Real-Time Detection of Organic Compounds in Liquid Environments Using Polymer-Coated Thickness Shear Mode Quartz Resonators

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The selection of sensitive coatings is a critical task in the design and implementation of chemical sensors using coated thickness shear mode quartz crystal resonators (QCRs) for detection in liquid environments. This design or selection is performed through a study of the sorption process in terms of the partition coefficients of the analytes in the coatings. The partition coefficient, which is controlled by the chemical and physical properties of the coating materials, determines the inherent selectivity and sensitivity toward analyte molecules. The selection of the coatings is logically determined by the interactions between coating and target analyte molecules, but can also be made through a systematic variation of the coating's properties. The determination of the partition coefficients is only accurate if all contributions to the total measured frequency shifts, Δf_s, of the coated QCR can be established. While mass loading is often assumed to be the dominant factor used in determining partition coefficients, viscoelastic effects may also contribute to Δf_s. Both the effect of viscoelastic properties and the effect of mass loading on the sensor responses are investigated by using a network analyzer and oscillator circuit and by characterizing the total mechanical impedance of the loaded sensor. Different types of coatings including rubbery and glassy polymers are investigated, and the targeted analytes include classes of polar compounds (methanol), nonpolar compounds (toluene, xylenes), and chlorinated hydrocarbons (trichloroethylene, tetrachloroethylene, etc). It is seen that changes in viscoelastic properties due to analyte sorption may be significant enough to place the sensor in the nongravimetric regime. However, for most applications involving the detection of relatively low concentrations of organic compounds and the use of acoustically thin films, changes in the complex shear modulus of the coatings contribute less than 5% of the total shift in the series resonant frequency, depending on the coating. In that case, the measured Δf_s and, hence, the calculated sensitivity/partition coefficients can still be used for an approximate classification and selection of the coatings for operation in a complex solution of water/analyte molecules.

Direct monitoring of trace organic compounds in ambient air and liquid environments requires highly sensitive chemical sensors.[1−10] For this purpose, acoustic wave-based chemical sensors have been extensively investigated. Acoustic wave devices are capable of detecting very low concentrations (ppm, ppb) of the organic compounds in these environments. The commonly investigated acoustic wave devices are thickness shear mode quartz resonators, (also known as quartz crystal resonators (QCRs)), acoustic plate mode (APM), surface acoustic wave (SAW), shear horizontal surface acoustic wave (SH-SAW), flexural plate wave (FPW), and shear horizontal acoustic plate mode (SH-APM) devices. Among these devices, shear horizontal (SH) acoustic wave devices are particularly attractive for liquid-phase applications because they do not couple energy via mode conversion into the liquid. To date, most applications have been performed in gas environments and utilize coated or uncoated SAW or QCR as the sensing platform.[1] Compared to gas-phase sensing, relatively few research papers exist in the literature on direct detection in liquid environments. One approach that has

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(8) Menon, A.; Patel, R.; Zhou, R.; Josse, F. *Proc. IEEE Int. Freq. Control Symp.*, Pasadena, CA, 1998; pp 667−675.
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(10) Grate, J. W.; Martin, S. J.; White, R. M. *Anal. Chem.* **1993**, *65*, 940A−948A, 987A−996A.

been investigated involves vapor detection in the headspace above the liquid sample. Such headspace gas analyzers consist of an array of SAW[11] or QCR gas sensors with various sensitive polymer coatings and rely on the volatility of the organic compounds. While this technique can provide a limited ability to characterize aqueous samples, it is impractical or unsuited for the detection of leaks in underground storage tanks and, in general, of some organic compounds with hydroxy, acid, and amino sites. Therefore, there is a need to investigate and develop sensors for the direct detection of organic compounds in aqueous solutions. In general, an acoustic wave-based chemical sensor is a multicomponent system consisting of an appropriate acoustic wave device and a (bio)chemically sensitive and selective coating used for both the detection and identification of organic compounds. The sensor sensitivity depends on both the device platform and the coating material, while the interaction between the coating and the targeted organic compounds determines the sensor selectivity. It is known that interaction forces usually lack an absolute specificity toward the target analytes; however, sensitivity and partial selectivity of each individual coating material are obtained through the difference in chemical and physical properties. Therefore, a sensor array with several devices, each with a different coating, is often needed to detect a given target analyte or class of analytes.

The design of sensor arrays using coated QCRs for the practical detection and identification of organic analytes in aqueous environments requires the appropriate selection of diverse, sensitive coatings. However, to select an appropriate coating material, there is a need to understand the various sorption processes and the sensing mechanisms between the coating materials and the target analytes. This can be understood through a study of the partition coefficients for analyte sorption in the coatings. The determination of these partition coefficients is only accurate if all contributions to the total measured frequency shift, Δf_s, of the loaded acoustic sensor can be established. In general, both mass loading and viscoelastic effects contribute to Δf_s, but mass loading is often assumed to be the dominant factor.

Two methods have been used to interpret QCR sensor data depending on the coating properties. One method utilizes the Sauerbrey equation, which relates mass changes to corresponding shifts in device operating frequency. This method has been widely used throughout the field of chemical sensors but has obvious limitations due to the acoustically thin film approximation used in converting frequency shift to mass.[1] Often it is difficult to distinguish between changes in mass load on the surface and viscosity changes of the liquid or changes in the viscoelastic properties of the coating. To overcome these limitations, the crystal impedance method has been developed.[12−14] This method allows the quantification of physical parameters (viscosity, density, shear modulus) from chemically and physically different systems on the QCR. Since the viscoelastic properties of the coatings can make a large contribution to the final sensor response, the crystal
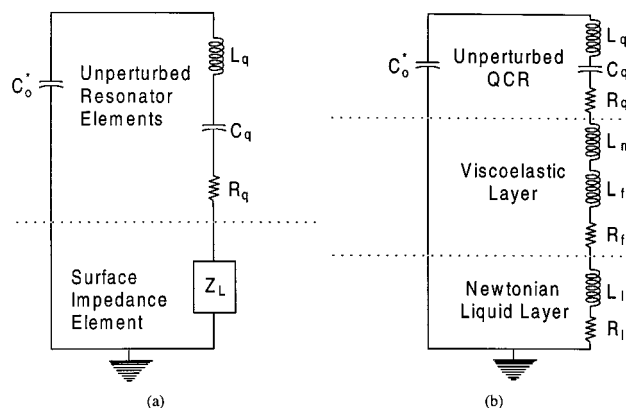
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(12) Cernosek, R. W.; Martin, S. J.; Hillman, A. R.; Bandey H. L. *Proc. IEEE Int. Freq. Control Symp.*, Orlando, FL, 1997; pp 96−104. *IEEE Trans. Ultrason. Ferroelect. Freq. Control* **1998**, *45*, 399−1407.
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Figure 1. (a) Electrical equivalent-circuit model of a QCR with an arbitrary composite surface load and (b) lumped-element electrical equivalent-circuit model for a QCR with a thin viscoelastic film in contact with a semi-infinite Newtonian liquid. Note that L_m represents the mass of the viscoelastic layer, and L_f and R_f respresent the viscoelasticity of the layer.

