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Modifying the response of a polymer-based quartz crystal microbalance hydrocarbon sensor with functionalized carbon nanotubes

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ABSTRACT

This report compares the performance of polymer and carbon nanotube–polymer composite membranes on a quartz crystal microbalance (QCM) sensor for the detection of aromatic hydrocarbons (benzene, toluene, ethylbenzene, p-xylene and naphthalene) in aqueous solutions. Several different polymers (polystyrene, polystyrene-co-butadiene, polyisobutylene and polybutadiene) and types of functionalized carbon nanotubes (multi-walled and single-walled carbon nanotubes) were investigated at varying carbon nanotube (CNT) loading levels and film thicknesses. In a majority of instances, the difference in response between membranes comprising pure polymer and membranes containing 10% (w/w) carbon nanotubes were not statistically significant. However, a notable exception is the decreasing sensitivity towards p-xylene with increasing carbon nanotube content in a polybutadiene film. This variation in sensitivity can be attributed to a change in the sorption mechanism from absorption into the polymer phase to adsorption onto the carbon nanotube sidewalls. With much thicker coatings of 10% (w/w) carbon nanotube in polybutadiene, the sensitivity towards toluene was higher compared to the pure polymer. The increased toluene sensitivity may be partially attributed to an increase in the sorption capacity of a carbon nanotube polymer composite film relative to its corresponding pure polymer film. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) measurements were performed to understand the mechanism of sorption and these studies showed that the addition of functionalized CNT to the polymer increases the absorption of certain types of hydrocarbons. This study demonstrates that carbon nanotubes can be incorporated into a polymer-coated QCM sensor and that composite films may be used to modify the QCM response and selectivity during the analysis of complex hydrocarbon mixtures.

1. Introduction

Certain hydrocarbon compounds (e.g. benzene, toluene and polycyclic aromatic hydrocarbons) pose a serious health and environmental risk at trace levels that they need to be frequently monitored to ensure regulatory compliance. Considerable effort has been devoted to developing sensitive, reliable, low cost and autonomous analytical tools which can be deployed directly in the field [1]. It is proposed that chemical sensors are capable of providing rapid and real-time quantitative information about hydrocarbon derived contaminants in the biosphere [2,3]. In particular, mass-based sensors using piezoelectric transduction [e.g. quartz crystal microbalance (QCM), surface acoustic wave (SAW)] are promising analytical tools that have been investigated extensively for the detection of a range of organic compounds in water [4]. These involve the measurement of a frequency change which is related to the amount of mass absorbed on a surface according to the Sauerbrey equation [5]. A polymer membrane coating is normally used to selectively interact with the analyte of interest and the quartz crystal microbalance detects the small mass changes associated with molecule adsorption/absorption. Although non-gravimetric contributions (e.g. viscoelastic effects) can be problematic for environmental monitoring applications [6], various groups have shown that hydrocarbons down to very low levels (ppb to ppm) can be detected, provided that certain conditions are met [7–10].

The analytical performance of a number of polymers have been compared and the sensitivities vary widely for a range of different types of hydrocarbons [7,11]. Generally, low density hydrophobic polymers with a low glass transition temperature are more sensitive towards non-polar hydrocarbons [12]. Despite some major improvements in sensitivity over the last several decades, analyte

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Table 1
Properties of various polymers used in the QCM study.

Polymers	Acronym	Source	MW (g/mol)	T_g (°C)	Density (g/ml)
Polystyrene	PS	Aldrich	77,000 (bimodal)	79	1.06
Polybutadiene	PB	Aldrich	456,000	−91	0.9
Polyisobutylene	PIB	Scientific Polymer Products	400,000	−64	0.92
Polystyrene-co-butadiene	PSB	Aldrich	160,000	102	1.04

T_g, glass transition temperature; MW, average molecular weight obtained by gel permeation chromatography (GPC).

selectivity remains a major challenge impeding the acceptance of QCM sensors for the assay of real environmental water samples. It is suggested that molecular imprinting may improve selectivity [13], however, these studies were performed in simple solutions rather than a mixture of hydrocarbons. Another strategy is to employ an array of sensors with different material coatings which have differential response towards the analytes of interest [14,15]. Statistical methods or artificial neural networks are then used to help discriminate between the different responses. Despite a significant amount of research, there are no reports showing that the sensor array can accurately quantify the concentration of a single hydrocarbon analyte in the presence of a complex mixture of other interfering compounds.

Carbon nanotubes (CNTs) have been shown to be promising materials for chemical sensing in environmental monitoring applications [16,17]. These are high surface area materials with large adsorption capacities that can be chemically tuned to interact with certain compounds. The adsorption properties of CNT have been studied by a number of groups. Chin et al. [18] investigated the adsorption capacity of single walled carbon nanotubes (SWCNTs) and showed that chemical treatment has a significant influence on the adsorption properties. After oxidation, the adsorption capacity of p-xylene increased while o-xylene decreased, and this difference was explained in terms of π–π electron donor–acceptor interactions. Recent studies have demonstrated that adsorption of phenolic compounds on CNT depends significantly on the micropore volume and surface area [19]. Penza and coworkers have performed QCM sensors studies with carbons nanotubes and showed that they can be used to distinguish between different types of hydrocarbon molecules [20–23]. Recent SAW measurements by Sayago et al. [24] has shown that there is a modest increase in the response towards octane with a multiwalled carbon nanotube/polyisobutylene composite. However, these studies were conducted in the gas phase and it is not known how the materials will perform in the aqueous phase.

Several reports have shown that sensors based on polymer composite materials typically outperform polymer based ones [25,26]. Carbon black-polymer based composite films have been used extensively in chemiresistor sensors [27,28]. The response mechanism is based on a change in the film resistance due to an increase in the distance between conductive carbon particles caused by analyte diffusion into the membrane. Compared to the chemiresistor, very little has been published investigating the potential of composite films with the QCM sensor. In addition, studies have been performed only in the vapour phase and it is not known how well the composite material will respond in aqueous solutions. In this work, a QCM sensor incorporating different carbon nanotube–polymer composite coatings was investigated for the detection of aromatic hydrocarbons in water. The analytical performance of polymer and carbon nanotube–polymer composite membranes was compared during QCM sensing of various hydrocarbons in water. The objectives of this paper are to understand the possible impact of carbon nanotube addition on the sensitivity and selectivity of a polymer-coated QCM sensor.

