A sensor of alcohol vapours based on thin polyaniline base film and quartz crystal microbalance

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ABSTRACT

Thin films of polyaniline base, emeraldine base (EB), coating on the quartz crystal microbalance (QCM) electrode were used as a sensitive layer for the detection of a number of primary aliphatic alcohols such as ethanol, methanol, 2-propanol and 1-propanol vapours. The frequency shifts (Δf) of the QCM were increased due to the vapour adsorption into the EB film. Δf were found to be linearly correlated with the concentrations of alcohols vapour in part per million (ppm). The sensitivity of the sensor was found to be governed by the chemical structure of the alcohol. The sensor shows a good reproducibility and reversibility. The diffusions of different alcohols vapour were studied and the diffusion coefficients (D) were calculated. It is concluded that the diffusion of the vapours into the EB film follows Fickian kinetics.

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1. Introduction

Detection of volatile organic compounds (VOCs) such as, alcohols, ethers, esters, halocarbons, ammonia, NO_2, warfare agent stimulants [1,2], toxic gases released in subways by terrorist and by military in the field of monitoring of old military dumps [3] are important in sensor technology. The development of sensors with selectivity, rapidly, reliability and reproducibility to VOCs becomes more interest. Direct spectroscopic and electronic conductivity measurements have been used due to the change in optical and electrical properties, respectively of the material exposed to the organic vapour [4]. Infrared spectroscopy [5] used for detection of methanol vapour in air, but this need expensive instrumentation and is not suitable for on-line monitoring. Ethanol detection was based on the using of metal oxides and powders [6] which catalyze the oxidation of ethanol.

A number of electronic devices and chemical sensors based on the using of different polymer coatings such as, mass sensitive quartz crystal microbalance (QCM) and surface acoustic wave (SAW) devices, and chemical field effect transistors (ChemFETs) have been developed. Amongst the various types of chemical sensors, there is a considerable interest in QCM [7–9] for detection of VOCs.

Bartlett and Ling-Chung have used polypyrrole as a gas sensor for alcohols and other organic vapours [8], however it shows a low sensitivity, and an incomplete desorption of the gas molecules [10], so the researches were extended towards polyaniline (PANI) as a gas sensing material [11,12]. PANI has been demonstrated as a good gas sensing ability due to its environmental stability, high electrical conductivity, good reversibility and reproducibility.

QCM is extremely sensitive to mass change, when the surface of a quartz crystal electrode is coated with a sensitive polymeric material, capable of interacting with the environment of interest, due to the ability of the polymer material to sorb vapour reversibly [13]. The change in mass onto the quartz crystal electrode during the reaction with the analyte was used as sensor for interested vapours and gases. The changes in mass (m') of the polymer film can be measured by the oscillating frequency of the quartz electrode. The frequency change (Δf) to the mass loaded is calculated from Sauerbrey equation [14]:

$$\Delta f = -\left(\frac{2f_0^2}{\sqrt{\rho_Q \mu_Q}} \right) m' \tag{1}$$

where f_0 (Hz) is the natural frequency of the quartz crystal, ρ_Q is the quartz density ($2.649\,g\,cm^{-3}$) and μ_Q is the shear modulus ($2.947 \times 10^{10}\,N/m^2$).

In previous studies [15,16], we studied the application of PANI coated the QCM electrode as sensors for pH and chlorinated hydrocarbons. The present work, presented an on-line detection of primary aliphatic alcohols vapour: ethanol, methanol, 1-propanol and 2-propanol using thin film of PANI in the form of emeraldine base (EB) coating on the electrode of QCM. A sensitive, reproducible and rapid sensor was developed.