impedance method has become more widely used for modeling the loaded sensor system.[13,14]

In the present work, thickness shear mode (TSM) QCRs with various coatings are investigated for the direct detection and identification of organic compounds in liquid environments. For a practical sensor application, the loaded QCR can be incorporated as the control element in an oscillator circuit capable of maintaining stable operation at low Q. The oscillation frequency tracks the crystal resonance and indicates both the viscoelastic loading and the surface mass accumulation. For the coating and sensor characterization, both the effect of viscoelastic properties and the effect of mass loading on the sensor responses are studied by using a network analyzer and by analyzing the total mechanical impedance of the loaded QCR. Different types of coatings including rubbery and glassy polymers are investigated, and the targeted analytes include classes of polar compounds (methanol), nonpolar compounds (toluene, xylenes), and chlorinated hydrocarbons (trichloroethylene, tetrachloroethylene, etc). Despite the drastic decrease in the sensor quality factor, Q, the ability to analyze the various loading parameters and to implement chemical sensors for direct detection of some chemical compounds in aqueous environments is shown. For most applications involving relatively low concentrations of organic compounds and acoustically thin films, the extraction of the partition coefficients indicates some levels of confidence in the selection of coatings and the identification of analytes.

THEORY

QCR Sensor Responses in Liquids. In liquid-phase applications, the QCR is usually coated with chemically sensitive materials possessing an affinity for the target molecules in solutions. As a result, mass, viscoelastic effects, and liquid loading combined affect the resonant frequency of the loaded QCR. This effect can be studied via the QCR electrical characteristics evaluated using motional impedance elements. Figure 1a illustrates a lumped-element model (LEM) of a QCR loaded by an arbitrary surface impedance. This model consists of an electrical (or static) branch and a mechanical (or motional) branch. The electrical branch represents the total electrostatic capacitance, C_0^*, that is associated

with the dielectric constant of the quartz plate and the geometric configuration of the electrode as well as any parasitic capacitance due to fixtures and the liquid environment. The mechanical branch represents the physical properties of the loaded quartz crystal. It includes the motional elements (L_q, C_q, R_q) of the unperturbed QCR, and a single element associated with the surface load. Here, the total motional impedance of the perturbed QCR is obtained from the sum of the unperturbed quartz crystal and surface load impedance. The motional impedance associated with the total surface load is obtained from the transmission line model (TLM) of the crystal with a surface load as[13,14]

$$Z_{L(TLM)} = \frac{N\pi}{4K^2\omega_s C_0}\left(\frac{Z_s}{Z_q}\right)\left[1 - \frac{j(Z_s/Z_q)}{2\tan(N\pi\omega/2\omega_s)}\right] \quad (1)$$

where K^2 is the quartz electromechanical coupling coefficient; N is the resonator harmonic number ($N = 1, 3, 5, ...$); $\omega = 2\pi f$ is the angular excitation frequency and $\omega_s = 2\pi f_s$ is the unperturbed crystal series resonance frequency; C_0 is the quartz electrostatic capacitance; Z_q, a real quantity, is the characteristic impedance of the quartz plate, given by $(\rho_q \mu_q)^{1/2}$; μ_q is the shear stiffness; ρ_q is the quartz density; and Z_s, a complex quantity, is the shear mechanical impedance at the device surface. If the surface mechanical impedance is much less than the quartz characteristic impedance, i.e., $Z_s \ll Z_q$, which is typically true for all sensing systems,[12] eq 1 reduces to a much simpler form of the motional impedance,[15] for the fundamental resonance frequency:

$$Z_L = \frac{\pi}{4K^2\omega_s C_0}\left(\frac{Z_s}{Z_q}\right) \quad (2)$$

For the QCR loaded with a finite viscoelastic coating and without a liquid overburden, the input impedance at the quartz surface/coating interface can be defined as[13,14]

$$Z_s = Z_0 \tanh\left(j\omega\left(\frac{\rho_f}{G}\right)^{1/2}h_f\right) \quad (3)$$

where Z_0 is the characteristic impedance of the viscoelastic coating, given by $(\rho_f G)^{1/2}$, $G = G' + jG''$ is the complex shear modulus (G' is the storage modulus and G'' is the loss modulus of the coating), ρ_f is the film density, and h_f is the film thickness. For a QCR loaded with a finite viscoelastic coating and a liquid layer, the total surface mechanical impedance at the viscoelastic coating/liquid interface can be defined as[15]

$$Z_s = Z_0\left[\frac{Z_l \cosh(\beta h_f) + Z_0 \sinh(\beta h_f)}{Z_0 \cosh(\beta h_f) + Z_l \sinh(\beta h_f)}\right] \quad (4)$$

In eq 4, the complex wave propagation constant, β, is equal to $j\omega(\rho_f/G)^{1/2}$ and Z_l is the characteristic mechanical impedance of the liquid layer in contact with the coating. It is noted that when the QCR is only loaded with a viscoelastic coating, $Z_l = 0$, and eq 4 reduces to eq 3. Without loss of generality, eq 4 can be rearranged into a more useful form:

(15) Granstaff, V. E.; Martin, S. J. J. Appl. Phys. 1994, 75, 1319−1329.

$$Z_s = \frac{Z_l + Z_0 \tanh(\beta h_f)}{1 + (Z_l/Z_0)\tanh(\beta h_f)} \quad (5)$$

The combined surface effects due to the viscoelastic coating and the liquid overlayer are heavily dependent on the impedance ratio, Z_l/Z_0, at the coating/liquid interface. If Z_l is comparable in magnitude to Z_0, the shear acoustic wave propagating in the viscoelastic film loses a portion of its energy to the liquid. However, if $Z_l \ll Z_0$, the acoustic wave sees a low impedance boundary at the coating/liquid interface and essentially all of the energy is reflected back into the viscoelastic layer. This latter case is representative of the sensor systems being treated here, in which high-modulus polymers are used as coatings and low-viscosity Newtonian liquids, primarily water, contact the coating. Under these conditions, eq 5 reduces to

$$Z_s = Z_l + Z_0 \tanh(\beta h_f) \quad (6)$$

which is a simple linear combination of the motional impedances due to the liquid and a finite thickness viscoelastic film (eq 3).

If the viscoelastic coating is acoustically thin, i.e., ($\beta h \ll \pi/2$), and analyte sorption produces only minor perturbations in the coating properties (modulus, density, and thickness), then approximations for the film mechanical impedance are appropriate. We first note that $\tanh(jx) = j\tan(x)$, so the surface impedance of the film is rewritten as $Z_{s(film)} = j(\rho_f G)^{1/2}\tan[\omega h_f(\rho_f/G)^{1/2}]$. The tangent function can be expanded in a Taylor series and the first two terms retained, $\tan(x) \approx x + {}^1/_3 x^3$. This leads to[16]

$$\tan\left(\omega h_f \sqrt{\frac{\rho_f}{G}}\right) \approx \omega h_f \sqrt{\frac{\rho_f}{G}} + \frac{1}{3}\omega^3 h_f^3\left(\frac{\rho_f}{G}\right)^{3/2} \quad (7)$$

The surface mechanical impedance of the viscoelastic layer can then be written as[16]

$$Z_{s(film)} \approx \frac{\omega^3\rho_f^2 h_f^3}{3}\frac{G''}{|G|^2} + j\left(\omega\rho_f h_f + \frac{\omega^3\rho_f^2 h_f^3}{3}\frac{G'}{|G|^2}\right) \quad (8)$$

The first term (the real component of $Z_{s(film)}$), proportional to G'' is the attenuation due to the coating. The second term (the imaginary component of $Z_{s(film)}$) represents the energy storage in the film; it consists of a mass component, $\omega\rho_f h_f$, and a viscoelastic component proportional to G'.

The surface mechanical impedance contributed by a semi-infinite Newtonian liquid is given by[14]

$$Z_l = \sqrt{j\omega\rho\eta} = \sqrt{\frac{\omega\rho\eta}{2}}(1 + j) \quad (9)$$

which contains both real and imaginary components (proportional to the liquid density−viscosity, $\rho\eta$) representing the power dissipation and energy storage in the liquid. Substituting eqs 8 and 9 into eq 6 and then using the result for the shear mechanical

(16) Wolf, O.; Seydel, E.; Johannsmann, D. Faraday Discuss. Chem. Soc. 1999, 107, 91−104.

impedance in eq 2 gives the lumped-element electrical components for the simplified film/liquid model:

$$Z_{L(LEM)} = R_f + R_l + j\omega(L_m + L_f + L_l) \qquad (10)$$

where the inductance attributed to the mass of the viscoelastic layer is

$$L_m = \frac{\pi}{4K^2\omega_s C_0 Z_q}\rho_f h_f \qquad (11)$$

the resistance and inductance due to the viscoelasticity of the layer are

$$R_f = \frac{\pi\omega_s^2\,\rho_f^2\,h_f^3}{12K^2 C_0 Z_q}\frac{G''}{|G|^2} \qquad (12a)$$

$$L_f = \frac{\pi\omega_s^2\,\rho_f^2\,h_f^3}{12K^2 C_0 Z_q}\frac{G'}{|G|^2} \qquad (12b)$$

and the resistance and inductance due to the liquid overlayer are

$$R_l = \frac{\pi}{4K^2 C_0 Z_q}\sqrt{\frac{\rho\eta}{2\omega_s}} \qquad (13a)$$

$$L_l = \frac{\pi}{4K^2 C_0 Z_q}\sqrt{\frac{\rho\eta}{2\omega_s^3}} \qquad (13b)$$

Equations 10−13 represent the simplified lumped-element model for a thin viscoelastic layer in liquid, and the equivalent lumped-element circuit model is illustrated in Figure 1b.

Changes in the mechanical properties of the surface loads are reflected through changes in the electrical elements of the motional arm of the equivalent circuit. By measuring Δf_s from that of the unperturbed quartz resonator, the information about the surface load is determined. The shift in series-resonant frequency produced by the loaded QCR is given by

$$\Delta f_s = f_s' - f_s = \frac{1}{2\pi\sqrt{L'C_q}} - \frac{1}{2\pi\sqrt{L_q C_q}} \qquad (14)$$

where $L' = L_q + L_m + L_f + L_l$. For small changes in the inductance due to the load, eq 14 reduces to

$$\Delta f_s \approx -f_s(\Delta L/2L_q) \qquad (15)$$

Here, $\Delta L = L_q - L' = L_m + L_f + L_l$. Note that Δf_s reflects both the viscoelastic properties and mass loading of the surface film and the viscous properties of the liquid overlayer. Thus, eq 14 cannot be used directly to determine the partition coefficients, since these are derived only from mass loading information.[1,18]

However, in many sensing applications, liquid properties remain unchanged during analyte sorption, and L_l can be treated as a constant. A simple preliminary determination of L_l is made by operating an uncoated QCR directly in contact with the liquid.