2. Experimental

2.1. Materials and reagents

The polymer materials used are listed in Table 1 along with some of their key properties. All reagents were AR grade and used without further purification. Table 2 shows the properties of different carbon nanotubes used. To aid the dispersion of the CNT in organic solvents and in the polymer matrix, the carbon nanotube samples were functionalized by covalent attachment of octadecylamine (ODA) to the nanotube sidewalls. The two multi-walled carbon nanotube samples were first oxidized using solutions of nitric acid/sulphuric acid. The single-walled carbon nanotubes had been previously oxidized and were functionalized without further oxidation. The oxidized carbon nanotube samples were reacted with thionyl chloride/DMF to create acyl chloride functional groups on the sidewalls which were then functionalized with ODA [29,30]. Carbon nanotube–polymer composites were then prepared by mild sonication of different ratios of functionalized CNT and polymers in organic solvent.

2.2. Surface preparation and film deposition

An AT-cut gold-coated quartz crystal (supplied by Stanford Research Systems, USA) was cleaned by soaking it in nitric acid (1:1 conc. nitric acid–deionized water) for ~30 min, followed by rinsing with deionized water, acetone, ethanol, and drying under high purity nitrogen. A thin film was deposited by placing ~200 μl of either a polymer or CNT–polymer solution on the quartz crystal and spin coating for 30 s using a Laurell Technologies spin processor (model WS-400B-NPP-Lite). The polymer solution concentration (0.5–3.5%, w/w) and spin coating speed were varied in order generate films of varying thickness. However, effort was taken to ensure that thin coatings were used in order to minimize the effect of viscoelastic processes occurring in the polymer film on the QCM response [6]. The coated crystals were dried overnight in an oven at ~60 °C prior to QCM sensor measurements. All of the coatings were fairly reproducible in thickness (<5% variation) and uniform in terms of film quality and integrity.

Table 2
Properties of various CNTs used in the polymer composite film preparation.

Carbon nanotube type	Acronym	Source	Length (μm)	Outer diameter (nm)	Purity
Short multi-wall carbon nanotube	Short-MWCNT	Cheap Tubes, Inc.	0.5–2	<8	>95%
Long multi-wall carbon nanotube	Long-MWCNT	Cheap Tubes, Inc.	10–30	<8	>95%
Single-wall carbon nanotube	SWCNT	Carbon Solutions, Inc.	0.5–3	1–2	>90%, high functionality

2.3. QCM measurements

The frequency of the quartz crystal was recorded using a Stanford Research Systems microbalance (QCM 200). The nominal frequency of oscillation of the quartz crystal is 5 MHz and experiments were undertaken by exposing one crystal face to aqueous solutions. An automated flow cell system which contains a four QCM array was used to perform parallel experiments. The system comprises a stainless steel flow cell, a Hamilton MVP valve selector and an Ismatec peristaltic pump (IDEX Corporation). The data transfer, pump speed and the position of the valves were controlled with Labview. All solutions were pumped through the cell using a flow rate of 150 μl min^{-1}. The coated quartz crystals were exposed to the hydrocarbon analyte solutions until a stable baseline was first obtained in deionized water (~2 h). QCM measurements were made at a temperature of $21 \pm 0.2\,^{\circ}$C and the frequency was recorded using a stability criterion of ± 0.2 Hz min^{-1}. Parallel resistance measurements were also made to check for motional losses induced by the various solutions. All QCM measurements were made within ~4 h, noting that previous studies found that soaking the polymer coated quartz crystal in water for long periods of time has a significant effect on sensitivity and reproducibility [31].

Analytical calibration curves were constructed by dissolving the hydrocarbon compounds in deionized water in the concentration range between 0 and 100 ppm. Naphthalene standards were made by serial dilution of a saturated solution which was prepared by weighing naphthalene (0.2 g, AR grade) into a glass Schott bottle that comprised deionized water (1000 ml) followed by constant stirring (~500 rpm) at room temperature ($21 \pm 2\,^{\circ}$C) for 3 days. The solution was filtered through a 0.45 μm filter paper and the naphthalene concentration was verified by GC–MS (20.5 ± 0.5 ppm, experiment repeated on 3 separate occasions). To limit losses by volatility and degradation, all standards were prepared freshly and the QCM studies were performed within several hours.

2.4. Film characterization by FTIR

Attenuated total reflectance (ATR) measurements were made using a Bruker Vertex 70 Fourier transform infrared spectrometer equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector. A Pike ATR accessory in combination with a trapezoidal (4 mm thick, 80 mm long, angle of incidence 45°) zinc selenide (ZnSe) internal reflection element (IRE) and a stainless steel flow cell were used. The IRE was coated by depositing 500 μl of the polymer solution (0.5%, w/w) on the ZnSe and leaving it to dry overnight. Analyte solutions were prepared in deionized water and pumped over the polymer-coated ZnSe surface using an Ismatec peristaltic pump (IDEX Corporation) at a constant flow rate of ~0.5 ml min^{-1}. Data were recorded in the 4000–650 cm^{-1} range using a spectral resolution of 2 cm^{-1} and a total of 32 scans were averaged for each spectrum. All experiments were conducted at room temperature (~21 °C).

2.5. Preparation of total petroleum hydrocarbon (TPH) solution

Total petroleum hydrocarbons (TPH) dissolved in water were prepared according to the procedure outlined elsewhere [32]. Briefly this involved placing North West Shelf (Australia) crude oil (70 ml) into a glass flask that contained deionized water (900 ml) and allowing the mixture to equilibrate for a period of 3 days at room temperature (~21 °C). The flask was sealed and the solution constantly stirred using a magnetic stirrer bar at a rotation speed of ~500 rpm. The water fraction was separated from the crude oil and the TPH was determined to be 19.0 ± 0.6 ppm (triplicate measurements) using GC–MS and GC–FID.

2.6. GC–MS analysis

GC–MS was used to determine the concentration of the various solutions used during the QCM study. The GC–MS analysis of BTEX compounds was carried out on a HP 6890 GC/Agilent 5973 MSD with an EST Encon purge and trap concentrator. Helium was bubbled into the water sample and the vapour swept through a sorbent trap (Vocarb 3000). Naphthalene was liquid/liquid extracted with dichloromethane and analyzed on a HP 6890 GC/Agilent 5973N MSD. Concentrations were determined by comparison with standards using electronic integration.