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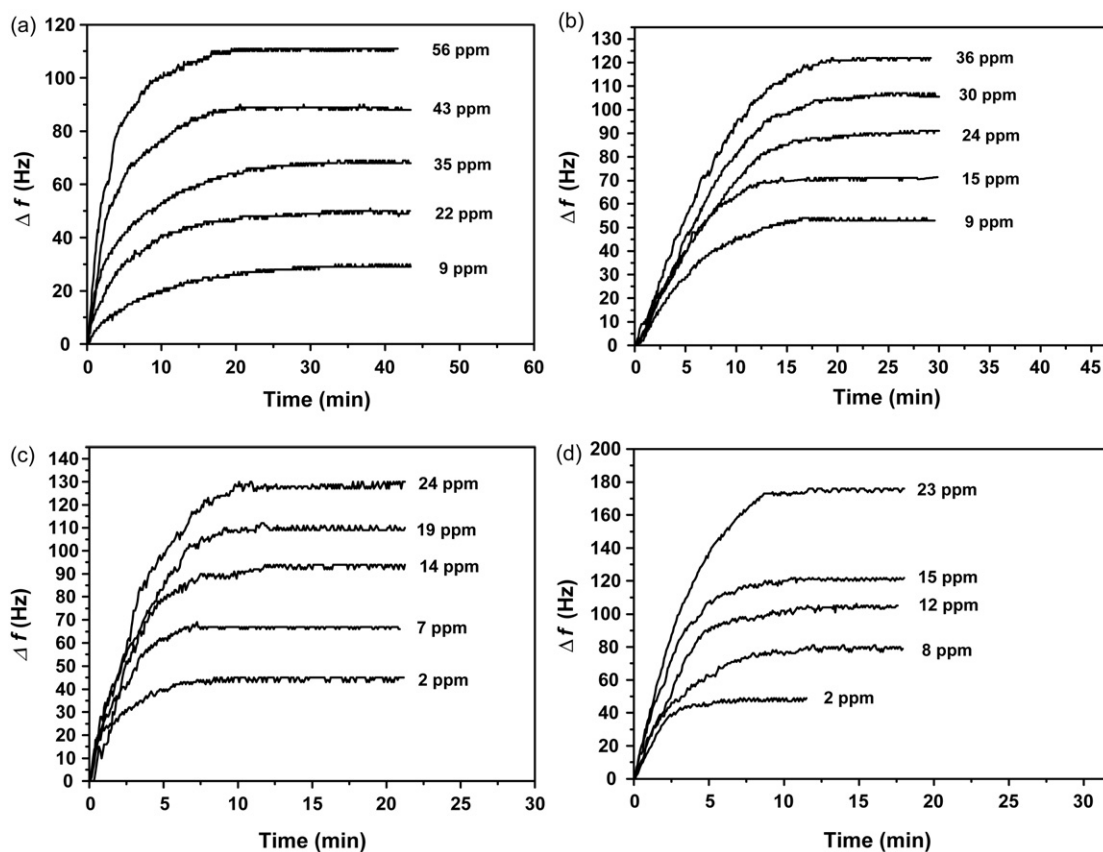*E-mail address:* mayad12000@yahoo.com (M.M. Ayad).

Fig. 1. Frequency shift of the EB film coated QCM when exposed to the vapours of various concentrations: (a) methanol (film thickness 123 nm), (b) ethanol (film thickness 152 nm), (c) 2-propanol (film thickness 171 nm), and (d) 1-propanol (film thickness 152 nm).

2. Experimental

2.1. Reagents and materials

Aniline (ADWIC, Egypt) was distilled twice under atmospheric pressure using zinc dust. Ammonium peroxydisulphate (APS) (WINLAB, UK) and sulfuric acid (ADWIC) were used as received. Ethanol and methanol were (ADWIC, Egypt), 1-propanol was (Aldrich, England) and 2-propanol was (BDH, England). All alcohols were used without any further purification. Double distilled water was used to make up the solutions.

2.2. Instrumentation

5 MHz AT-cut quartz crystal, one inch in diameter covered this hole, sealed with silicon rubber (RTV). This resonator formed the frequency determining element for an electronic counter. The frequency was measured using GW frequency counter, Model GFC-8055G. The design and experimental arrangement has been described in earlier studies [17].

2.3. Coating on the electrode of QCM with PANI emeraldine base film

A 0.08 M solution of aniline was prepared in 50 mL of 0.1 M H_2SO_4 and a solution of 0.1 M APS was prepared in 50 mL of 0.1 M H_2SO_4. The APS/aniline molar ratio after mixing was 1.25. The solutions of the reactants were added to the polyethylene cell. As the polymerization proceeds, the *in situ* PANI films were deposited onto the electrode of QCM. PANI salt, emeraldine salt (ES), formed at

the end of the polymerization was rinsed with 0.1 M H_2SO_4. The de-doping process was made by exposure of the ES film to 0.1 M ammonia to give PANI base, emeraldine base (EB), film. The EB film coating on the electrode of QCM was dried in an oven at 50–60 °C for at least 30 min. The thickness of the film can be determined as described elsewhere [16].