Also, changes in the coating viscoelastic properties are often small (<3%) or negligible upon sorption of low concentration analytes, and L_f can be treated as a constant. Under the conditions of constant liquid and viscoelastic properties, Δf_s can be related directly to the added mass of the sorbed analyte. A new expression for the measurable shift in series-resonant frequencies is given by

$$\Delta f_s' \approx -f_s'\frac{\Delta L_m}{2L'} \qquad (16)$$

where f_s' and L' are defined in eq 14 and ΔL_m is the change in coating mass. Equation 16 references the frequency shift to the coated QCR in liquid prior to any analyte sorption. Because of the direct relationship to mass loading, eq 16 can be used to determine partition coefficients, assuming that the above stated assumptions, i.e., negligible change in viscoelastic properties hold.

In some cases, analyte sorption in the coating material produces nonnegligible changes in the viscoelastic properties. Then, eq 16 is no longer valid, since ΔL_f must also be included in computations of the frequency shift. Fortunately, for small changes in viscoelasticity (an original assumption for the equivalent-circuit LEM development), the relationship between R_f and L_f given by eqs 12 allows for determination of ΔL_f from a straightforward resonance resistance measurement and an a priori estimate of the coating loss tangent, G''/G'.[17] Once ΔL_f is determined, a direct investigation of mass loading is possible.

An inspection of eq 16 indicates that L' includes the inductance due to the liquid and, thus, influences the sensitivity of $\Delta f_s'$ to the added mass. In comparison, for an identical mass sorption in gas sensing, L_l is nonexistent and $L' = L_q + L_m + L_f$, which will result in larger values of $\Delta f_s'$. In conclusion, a reduction in the sensitivity to the sorbed mass is expected in liquid environments. Note that this reduction in sensitivity can also be explained through the decrease in the crystal quality factor Q, as outlined in the section on result and discussion.

EXPERIMENTAL SECTION

Apparatus. Piezoelectric quartz crystals, 9 MHz AT cut, with diameters of 14 mm were used. The QCRs were fabricated with electrodes made of a 1400-Å-thick layer of gold deposited on a 50-Å-thick chromium adhesion layer. Two different electrode geometries were used: a QCR with two identical circular and concentric electrodes both 7-mm diameter, and a QCR with an upper electrode of 4-mm diameter and a lower electrode of 7 mm. The electronic instrumentation consists of a network analyzer (HP8753C), and oscillator circuits. The oscillator circuits incorporate the quartz crystal in a feedback loop as the active control element. The amplifier stage of the oscillator is a monolithic IF amplifier with a 3-dB bandwidth of 90 MHz and includes an automatic gain control (AGC) maintaining a voltage level proportional to the loss in the crystal. Note that this is required because of the relatively high loss (low-quality factor, Q) of the loaded crystal resonator.

Selection of Sensor Coatings for the Design of Sensors. The initial considerations of the coating material selection for a

(17) Cernosek R. W.; Martin, S. J.; Hillman, A. R. *ECS Abstr.* **1998**, 98-2 (No. 1182).

chemical sensor for aqueous environments are identical to those described in gas sensing. This is because the general sorption process between polymer coatings and analytes in aqueous environments are considered similar to those described for coatings used in the gas phase. However, a primary requirement in the selection of the coating material is the coating stability in water. Other criteria for the selection of coating materials can be derived from the preliminary work done in aqueous environments that include reversibility, reproducibility, and functionalization process of the coating.

Reagents. The liquids were prepared from analytical-grade reagents, purchased from Aldrich (Milwaukee, WI), and used as received. The polymers used were also purchased from Aldrich. Deionized (DI) water was used.

Experimental Setup and Procedures. The experimental setup is composed of the sensing system, the sample delivery system, and the electronic instrumentation as described in ref 18. The sensing system consists of QCRs, the mounting elements, and a measurement cell made from Plexiglas. The liquid delivery system consists of a sample tank, a flow injection analyzer (Eppendorf), and a working solution. Well-defined concentrations of organic analytes are prepared by diluting the organic compounds in a methanol/water solution that is injected into the working solution by the computer-controlled flow injection analysis system. Control tests have been run with the methanol/water solution alone to determine the effects of methanol on the coating and, hence, the sensor response. Note that the effects of methanol on the sensor response are additive and linear for the measured concentration ranges. Thus, the obtained results for the analytes can still be used to calculate the sensitivity. A typical run is started by pumping DI water through the cell at a selected flow rate. A low flow rate of 0.45 mL min^{-1} is used to minimize the hydrodynamic coupling between flowing liquid and crystal surface, the pressure and pulsating flow effects on the sensor surface which may add to the device noise.[18] Stability of the frequency response is first established for 20 min. This DI water baseline is then followed by a series of 20-min exposures to the analyte solutions.

Polymer solutions of 2−5 wt % are prepared by dissolving the polymer in either toluene or chloroform. A layer of this chemically sensitive polymer is applied over the clean surface (upper electrode) of the device by spin coating the polymer solutions at 2000 rpm for 30 s. The adhesion of the film is improved by exposing the coated device to ambient air for 30 min or by heating the coated device for 15 min at 100 °C. The coating thickness is calculated by utilizing the technique described in ref 19. This technique is based on the Sauerbrey equation, which is suitable for frequency shifts due primarily to mass loading. Since the coating thicknesses used in this study are very thin, the approximation is valid. The tested organic analytes are tetrachloroethane, tetrachloroethylene, trichloroethylene, tetrachloromethane, chloroform, toluene, and xylenes.