3. Results and discussion

3.1. Polymer and CNT–polymer composite sensitivity

QCM sensor measurements on quartz crystals coated with different polymer films (approximately 200 ± 70 nm thick, based on the frequency response of the QCM and the Sauerbrey equation) were made to assess their response to benzene, toluene, ethylbenzene, p-xylene (BTEX) and naphthalene. It is important to note that most studies in the literature have neglected to determine the exact hydrocarbon concentration during QCM analysis of the hydrocarbon analytes at ppm levels. We found with the GC–MS that the hydrocarbon loss during the preparation of the standards in deionized water varied between 20 and 60%, and this depended on the type of hydrocarbon, the hydrocarbon concentration and the method of preparation. Subsequently, all of the hydrocarbon concentrations used in the construction of the QCM calibration curves were GC–MS corrected. Fig. 1 shows a typical QCM sensor response for the various polymer coatings when exposed to different concentrations of p-xylene dissolved in deionized water. It can be seen that the frequency decreases (shifts more negative) with increasing levels of p-xylene and this is consistent with the hydrocarbon partitioning into the polymer films.

The responses for PB and PIB were relatively fast (1–5 min) and reversible for most analytes tested. However, the response times of PS and PSB were significantly longer (2–15 min) compared to PB and PIB, which agrees favourably with literature reports showing that glassy polymers with a high glass transition temperature respond much slower [11]. It is important to note that the response times varied considerably with hydrocarbon concentration for all polymers and the time taken to reach equilibrium was typically longer at higher concentrations. Some reports suggest that the diffusion coefficient is concentration independent [33], while others show that the diffusion coefficient is larger at higher hydrocarbon concentrations [34]. Presumably some swelling process occurs at elevated hydrocarbon levels which may be responsible for changes in the diffusion coefficient and subsequently the response time. Consistent with smaller diffusion coefficients for the large molecules, the response times were generally higher for naphthalene, p-xylene and ethylbenzene compared to toluene and benzene.

Fig. 2 shows the concentration versus response curves of the various polymer coated QCM crystals to BTEX and naphthalene dissolved in deionized water. In terms of analytical performance, PB and PIB responded linearly over the 0–80 ppm range with a correlation coefficient (r^2) much greater than 0.97. By contrast, PS and PSB were generally less linear ($0.80 < r^2 \leq 0.99$) and reversible over a similar concentration range. This is partly due to plasticization processes occurring in these polymer films and is consistent with recent studies showing that the hydrocarbon sorption/diffusion properties in glassy polymers vary consider-

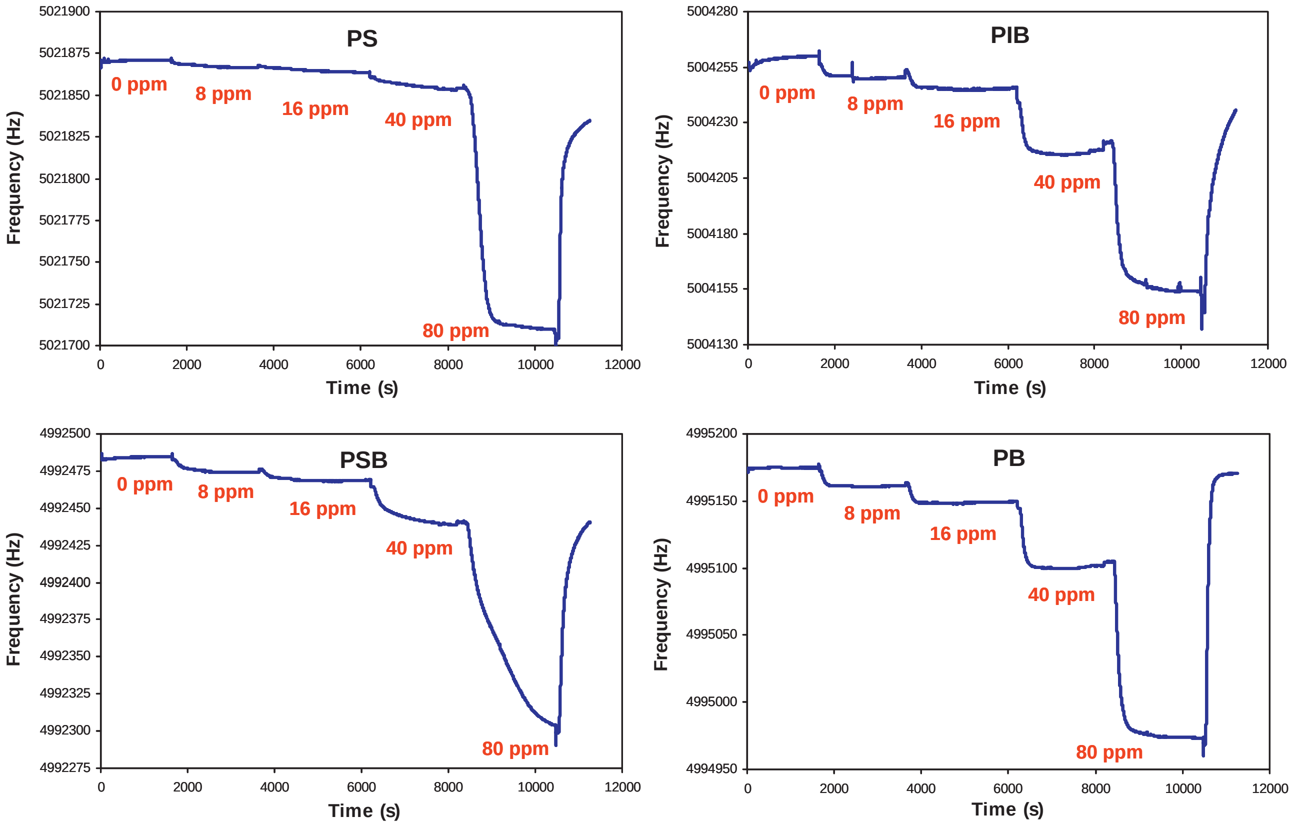

Fig. 1. Transient response of a QCM sensor coated (1 kHz film thickness) with different polymer films after exposure to step changes of increasing p-xylene concentration in deionized water.

ably with the hydrocarbon concentration and water aging [35]. The hydrocarbon sensitivity was determined from the slopes of the calibration curves by regression in the linear region (between 0 and 40 ppm for benzene, toluene, ethyl benzene and p-xylene and 0–10 ppm for naphthalene). Fig. 3 compares the sensitivity of the various polymers for the different aromatic hydrocarbons, noting that the data was normalized with respect to polymer film thickness. It is evident that PB was the most sensitive for all analytes and PS was the least sensitive for toluene, ethylbenzene, p-xylene and naphthalene. It should be noted that for benzene the data is prone to large errors since the resulting QCM frequency shift is relatively small compared to the other analytes. As such, no appreciable difference was discernable in benzene sensitivity when comparing the various polymers. Except for PS, the polymer sensitivity decreased according to the following trend: naphthalene > p-xylene > ethylbenzene > toluene > benzene and this correlates reasonably well with the octanol–water partitioning coefficients [36]. The following correlations were obtained between the hydrocarbon sensitivity and octanol–water partitioning coefficient: PB ($r^2 = 0.90$), PIB ($r^2 = 0.91$), PSB ($r^2 = 0.97$), and PS ($r^2 = 0.51$). The QCM response patterns for the various aromatic hydrocarbons shown in Fig. 3 are very similar suggesting that pure polymer films alone may not be sufficient to discriminate between these compounds when present in a mixture.