2.4. Procedures

All measurements were carried out in a polyethylene cell with an internal volume of 140 mL. Hamilton microliter syringe (Hamilton Bonaduz AG, Switzerland) was used for analyte injections. The concentration of injected analyte in the cell was calculated in part per million (ppm) according to the following equation:

$$C = \frac{22.4\rho TV_s}{273MV} \times 10^3 \tag{2}$$

where C is the concentration in ppm, ρ is the density of liquid sample in g/mL, T is the temperature of detection chamber in Kelvin, V_s is the volume of liquid sample in µL, M is the molecular weight of sample in g, and V is the chamber volume in liter.

The EB film coating on the QCM after exposed to a specific concentration of the alcohol vapours and the frequency variation with time attained the steady state, was exposed to hot air to desorb the vapour and recover the electrode. The backshift of the crystal frequency to its initial value was taken as an indication of full desorption. All measurements were carried out at room temperature (~25 °C).
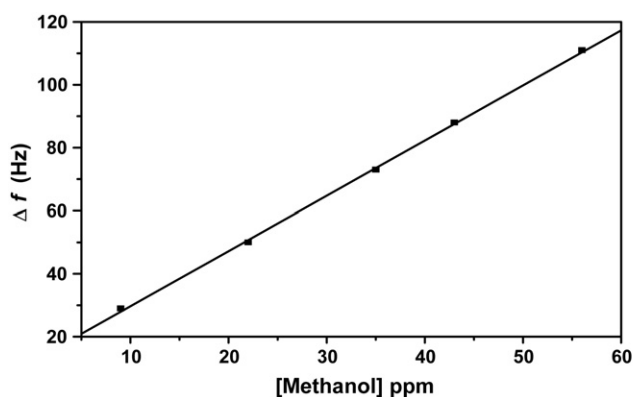
Fig. 2. Calibration curve for the determination of the methanol vapours using the EB film coated QCM electrode.

Fig. 3. The effect of film thickness on the detection of methanol vapours.

3. Results and discussion

3.1. EB coated QCM electrode for detection of alcohols

A thin film of the EB coating on the electrode of QCM shows a sensitive detection for primary aliphatic alcohols. The electrode was exposed to various concentrations of methanol vapour and the frequency of the quartz crystal decreased due to the adsorption of the vapours into the EB film according to Eq. (1). The equilibrium reached after few minutes. The relation between frequency shift (Δf) and time was plotted and is shown in Fig. 1(a). From the figure, it is observed that Δf increases linearly with increasing methanol vapour concentration. This is expected, since more vapour molecules in the test atmosphere, more vapour molecules would adsorbed into the EB film. The interaction between the EB film and methanol is electrostatic interaction through hydrogen bonding between imines and amines groups of the polymer chain and oxygen atom of the alcohol [18]. After each injection of methanol vapour, the frequency of the crystal back shifted to its initial value by drying the electrode using hot air, which indicates fully desorption of methanol from the electrode surface.

A calibration curve was constructed for determination of methanol vapour by plotting of Δf against various concentration of methanol vapour and is shown in Fig. 2. A linear correlation was obtained with a correlation coefficient (R) and slope equal 0.999 and 1.754 Hz/ppm, respectively.

It would be expected that the polymer thickness would affect the response time and sensitivity of the sensor. The frequency of the QCM electrode having different EB film thicknesses was recorded upon exposure to various concentrations of injected methanol vapour. Plots of Δf with the concentration of methanol for the different EB films of different thicknesses are shown in Fig. 3. It is obvious that as the film thickness increases, the magnitude of Δf and hence the slope of the correlation also increases. This is due to the increasing of the active sites, imines and amines, of the polymer. The correlation coefficients and the slopes of these correlations were calculated and are given in Table 1.

Ethanol vapours detection was also carried out, and the frequency of the crystal was recorded when the EB film of thickness 152 nm coated QCM electrode was exposed to various concentrations of ethanol vapours. The plot of Δf versus time was constructed as shown in Fig. 1(b). The same profile was obtained like that of methanol. A calibration curve of Δf against concentration of ethanol vapours in ppm was made and a linear relation was obtained with a correlation coefficient of 0.999 and a slope of 2.501 Hz/ppm.