(18) Menon, A.; Zhou, R.; Josse, F. *IEEE Trans. Ultrason. Ferroelect. Freq. Control* **1998**, *45*, 1416−1426. Menon, A.; Patel, R.; Zhou, R.; Josse, F.; *Proc. 1998 IEEE Int. Freq. Control Symp.*, Pasadena, CA, 1998; pp 667−675. Josse, F.; Zhou, R.; Patel, R.; Menon, R. *Proc. SPIE, Chem. Microsens. Appl.* **1998**, *3539*, 64−73. Menon, A.; Zhou, R.; Josse, F. *The 193rd Meeting of the Electrochemical Society, Meeting Abstract*, **1998**, 98-1, Abstr. 1126. Patel, R.; Menon, A.; Zhou, R.; Josse, F. *The 194th Meeting of the Electrochemical Society, Meeting Abstract*, **1998**, 98−2, Abstr. 1193.
(19) Lu, C. S.; Lewis, O. *J. Appl. Phys.* **1972**, *43*, 4385−4390

The network analyzer is used to characterize the unloaded and loaded QCR in the cell together with the test fixture and lead wires. This characterization will help determine secondary loading effects that may affect the sensor response. The network analyzer is also used to measure the complex reflection coefficient, $S_{11}(f)$, from which a complex admittance can be determined as

$$Y(f) = \frac{1}{Z(f)} = \frac{1}{Z_0} \frac{1 - S_{11}(f)}{1 + S_{11}(f)} \tag{17}$$

where Z_0 is the characteristic impedance of the measurement system, which is typically 50 Ω in the present case. To characterize the effects of changes in the viscoelastic properties of the coating on the complex admittance, measurements were taken for the uncoated QCR, coated QCR, coated QCR in water, and coated QCR exposed to analytes in water. The measured data were then fitted to the lumped-element equivalent circuit of Figure 1b.

RESULTS AND DISCUSSION

Sensor Measurements in Liquid Environments. In a piezoelectric material such as quartz, confinement of the induced elastic wave motions produces resonance with a very high Q (10^4−10^7).[20] The quality factor, Q, is the ratio of energy stored to energy dissipated per cycle at the resonance frequencies and in our context is defined by $\omega L/R$, with L the total motional inductance and R the total motional resistance. It is noted that a bare QCR has the ability to resonate with minimal loss (usually $R \approx 8-20$ Ω). However, this is not the case in liquid sensing, where the QCR is loaded with a viscous coating and/or a liquid layer and the increase in the energy storage is not as significant as the increase loss. As a result, there is a noticeable drop in resonator Q. This will consequently affect the design of an appropriate oscillator circuit capable of maintaining good short and long-term frequency stability. Therefore, prior to conducting the experimental measurements of the sensor response in liquid environments it was necessary to characterize the QCR operating under the various loading conditions.

The characterization of a QCR is performed by measuring the admittance phase response of the bare and composite loaded (polymer coating + water) QCRs. Figure 2 shows the admittance phase responses for the QCR under three conditions: with the test fixture O-ring secured against the crystal, with water loading only, and with the composite load. The QCR is coated with poly(methyl acrylate) (PMA) with a calculated thickness of 0.77 μm. The results clearly show that the loading by the polymer layer produces a relatively small drop in the resonator Q and that liquid loading produces the most substantial drop in the Q as well as decreasing the admittance phase slope at resonance (frequency where the phase is zero). It is noted that any instability in the QCR oscillator circuit is related to this decrease in the admittance phase slope. However, despite the decrease in the admittance phase slope and the quality factor Q, the loaded QCR still can be used as a sensing element, provided other noise or unwanted frequency variations can be minimized.

(20) Meeker, T.; Shreve, W.; Cross, P. *Precision Frequency Control: Acoustic Resonators and Filters*; Academic Press: New York, 1985; Vol. 1, pp 47−145.
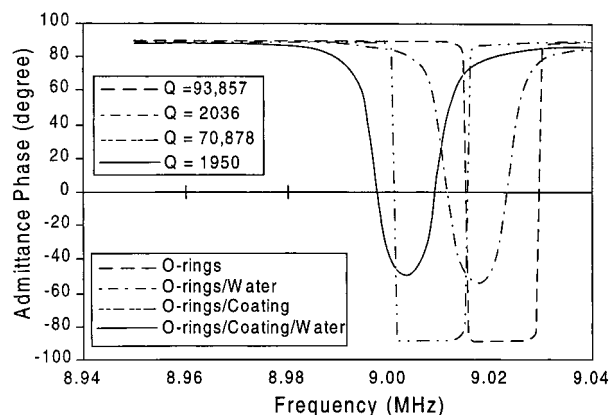
Figure 2. Admittance phase response for a PMA-coated QCR in contact with the O-ring and composite load (polymer coating + water) showing a decrease of admittance phase slope with increasing load. The coating thickness is 0.77 μm.

Prior to conducting measurements for the identification and detection of low concentrations of analytes in liquids, one also needs to minimize unwanted frequency variations, i.e., the induced noise in the sensor signal. The noise can be categorized as direct and indirect frequency variations. Indirect frequency variations are mainly caused by parasitic reactance, a function of the active and passive components of the circuit, and can be minimized by maintaining the highest possible Q value of the circuit. A detailed discussion on indirect noise can be found in refs 18, 20, and 21. Direct noise, i.e., direct frequency shifts, is caused by any change to the QCR environment due to mass and viscoelastic loading, liquid flow, and pressure. However, of all the direct frequency variations, only those due to changes in the QCR loading caused by the sorbed analyte are desired and any other induced frequency are considered as noise. Direct frequency variations can be expressed as

$$\frac{\Delta\omega}{\omega_0} = \frac{1}{\omega_0}\sum_{i=1}^{n}\frac{\partial\omega}{\partial\alpha_i}\Delta\alpha_i \qquad (18)$$

where $\omega_0(=2\pi f_0)$ is the fundamental resonant frequency of the crystal and α_i are the various parameters on which the fundamental resonant frequency depends. Thus, in our context, since ω_0 is only a function of the total motional inductance of the loaded resonator and motional capacitance of the quartz, eq 18 can be reduced to

$$\frac{\Delta\omega}{\omega_0} = \frac{1}{\omega_0}\left(\frac{\partial\omega}{\partial L}\Delta L + \frac{\partial\omega}{\partial C_q}\Delta C_q\right) \qquad (19)$$

Thus, the observed noise in the sensor measurements can be considered as a combination of the unwanted direct and indirect frequency variations.

Other sources of noise may be caused by compressional wave interference on the sensor signal.[22-24] Compressional waves are generated by QCRs in liquid environments due to the gradient in the shear particle displacement profile. These waves propagate unattenuated in the liquid reflecting at the liquid/cell (cell surface in contact with liquid) interface and can interfere with the shear acoustic sensor signal at the resonator surface. Therefore, to minimize reflection from any generated compressional wave, the cell surface in contact with the aqueous solution is roughened.