Very few papers have been published investigating the analytical performance of carbon nanotube–polymer composites for the detection of hydrocarbons. Studies were performed to determine the effect of CNT doping on the polymer response and Fig. 2 shows the calibration plots of various carbon nanotube–polymer composites. It appears that the addition of ODA functionalized short MWCNTs to the polymers PS, PSB, PB and PIB at a 1:10 ratio did not significantly improve the response characteristics of the polymer coating. Furthermore, no changes were observed in the linearity and response time. However, for both PSB and PB composites the calibration reproducibility improved slightly compared to the polymer alone. Fig. 3 compares the hydrocarbon sensitivity of the various polymer composites. Generally, the addition of ODA functionalized short MWCNT to the polymer membrane had no considerable impact on the detection sensitivity towards benzene, ethylbenzene and naphthalene. One exception was ethylbenzene, in which the sensitivity of PS-CNT was substantially higher compared to PS, and in other cases there was even a slight decrease in sensitivity. For example, the sensitivity of PB-CNT for toluene, p-xylene, and naphthalene were slightly lower compared to PB, and this is probably due to either a change in the response mechanism (absorption versus adsorption) or variations in the viscoelastic properties of the film coating. The slight variation in the hydrocarbon response suggests that the carbon nanotube–polymer composite films may aid in analyte discrimination when incorporated into a QCM sensor array. It will be shown in the subsequent section that the CNT content in the polymer plays some role in modifying the sensitivity of certain hydrocarbons.

Environmental water monitoring requires sensitive sensors that can detect down to ppb levels. Although polystyrene, polybutadiene, polyisobutylene, and polystyrene-co-butadiene have been previously studied for different types of hydrocarbons (for example chlorinated and aromatic) [11,37,38], very few reports have compared the limit of detection of the aforementioned polymers in the presence of the following hydrocarbons: benzene, toluene, ethylbenzene, p-xylene and naphthalene. The detection limit was calculated using the IUPAC recommendation where the response is 3 times the signal to noise ratio. Table 3 compares the detection limit of the various polymers which was determined by linear extrapolation of the calibration curve. It is evident that PB was the

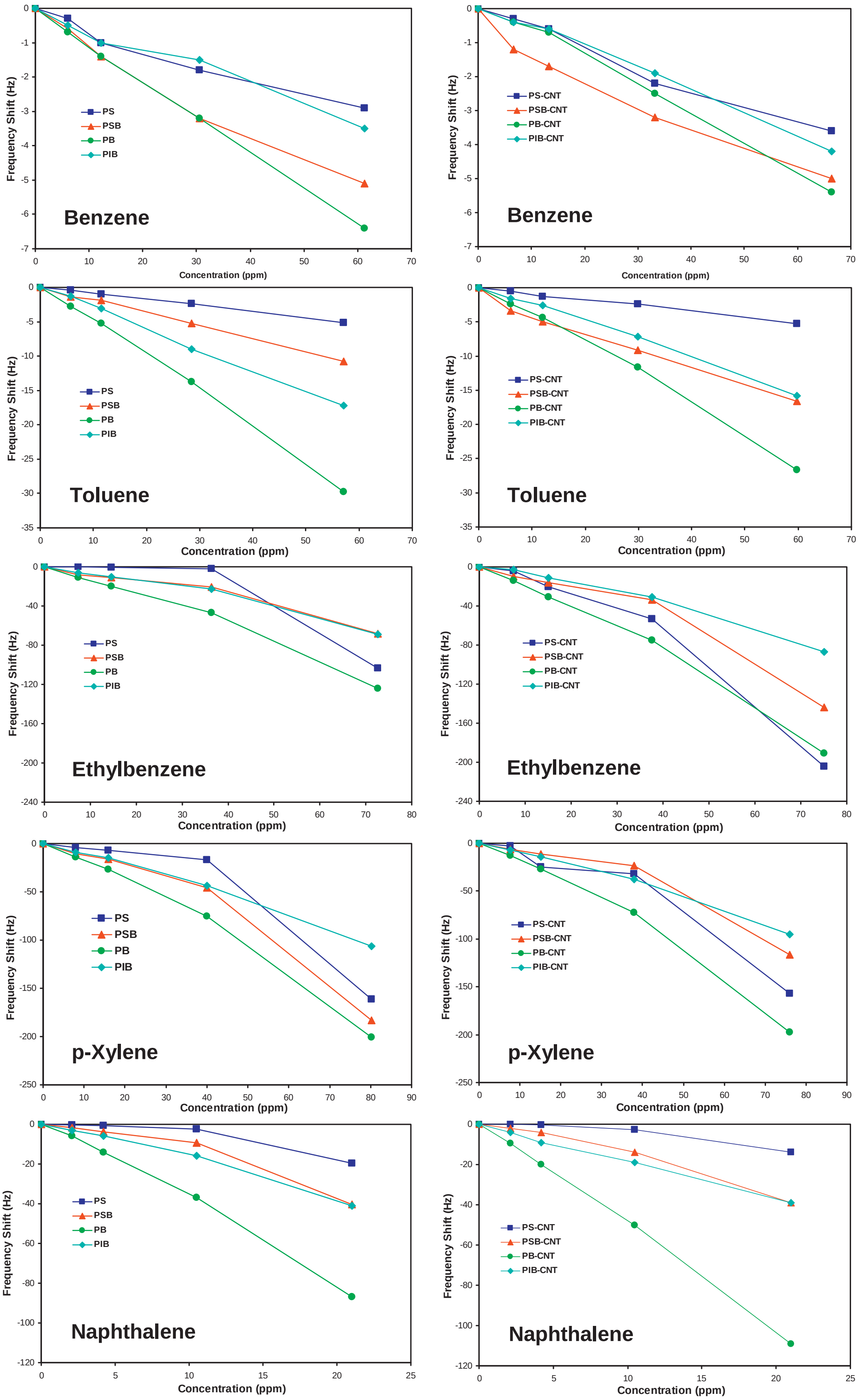

Fig. 2. QCM calibration graphs of various polymeric-based films exposed to different aromatic hydrocarbon compounds dissolved in deionized water (left: polymer only; right: 1:10 ODA functionalized short MWCNT–polymer composite).