The detection of 2-propanol and 1-propanol was also carried out and gave the same profiles like those of methanol and ethanol. Fig. 1(c)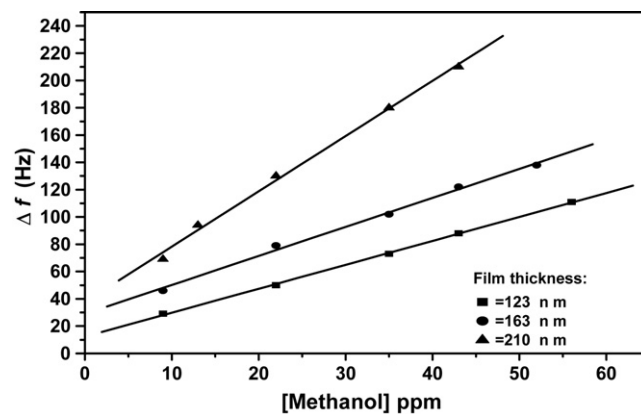 and (d) shows the Δf variation with time at various concentrations of 2-propanol and 1-propanol vapours. Calibration curves were constructed and linear correlations with $R = 0.999$ and 0.998 and slopes = 3.765 and 6.162 Hz/ppm were calculated, respectively for 2-propanol and 1-propanol. 1-Propanol has the same molecular weight of 2-propanol, but exhibit higher Δf values and hence higher slope than its isomer. This is could be due to the steric hindrance which prevents 2-propanol molecules from further adsorption into the EB film coated QCM electrode. Generally, it is concluded that as the molecular weight of the tested analyte molecule is increased the sensitivity of the EB film increased and the response of the quartz crystal increased except 1-propanol and 2-propanol due to the steric hindrance.

The sensitivity of the EB film coated QCM electrode that defined as the slope of calibration graph for each analyte injected is listed in Table 1.

3.2. Reproducibility and reversibility of the sensor

The sensor shows a good reproducibility and reversibility. Fig. 4 shows the exposure of 13 ppm methanol to the EB film of thickness 103 nm. Δf was recorded versus time till reached to the steady state and then the fully desorption of the crystal was obtained by using a hot dry air. The presence of about 2 and 3 Hz in methanol injection is considered to be the stability in the quartz crystal electrode. The experiment was repeated for five times to insure complete reproducibility and reversibility of the sensor.

3.3. Vapours diffusion

The diffusion of the alcohols vapours into the EB film coated QCM electrode is an important study [19]. Diffusion is expressed in terms of diffusion coefficient (D), in which an EB film of thickness 191 nm was exposed to 5 ppm of different alcohols vapour as shown in Fig. 5(a). The experimental data were analysed using the

Table 1
Analytical characteristic parameters for the determination of aliphatic alcohols vapour using the EB coated QCM electrode.

Compound	Film thickness (nm)	Sensitivity (Hz/ppm)	R[a]	R.S.D.[b] ($n = 5$)
Methanol	123	1.75414	0.999	0.89485
	163	2.12513	0.997	2.69915
	210	4.05173	0.998	4.23381
Ethanol	152	2.50125	0.999	1.37831
2-Propanol	172	3.76557	0.999	1.35385
1-Propanol	152	6.1626	0.998	2.84581

[a] Correlation coefficient.
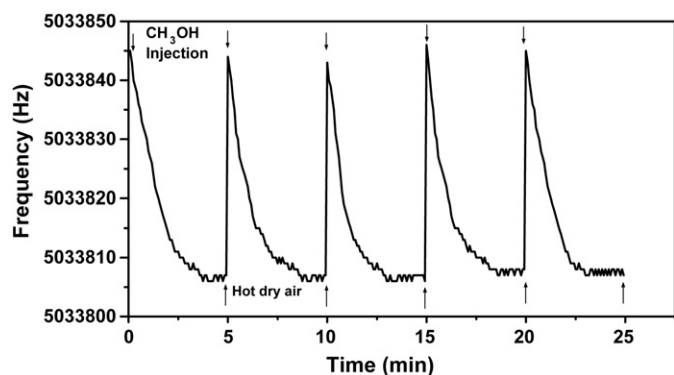[b] Relative standard deviation.