The observed unwanted frequency variations using oscillator circuits are less than ±0.25 Hz for the bare device in air, and ±6 Hz at a flow rate of 0.87 mL min^{-1}, ±4 Hz at 0.65 mL min^{-1}, ±2 Hz at 0.45 mL min^{-1}, and less than ±0.5 Hz at zero flow rate for the bare device in water, respectively. For the polymer-coated QCRs, similar experiments were conducted using PMA-coated and poly(styrene) (PS)-coated QCRs. The results show that the unwanted frequency variation is ±5 Hz at a flow rate of 0.87 mL min^{-1}, ±4 Hz at 0.65 mL min^{-1}, ±2 Hz at 0.45 mL min^{-1}, and ±0.5 Hz at zero flow rate. It is noted that the above values for the polymer-coated devices are not absolute and will vary depending on the coating thickness and the temperature stability of the environment. The results evidently show that unwanted variations are mainly due to the dynamic liquid and the pulsating effect of the flow injection analysis system. These can be eliminated or minimized by conducting the experiments at low flow rate. Although the zero flow rate, that is, static liquid has the lowest level of noise, a low flow rate of 0.45 mL min^{-1} is used for sensor measurements in this study.

Effect of Methanol Concentration and the Coating Thickness. Because the organic analytes of interest have very low solubility in water, methanol was added to increase the solubility of the organic analytes in water. However, the methanol molecules also interact with the polymer coatings and result in an additional frequency change. This, in turn, affects the polymer coating sensitivity to the analytes of interest and hence the partition coefficients. It is therefore necessary to determine the appropriate methanol concentration for optimum polymer coating sensitivity. Poly(ethyl acrylate) (PEA)-, poly(vinyl acetate) (PVAc)-, and PMA-coated QCRs exposed to different concentrations of tetrachloroethane with different methanol concentrations (0.05, 0.10, 0.20, 0.39 wt %) were investigated. The results indicate that the sensor response for the PEA-coated QCRs generally decreases with increasing methanol concentration. This is probably due to the increase in the interaction of the methanol molecules with the polymer coating. The methanol molecules may occupy more sites in the polymer coating, thus reducing the opportunity of interaction between the analyte molecules and the coating. Another reason may be due to the added methanol in the solution. The added methanol molecules in water will improve the solubility of analytes such as tetrachloroethane and give the analytes a preference for remaining in the liquid, and thus, sorption into the polymer is less favorable. This will result in a reduction in the sensitivity of the coating to the analytes. Similar results were also observed for the PVAc-coated QCR sensor. However, the sensor response of the PMA-coated QCR increases with increasing methanol concentration. This may be due to the interactions in the ternary system, i.e., coating/methanol/analyte. In this case, methanol molecules may not replace the analyte molecules in the

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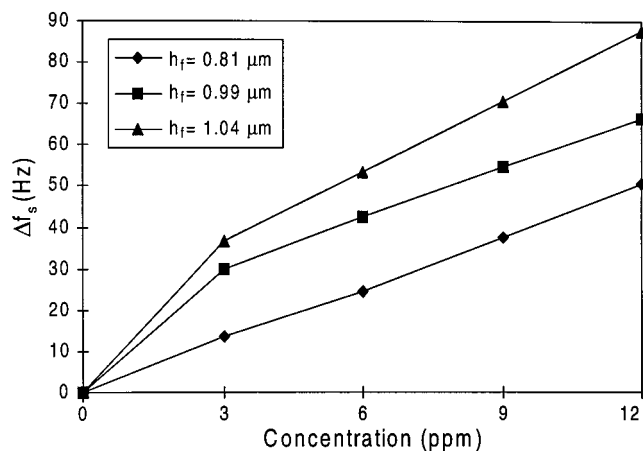
Figure 3. Frequency shifts, Δf_s, of the PEA-coated QCRs for different coating thicknesses exposed to different concentrations of tetrachloroethane. h_f is the thickness of the coating.
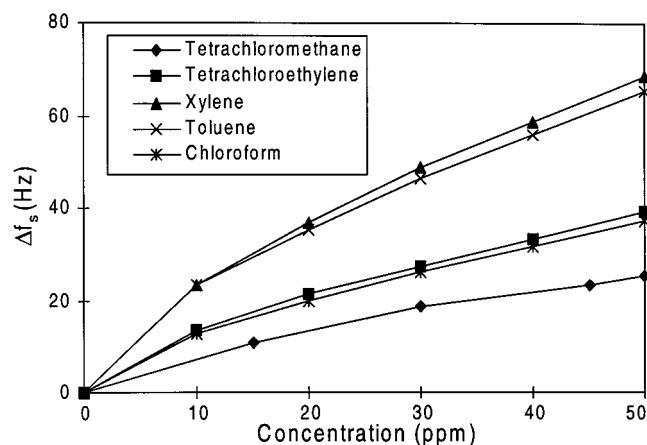

Figure 4. Frequency shifts, Δf_s, of the PEA-coated QCR exposed to different concentrations of tetrachloroethylene, tetrachloromethane, xylene, toluene, and chloroform. The coating thickness is 0.99 μm.

Figure 5. Admittance (a) amplitude response and (b) phase response for a PIB-coated QCR showing the effect of the O-rings and the composite load (coating +aqueous analyte solution), namely, a decrease of resonance magnitude and phase slope with increasing load. The methanol and trichloroethylene concentrations are 0.39 wt % and 50 ppm, respectively. The calculated coating thickness for the PIB is 1.25 μm using the Sauerbrey equation.

coating but participate in the interaction of the analyte/coating pairs. However, methanol sensitivity for the polymer coatings investigated is very small compared to that of the analytes; hence changes in frequency due to analyte alone can be used to evaluate the sensor sensitivity. The obtained sensitivity pattern can be still used for the selection of sensitive materials for sensor and sensor arrays. Figure 3 shows the response of the PEA-coated QCRs for three different coating thicknesses when exposed to increasing concentrations of tetrachloroethane. The calculated thicknesses are 0.81, 0.99, and 1.04 μm. As in the gas phase, the results clearly show that the thicker coatings give larger frequency shifts but a relatively longer response time. Similar results have been obtained for all the investigated polymer coatings.

