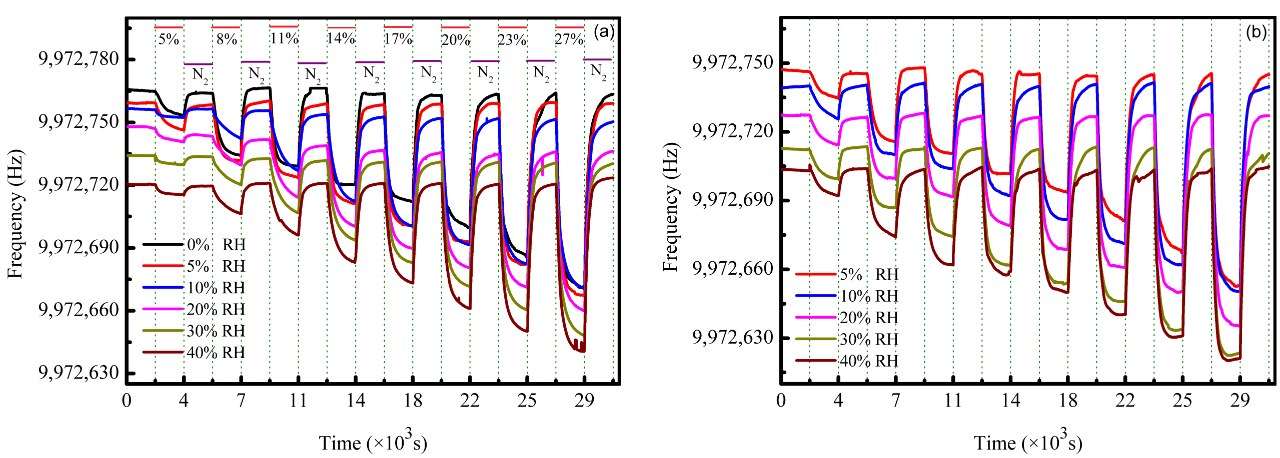


Figure 2. a) Benzene; b) acetone vapor response of **5**-coated sensor to indicated concentrations of analyte.

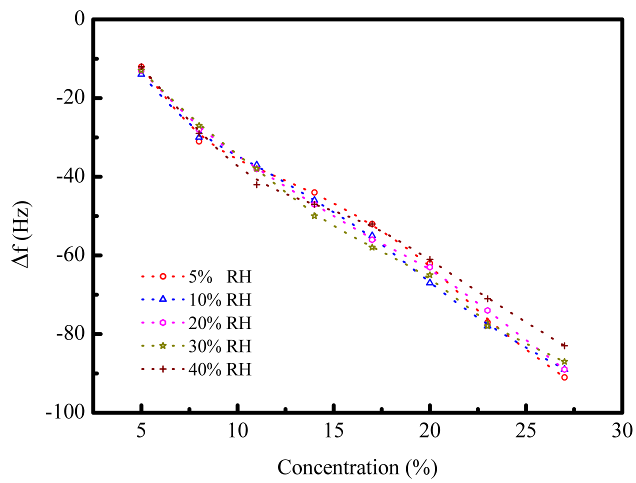


Figure 3. Variation in the sensitivity with acetone vapor concentration at various RH levels.

As a representative result, the influence of relative humidity (RH) on the acetone sensitivities of the sensor as a function of acetone vapor concentration is shown in Figure 3. It is clear from the Figure 3 that humidity level has a negligible effect on the acetone response of the film sample. This suggests the existence of two kinds of adsorption surface sites on the film surface. Patchwise and random models are frequently used to describe the adsorption processes on heterogeneous surfaces. In the patchwise model developed by Langmuir [12], the adsorption sites of equal adsorption energies are assumed to be grouped together into patches. This model also assumes that the patches are so large that the interactions between two molecules adsorbed onto different patches can be neglected. In the random model, the adsorption sites of equal adsorption energies are assumed to be distributed fully at random over a heterogeneous surface [13].

The obtained response/recovery characteristics and the RH level variation in the sensor sensitivities indicate the existence of a heterogeneous surface and surface energetic heterogeneity in the case of manganese phthalocyanine.