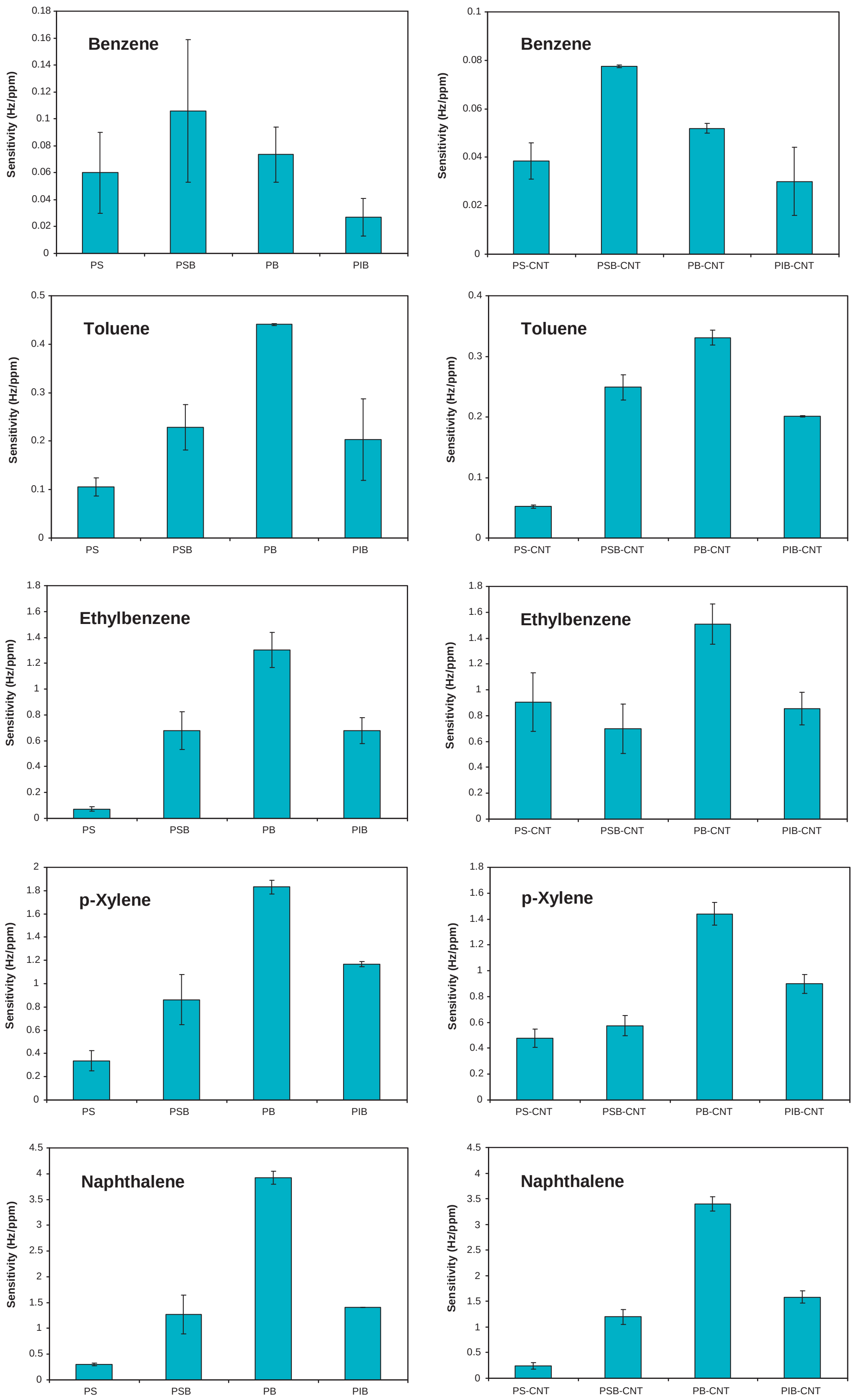

Fig. 3. QCM sensitivity of various polymeric-based films exposed to different aromatic hydrocarbon compounds dissolved in deionized water (left: polymer only; right: 1:10 ODA functionalized short MWCNT–polymer composite). The error bars show the range of results based on replicate measurements.

Table 3
Detection limit summary for various coatings using the QCM. All films were 1.1 ± 0.3 kHz thick and the carbon nanotube content in the ODA functionalized short MWCNT–polymer composite was 10 ± 1% (w/w).

Coating	Benzene (ppm)	Toluene (ppm)	Ethylbenzene (ppm)	p-Xylene (ppm)	Naphthalene (ppm)
PS	12	7	15	1	3
PS-CNT	13	7	1	1	4
PSB	6	3	0.7	0.5	0.7
PSB-CNT	5	1.5	0.6	0.8	0.6
PB	5	1	0.4	0.3	0.2
PB-CNT	10	1.5	0.3	0.3	0.1
PIB	7	2	0.7	0.5	0.4
PIB-CNT	10	2	1	0.6	0.3

most sensitive polymer and can detect toluene, ethylbenzene, and p-xylene down to 1 ppm, 0.4 ppm, and 0.3 ppm, respectively. These compare reasonably well to World Health Organization (WHO) drinking water guidelines of 0.7 ppm for toluene, 0.3 ppm for ethylbenzene, and 0.5 ppm for p-xylene [39]. The recommended WHO level of 0.01 ppm for benzene [39] could not be achieved with any of the films. However, the detection limits presented in Table 3 were obtained on polymer coatings that were between 800 and 1400 Hz thick (approximately 130–270 nm) and it will be discussed in a subsequent section that the QCM sensitivity can be significantly improved with increased film thickness. Interestingly, the limit of detection values obtained here for benzene and toluene using polybutadiene and polystyrene are comparable or in some cases slightly better than that reported elsewhere [11], despite the other group using a higher frequency QCM sensor.