Sensor Measurements. Several sensor experiments were conducted for the various coatings exposed to different concentrations of various analytes. Figure 4 shows the responses, Δf_s versus concentrations, for a PEA-coated QCR exposed to tetrachloroethylene, tetrachloromethane, xylene, toluene, and chloroform in water. The results indicate that the sensor responses increase linearly with increasing analyte concentration. Similar results were also obtained for all the investigated polymer-coated QCRs. Note that very low concentrations of analytes have not been investigated due to the unwanted frequency variations. The unwanted varia-
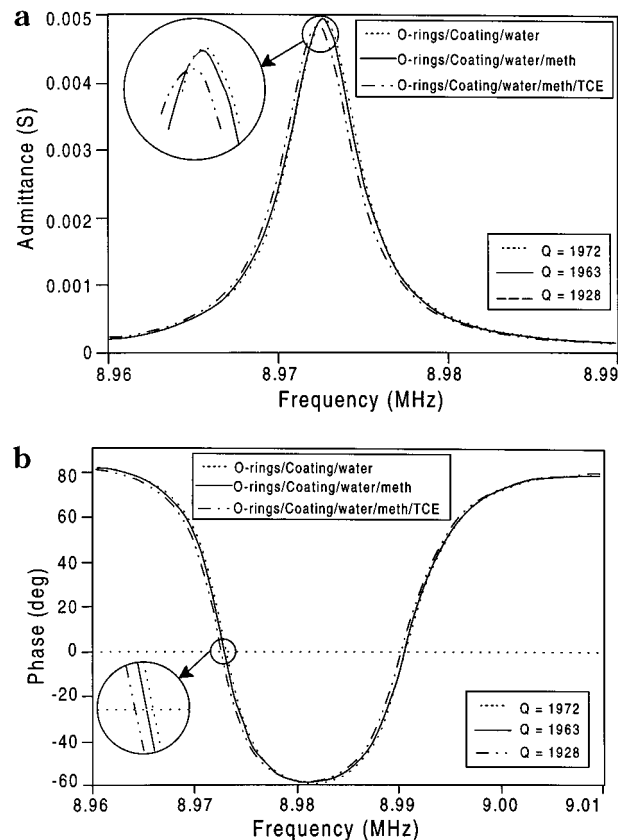
tions can be reduced by utilizing a stable oscillator circuit and/ or by operating the sensor under static liquid conditions. The different slope between 0 and 3 ppm seen in Figures 3 and 4 may be attributed either to a different rate of absorption at a very low concentration or to slightly higher responses at the initially measured concentration of 3 ppm.

Characterization of Polymer-Coated QCRs. The selection of the coatings can be performed through a study of the sorption process in terms of the partition coefficients of the analytes in the polymer coatings. However, the determination of the partition coefficients is only accurate if all contributions to the total measured frequency shifts, Δf_s, can be accounted for. While mass loading is often assumed to be the dominant factor used in determining partition coefficients, viscoelastic effect may also contribute to Δf_s. Therefore, it is necessary to study the effect of changes in viscoelastic properties of the coatings on the sensor responses. In this study, the QCR devices coated with PEA, poly-(isobutylene) (PIB), poly(*cis*-butadiene) (PBdE), and PS were investigated for the determination of any viscoelastic effect on the loaded QCRs. PBdE, PIB, and PEA represent rubbery polymers and PS represents the glassy polymers. Figure 5 shows the admittance amplitude and phase responses for the PIB-coated QCR (h_f = 1.25 μm, ρ_f = 0.92 g/cm³ in air) exposed to DI water, methanol, and trichloroethylene (TCE). The results indicate that the DI water loading has the most impact in lowering the Q of
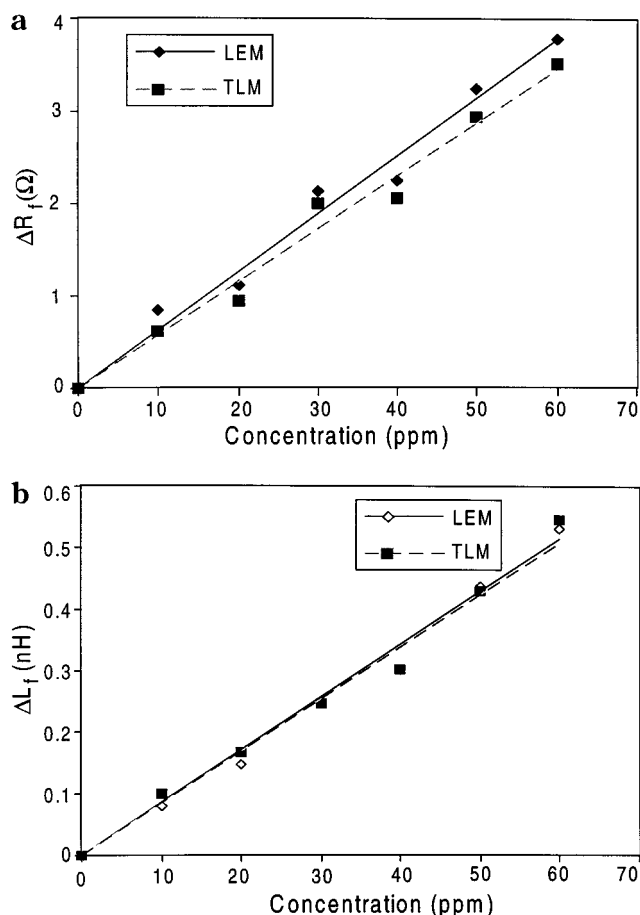
Figure 6. Changes in (a) motional resistance and (b) motional inductance of the PIB coating on a QCR exposed to different concentrations of trichloroethylene. The calculated coating thickness is 1.25 μm using the Sauerbrey equation.