3.2. Adsorption isotherms

Adsorption is usually described through isotherms, that is, an empirical relationship used to predict how much adsorbate can be adsorbed by an adsorbent. A quantitative description of this process is essential to model the adsorbate transport. Distribution of organic vapor between the gas phase and the solid phase can be described by several isotherm models such as Langmuir, Temkin, and Freundlich. The Langmuir isotherm arises from assuming that the energy of adsorption of the species is independent of the coverage or the atomic arrangement of the species on the surface [14]. Once a site is filled, no further sorption can take place at that site. This indicates that the adsorption is limited to one monolayer and evolution of θ is given by the following equation:

$$\frac{d\theta}{dt} = k_a C(\theta_0 - \theta) - k_d \theta, \tag{2}$$

where k_a is adsorption kinetic rate, k_d is desorption kinetic rate, and θ_0 is the total number of free sites on the surface. In equilibrium, $\frac{d\theta}{dt} = 0$, Eq. (2) becomes

$$\theta_e = \frac{k_a C_e \theta_0}{k_a C_e + k_d} \tag{3}$$

Eq. (3) can be rearrangement to obtain a linear form:

$$\frac{1}{\theta_e} = \frac{1}{kC_e\theta_0} + \frac{1}{\theta_0}, \tag{4}$$

where $k = \frac{k_a}{k_d}$, θ_0 is the maximum monolayer adsorption capacity, C_e is unadsorbed gas molecule concentration in the gas phase, and θ_e is the amount of adsorbed gas molecule per unit mass of sorbent.

If we assume that the frequency shift in the QCM is proportional to the amount of adsorbed gas molecules, the plot of $1/\theta_e$ as a function of $1/C_e$ should give a linear relationship. Figures 4a and 4b show a plot of the linearized form of the Langmuir model under various humidity conditions for benzene and acetone vapors, respectively.

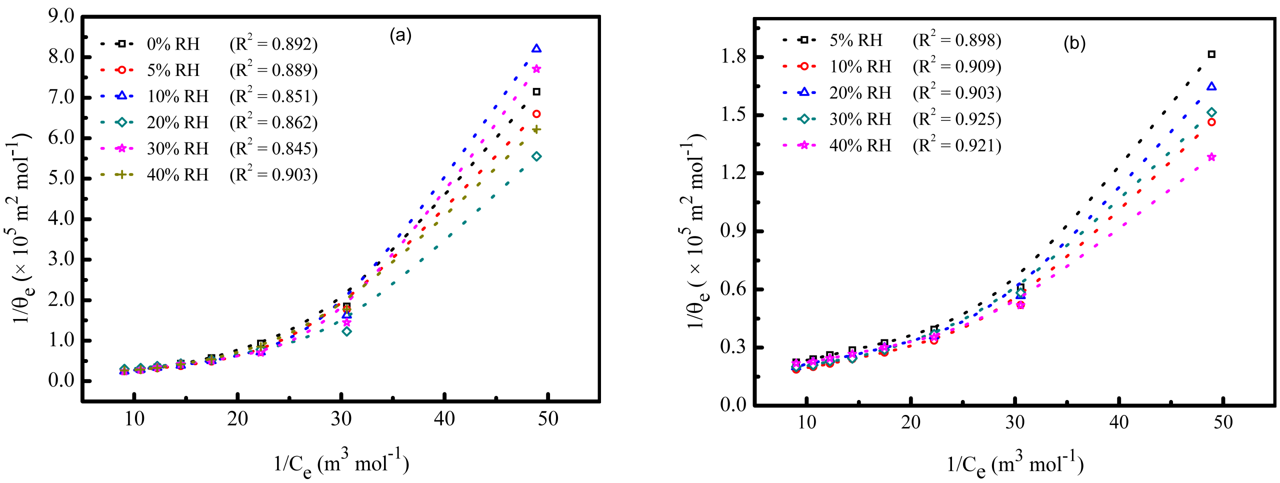


Figure 4. Langmuir plots for benzene (a) and acetone (b) vapors on the compound.

The applicability of the Langmuir model to experimental data was quantified by the correlation coefficient (R^2), which was obtained from the slopes of the $1/\theta_e$ vs. $1/C_e$ plots.

It was found from Figures 4a and 4b that the correlation coefficients are in the range of 0.845–0.903 for benzene vapor and 0.898–0.925 for acetone vapors. These values of R^2 suggest that the Langmuir isotherm is not appropriate to model the sorption of benzene and acetone vapors onto the Pc film investigated.