3.2. *Effect of CNT content*

The amount of ODA functionalized short MWCNT in the polybutadiene film was varied from 0 to 22% (w/w) and QCM measurements were made in aqueous solutions comprising toluene and p-xylene at different concentrations. Fig. 4 shows the variation in polybutadiene sensitivity as a function of CNT loading content. The toluene sensitivity remained unchanged, whereas the p-xylene sensitivity decreased slightly with CNT content. It is expected that the hydrocarbons interact with the CNT via adsorption rather than absorption processes. The adsorption of p-xylene onto CNT is thermodynamically more favourable (e.g. larger interaction energy), since p-xylene is slightly larger in size compared to toluene (the molar volume of p-xylene is ~124 cm^3/mol compared to toluene of ~107 cm^3/mol [36]). However, the decreased QCM response for p-xylene with higher CNT content suggests that other factors (e.g. π–π electron donor–acceptor interactions, steric hindrance) play an important role on the adsorption mechanism. In addition, as the polymer amount is lowered due to a higher proportion of CNT, the absorption of p-xylene will be less favourable since the partition coefficient of p-xylene into hydrophobic polymers is much larger relative to toluene [40]. The decrease in p-xylene sensitivity might be attributed to a reduction in the PB free volume as a result of an increased CNT loading content, noting that previous studies have shown that polybutadiene has a high free volume [35]. SEM analysis of the various films revealed that the CNT was uniformly distributed throughout the polymer in all cases (not shown).

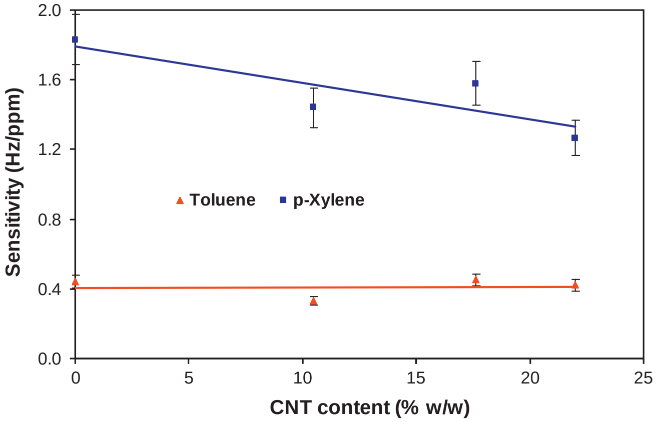

Fig. 4. The effect of CNT (ODA functionalized short MWCNT) content on the sensitivity of a polybutadiene-coated QCM sensor when exposed to toluene and p-xylene dissolved in deionized water. The error bars show the range of results based on replicate measurements.

Alternatively, it is possible that, as the hydrocarbon molecules are absorbed by the polybutadiene film, changes occur in its viscoelastic properties. The resistance of the various films were recorded in parallel with frequency measurements, noting that changes in the resistance provide information about the dissipation of the oscillation energy due to motional losses [41]. In fact, very little variations in the baseline resistance were observed during toluene solution exposure, whereas the resistance varied much

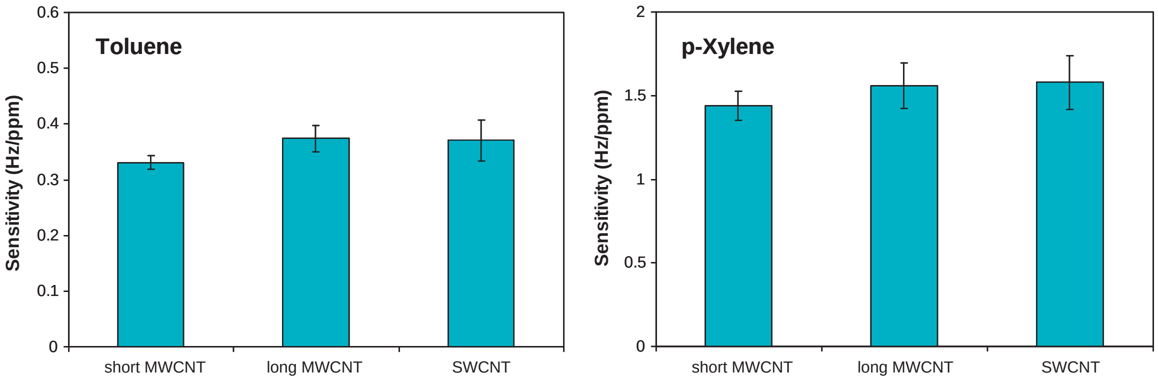

Fig. 5. The effect of ODA functionalized CNT type on the sensitivity of a PB coated QCM sensor when exposed to toluene and p-xylene dissolved in deionized water. In all cases a 1:10 CNT–polymer loading was used. The error bars show the range of results based on replicate measurements.

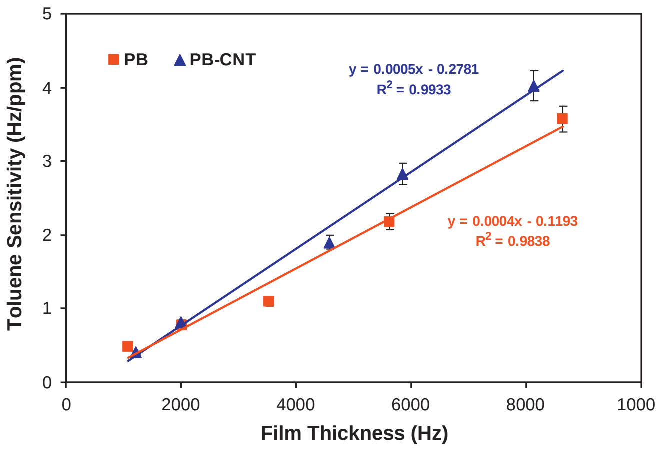

Fig. 6. The effect of film thickness on the toluene sensitivity of a polybutadiene (PB) and 1:10 ODA functionalized short MWCNT–polybutadiene (PB-CNT) coated QCM sensor. The error bars show the range of results based on replicate measurements.

more significantly when changing the p-xylene concentration. The much higher partition coefficient for p-xylene compared to toluene suggests that the p-xylene concentration in the polymer film will be larger and this may have a greater effect on the viscoelastic properties of the polymer film. This is consistent with reports which show that changes occur in the film viscoelastic properties when certain hydrocarbon compounds are absorbed [42,43]. Higher CNT contents were not studied due to problems with forming a uniform and adherent layer on the quartz substrate.