Fig. 4. Reproducibility test for frequency changes of the EB coated QCM exposed to 13 ppm methanol: (a) methanol injection and (b) methanol desorption using hot air.

following Fick's second equation which has been reviewed by Crank [20]:

$$\frac{\Delta f_t}{\Delta f_\infty} = 4\sqrt{\frac{D}{\pi}}\frac{t^{1/2}}{L} \tag{3}$$

where Δf_t is the frequency change due to the absorption of the vapour into the EB film at any time t and Δf_∞ is the frequency change in the equilibrium state at the end of the absorption process, these two parameters can be given as follows:

$$\Delta f_t = f_{EB} - f_t \quad \text{and} \quad \Delta f_\infty = f_{EB} - f_\infty$$

where f_t is the frequency during the exposure process at time t, f_∞ is the frequency at the equilibrium state and f_{EB} is the frequency of the EB film.
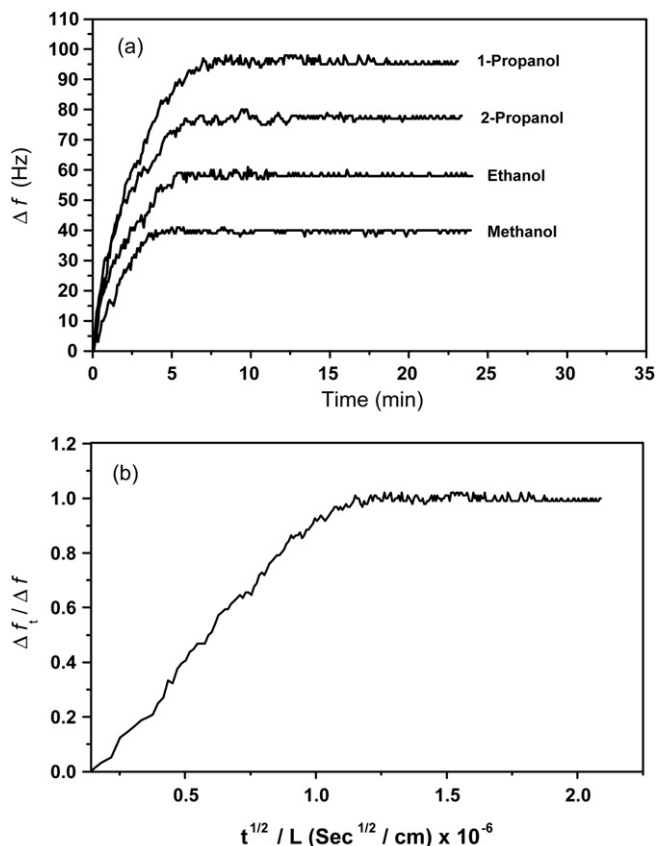

Fig. 5. (a) Frequency change of the EB film coated the QCM electrode of thickness 191 nm when exposed to 5 ppm vapours of methanol, ethanol, 2-propanol and 1-propanol. (b) $\Delta f_t/\Delta f_\infty$ as a function of $t^{1/2}/L$ when the EB film of thickness 191 nm was exposed to 7 ppm vapour of 2-propanol vapours.

Fig. 5(b) shows a plot of $\Delta f_t/\Delta f_\infty$ as a function of $t^{1/2}/L$ when the EB film was exposed to 2-propanol, in which the process obeys Fickian kinetics [20]. The D values were calculated from Eq. (3) for methanol, ethanol, 2-propanol and 1-propanol and are equal to 2.75, 2.80, 3.00 and 3.50×10^{-13} cm^2/s, respectively. It is clear that, D values are in the order: methanol < ethanol < 2-propanol < 1-propanol. The difference between the values of D is due to the differences in the structure and molecular weight of these aliphatic alcohols. However the difference between 2-propanol and 1-propanol can be explained on the difference in the molecular structure.

4. Conclusion

PANI film in the form of the EB coating on the electrode of QCM sensor show a good interaction with the tested alcohols vapours through hydrogen bonding. It was found that as the concentration of injected analyte increases, the magnitude of the response of the quartz electrode increases. Increasing the film thicknesses enhances the chances for more hydrogen bond formation with the EB chains. The diffusion of the alcohol vapours into the film depends on the structure of the alcohol. The sensor shows a higher sensitivity to the tested analyte species and satisfactory obtained linear correlations. The results indicated the reproducible and the reversible performance of the sensor.

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