The model of an adsorption surface considered by Jovanovic [15] was initially derived for adsorption of gases, but has also been used to describe adsorption of peptides and proteins on ion-exchange adsorbents [16]. The Jovanovic isotherm keeps the same assumptions contained in the Langmuir isotherm equation, only considering, in addition the possibility of some mechanical contacts between the adsorbing and desorbing molecules when the surface is homogeneous. The Jovanovic model leads to the following relationship:

$$\theta_e = \theta_{max}\,(1 - e^{K_J C_e}) \tag{5}$$

The linearized form of the Jovanovic equation is given as follows:

$$\ln\theta_e = ln\,\theta_{max} - K_J C_e, \tag{6}$$

where $\theta_{\max}$ is the maximum amount of analyte adsorbed per unit mass of sorbent and K_J, the Jovanovic constant, is related to the energy of adsorption. The applicability of the Jovanovic model can be tested by linear fitting of $(\ln \theta_e)$ versus C_e plot. Figures 5a and 5b display the variation in $(\ln \theta_e)$ with C_e for benzene and acetone vapors, respectively.

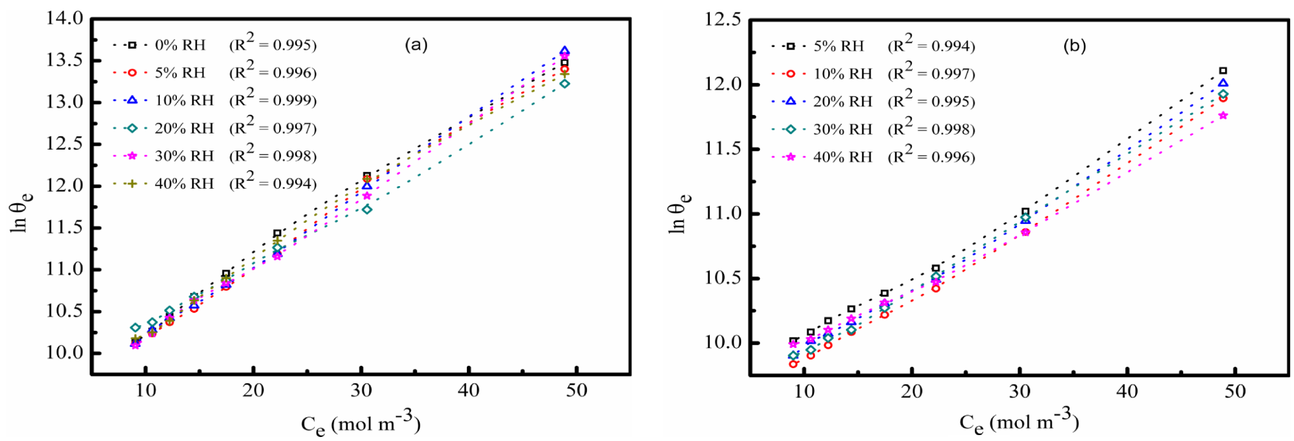


Figure 5. Plot of Jovanovic isotherm model for sorption of benzene (a) and acetone (b) onto compound **5**.

Examination of the adsorption data shows that good correlation coefficients (R^2) were obtained by fitting the experimental data to the Jovanovic isotherm. It reveals that the plots of $(\ln \theta_e)$ versus C_e plots are linear for all RH levels, indicating that the adsorption of benzene and acetone vapors onto compound **5** obeys the Jovanovic adsorption isotherm.

4. Conclusion

A spray-coated film benzene and acetone vapors sensor based on novel 1 (4), 8 (11), 15 (18), 22 (25)-tetra (4-(4-methoxyphenyl)-8-methylcoumarin-7-yloxy) manganese (III) phthalocyanine was successfully developed. All the observations demonstrated that benzene and acetone vapors detection can be achieved by the film of **5** even at room temperature. A comparative study of the applicability of isotherm models of Langmuir and Jovanovic isotherms to describe the experimental adsorption data of benzene and acetone vapors on Pc compound was carried out. The investigations indicated that the gas sensing process in Pc film is related to surface reactions and humidity interference led to modifying of the baseline frequency of the sensor. Comparing the regression coefficients R^2 shows that the adsorption of benzene and acetone vapors onto compound **5** can be successfully described by the Jovanovic adsorption isotherm.

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