3.3. *Effect of CNT type*

The type of CNT in the polybutadiene film was varied in order to determine the impact on QCM sensitivity and selectivity. The results are shown in Fig. 5 and it is evident that at a 1:10 CNT–polymer loading the type of CNT used does not significantly alter the hydrocarbon sorption properties of PB. This study suggests that the amount of hydrocarbon absorbed/adsorbed is independent on the type of CNT.

3.4. *Effect of film thickness*

Relatively thick films (e.g. 1–3 μm) are often required in order to achieve suitable sensitivity with a QCM sensor that oscillates at a fundamental frequency of 5 MHz. However, non-gravimetric contributions (e.g. viscoelastic effects) become more pronounced with increasing films thickness [6] and this can lead to significant quantification errors during the analysis of environmental samples. The following model developed by Johannsmann et al. [44]

$$m = \frac{m^*}{1+[\hat{J}(f)(\rho_q(2\pi f)^2 d^2)/3]}$$

gives a correction to the sensed mass obtained using the Sauerbrey equation (or m^*) where $\hat{J}(f)$ is the complex shear compliance, ρ_q is the specific density of quartz, f is the resonance frequency of the crystal in contact with the solution and d is the film thickness. For thick membranes or materials with a high shear compliance (soft materials), the correction term can be significant. The addition of carbon nanotubes to polymers to form a composite material is known to improve the mechanical strength and decrease the shear compliance [45], suggesting that thicker membrane films may be used on the quartz crystal without deleterious effects.

The QCM sensitivity towards toluene was studied as a function of film thickness for a polymer and carbon nanotube-polymer coated quartz crystal. Fig. 6 shows the effect of film thickness (var-

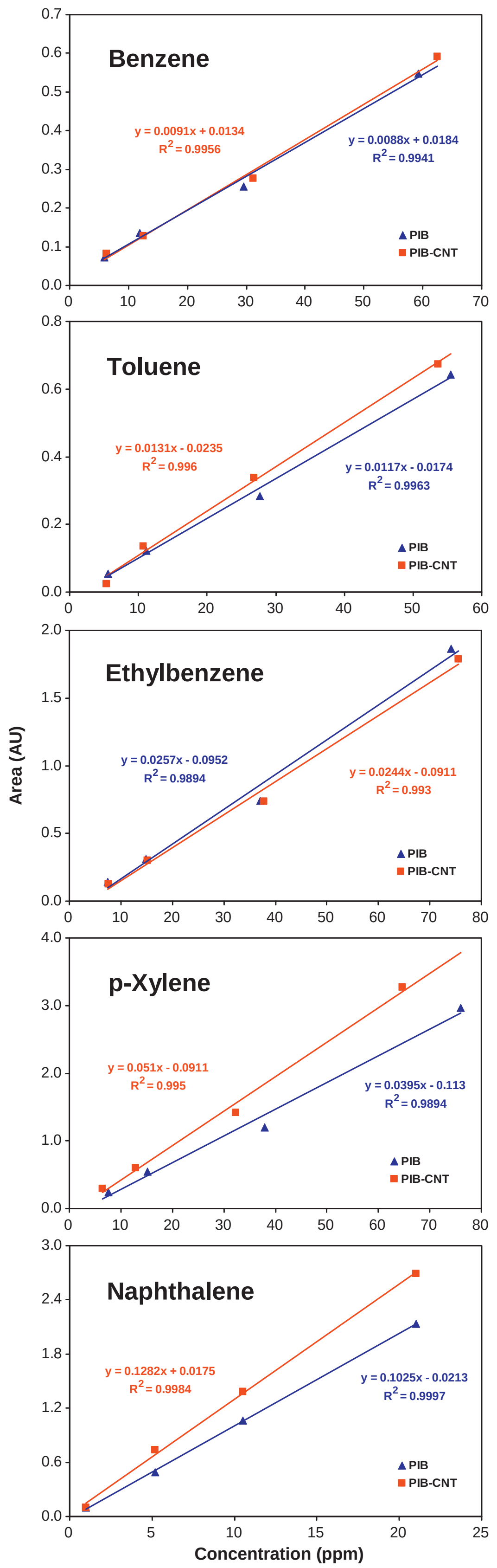

Fig. 7. Infrared response as a function of hydrocarbon concentration for a polyisobutylene and an ODA functionalized short MWCNT–polyisobutylene (1:10) coating when exposed to different hydrocarbons dissolved in deionized water.

Table 4
The concentrations of the main compounds present in the TPH water fraction.

Benzene (ppm)	Toluene (ppm)	Ethylbenzene (ppm)	m-, p-Xylene (ppm)	o-Xylene (ppm)	TPH C_6–C_9	TPH C_{10}–C_{14}	TPH C_{15}–C_{28}	TPH C_{29}–C_{36}	Naphthalene (ppm)
2.7	4.8	0.43	2.1	0.83	13.3	2.6	2.8	0.21	0.25

ied from ~1000 to ~9000 Hz) on the polybutadiene sensitivity with and without ODA functionalized short MWCNT (10%, w/w). It is evident that the carbon nanotube–polybutadiene (1:10) composite film is slightly more sensitive at higher coating thicknesses compared to the polybutadiene film. In addition, the sensitivity versus film thickness plot was slightly more linear for the PB-CNT film. For both the pure polymer and polymer/carbon nanotube composite films, the observed increase in QCM sensitivity with increasing film thickness is consistent with trends observed elsewhere [46], which show that non-polar hydrocarbon analytes partition into the polymer. The process of partitioning occurs mainly in the bulk of a polymer material, whereas adsorption takes place predominately at the polymer–solution interface. Adsorption is expected to remain relatively constant as the film thickness is changed, since adsorption is dependant on the surface area of the material rather than its volume. However, the increased sensitivity at higher film thicknesses for the carbon nanotube–polybutadiene composite compared to pure polybutadiene implies that the sorption capacity of the composite film is larger [47]. This increased QCM sensitivity for the PB-CNT coating agrees favourably with recent infrared studies by us which revealed that the uptake of toluene (~60 ppm) was higher for a polyphenylenevinylene (PPV) film comprising of single wall carbon nanotubes [26]. The increased sensitivity of the polymer/carbon nanotube composite film relative to that of the pure polymer at larger thicknesses is consistent with a more rigid film giving a smaller Johannsmann model correction factor.

3.5. Response mechanism

It is well established that the response mechanism of the QCM sensor is complicated by various non-gravimetric contributions [6]. Subsequently, ATR-FTIR studies were performed to compare the performance of the polymer with and without ODA functionalized short MWCNT. Polyisobutylene (PIB) was found to be the only polymeric material suitable for the detection of all the aromatic compounds studied in this report due to the presence of very few interfering absorption bands in the mid-infrared region of interest. Fig. 7 compares the PIB and PIB-CNT coating as a function of hydrocarbon concentration and type. It is important to note that the addition of CNT to the polymer significantly attenuated the IR signal, resulting in a slightly lower signal to noise ratio. The slopes of the PIB and PIB-CNT response curves are very similar for benzene, toluene and ethylbenzene, suggesting that the addition of carbon nanotubes (at 10%, w/w) to PIB does not significantly alter the sorption properties. This is consistent with the QCM results which revealed no difference in sensitivity with and without CNT. For naphthalene, the IR response slope of the PIB-CNT material was slightly higher compared to PIB and this compares reasonably well with the QCM data which revealed a similar trend. However, the IR response slope for p-xylene was significantly larger with PIB-CNT when compared to PIB, implying that the carbon nanotube particles have increased the sorption of p-xylene. This observation is inconsistent with the QCM data which revealed the reverse effect. The reason is probably due to variations in the IR sensitivity which has been found to depend significantly on the type of analyte and membrane thickness [48]. Unlike the membranes on the QCM crystals which are thin (~200 nm) and were spin coated, the membranes on the IRE crystal are thicker (~9 μm) and were drop casted. This slower evaporation process is likely to introduce heterogeneities throughout the thickness of the membrane. If CNT was only modifying the film sorption capacity then we would see either an increase or a decrease in the hydrocarbon sorption properties for all analytes. The fact that the absorption of some hydrocarbons increased more relative to others suggests that the CNT has probably changed the mode of sorption and modified the polymer selectivity. Further studies are being planned to study the effect of film preparation conditions (e.g. thickness) on the ATR-FTIR sensitivity.

3.6. Analysis of total petroleum hydrocarbons (TPH)

Very few QCM studies have been reported in the literature using complex mixtures that contain more than one type of hydrocarbon compound [49]. A study was undertaken to determine the QCM frequency response of the various coatings exposed to a total petroleum hydrocarbon solution, noting that this is a complex mixture which comprises mainly water soluble hydrocarbon molecules. Due to the presence of many different hydrocarbon compounds it was not possible to determine the limit of detection. Table 4 shows the concentrations of the main compounds present in the water fraction. It is evident that more than 69% of the TPH water fraction comprises C_6–C_9 compounds. QCM sensor measurements were made on the TPH water fraction and the responses for the different coatings are shown in Fig. 8. It is evident that the

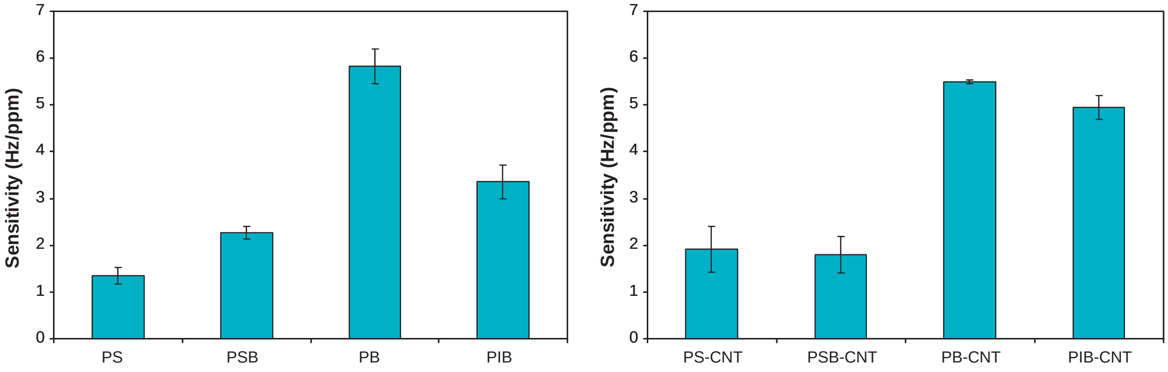

Fig. 8. QCM sensitivity of various polymeric-based films exposed to TPH solution (left: polymer only; right: 1:10 ODA functionalized short MWCNT–polymer composite). The error bars show the range of results based on replicate measurements.

highest response was achieved with the PB and PB-CNT coatings. The next most sensitive polymer for TPH was PIB. Interestingly, the response of PIB increased in the presence of ODA functionalized short-MWCNT whereas no considerable differences were observed for the PB, PS and PSB polymers. The reason for this is unknown but it is possible that the carbon nanotube has increased the sorption capacity of PIB for certain hydrocarbon compounds. It is important to note that the QCM frequency shift of the TPH water fraction (~19 ppm) was much greater for all of the coatings tested when compared to the frequency change of an individual hydrocarbon solution of similar concentration. This suggests that the other hydrocarbons present in the TPH solution are probably contributing significantly to the QCM response. GC–MS revealed that the water sample comprises a number of aromatic-based organic compounds (e.g. m-xylene, o-xylene, alkylated benzenes, methyl naphthalene, methyl phenols, $>C_{10}$) at low ppm levels and due to some of them (e.g. alkylated benzenes, methyl naphthalene, $>C_{10}$) having a larger octanol–water partition coefficient [36] compared to the ones studied here are expected to partition more favourably into the polymer film. Further studies are being planned to determine if the QCM sensor array can distinguish between different TPH water fractions.

4. Conclusions

This study has shown that the QCM sensor sensitivity varies slightly when a polymer film is doped with low levels of carbon nanotubes (10%, w/w). However, at higher CNT loading levels the sensitivity decreased more significantly for some compounds (e.g. p-xylene) compared to others (e.g. toluene), suggesting that the addition of CNT may play an important role in improving the polymer selectivity for certain hydrocarbon compounds. The hydrocarbon sensitivity seemed to be independent on the type of CNT. It has been shown that the QCM sensitivity of both the polymer and the CNT–polymer composite increase with increasing film thickness, and this is consistent with a film that undergoes a partitioning mechanism with non-polar hydrocarbon compounds. However, the sensitivity of the CNT–polymer composite film was much greater relative to the polymer alone when using thicker coatings on the quartz crystal. This probably implies a change in the sorption capacity at larger film thicknesses. ATR-FTIR measurements revealed that the CNT preferentially interacts with certain types of hydrocarbons. The QCM sensitivity for the various hydrocarbons was compared to the octanol–water partitioning coefficients and a reasonable correlation was obtained for the polymers PB, PSB and PIB.

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