Figure 7. Changes in the storage (G') and the loss (G'') shear moduli of the PIB coating on a QCR exposed to different concentrations of TCE) at a constant methanol concentration of 0.39 wt %. The calculated coating thickness is 1.25 μm using Sauerbrey equation.

the crystal and decreasing both the magnitude and the phase slope at resonance. Note that the measured loss (i.e., $R_q + R_f + R_l$) is 183 Ω and is mainly due to the liquid (i.e., R_l) as indicated by eq 13a for the 9-MHz QCR device. Figure 5 also shows that the admittance magnitude of the liquid-loaded QCR is slightly further decreased in the presence of analytes in the aqueous solution and the admittance response is further translated toward lower frequency. Similar effects have been observed for the PIB-, PBdE-, PEA-, and PS-coated QCRs with different coating thicknesses and the degree of changes a function of the thickness.

The measured admittance of the loaded crystal can be fitted to the LEM of Figure 1b to extract values of the changes in coating motional resistance (R_f) and inductance (L_m and L_f) as a function of analyte concentration. Figure 6 shows the variation of the calculated R_f and L_1 ($L_1 = L_m + L_f$) versus trichloroethylene concentration for the PIB-coated QCRs. Note that ΔR_f and ΔL_1 represent changes in R_f and L_1 due to trichloroethylene molecules only (the reference here is the coating exposed to water and methanol). It can be seen that both ΔR_f and ΔL_1 generally increase with increasing analyte concentration. Similar behavior was also observed for the PBdE-, PEA-, and PS-coated QCRs exposed to various analyte solutions. It is noted that knowledge of ΔL_1 alone does not provide adequate information on the individual contributions from mass loading and viscoelastic effects. However, the viscoelastic effects, if any, can be extracted after calculating
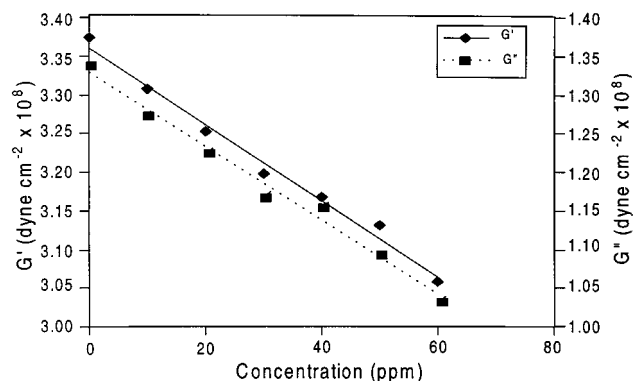
changes in the shear storage modulus G' and loss modulus G'' and determining the relationship established by eqs 12.

Equation 4 can be used to give a realistic description of viscoelastic coatings exposed to liquid media in terms of the shear modulus, G.[12–14] The complexity of this model accounts for the polymer coating and the DI water solution. The PIB coating was first characterized in air by measuring the admittance for the PIB-coated QCR (Δf_c = 20,129 Hz, which corresponds to h_f =1.25 μm using the Sauerbrey equation). The extracted values for the storage (G′) and loss (G″) moduli are found to be of the order of 10^9 dyn/cm² with a loss tangent of ~1, comparable to the published data on PIB.[25] Similar calculations were conducted for PBdE- coated QCRs, and the extracted shear moduli values are found in agreement with published results.[26]

Using the measured S parameters and eq 17, the storage and loss moduli versus trichloroethylene concentration for the PIB-coated QCR were calculated and are depicted in Figure 7. It is observed that the storage and loss moduli of the PIB coating under DI water + methanol are of the order of 10^8 dyn/cm², which is consistent with the characteristics of a rubbery, viscoelastic material. However, the observed relatively lower starting values of G′ and G″, extracted from the model, may be due to the uptake of water and methanol molecules and/or to errors in estimating the coating thickness. It is known that, to extract proper values for moduli, a reasonable level of viscoelastic response is needed.[27] Such response is best obtained for thick layers. The acoustically thin coatings investigated in the present study may result in a small level of viscoelastic response and thus will contribute to the error of the extraction. Furthermore, there is no accurate technique for controlling the thickness of polymer coatings, which may change dimension when subjected to water, and it has been shown[27] that films exhibiting small motional resistances lead to large errors in determination of moduli for small errors in coating thickness. While the initial extracted moduli values may have no great significance, the calculated trends in G' and G'' with

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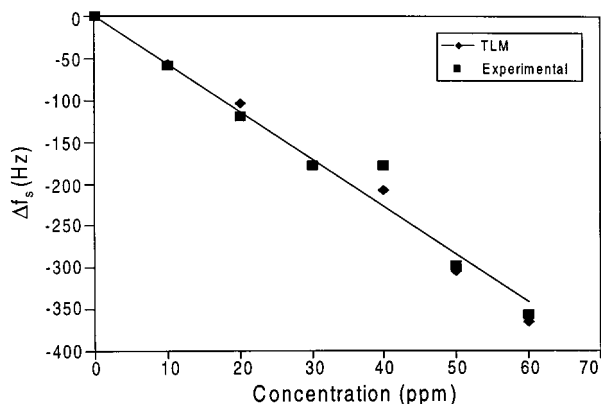(27) Lucklum, R.; Behling, G.; Haupmann, P. *Anal. Chem.* **1999**, *71*, 2488–2496.

Figure 8. Calculated shifts in the series resonance frequency of a PIB-coated QCR vs concentrations of TCE obtained using the transmission-line model. The line is a fit to the calculated data. Experimental data are shown for comparison. Note that the LEM and TLM results are indistinguishable.

Figure 9. Sensitivities of the PEA-, PMA-, PECH-, PBMA−MMA-, PIB-, and PVAc-coated QCRs for different organic analytes in water. Note that the methanol response has been subtracted from all other responses except for methanol itself.

increasing trichloroethylene concentration and the overall decrease in the magnitude of the shear modulus appear reasonable and consistent with observed motional resistances and inductance. The values also indicate that, as the analyte molecules sorb into the polymer, the coating behaves more rubberlike. It has also been found that glassy PS coating behaves as a rubbery solid in water since G' and G'' are on the order of 10^8 dyn/cm^2. This may explain the observed reversibility of the sensor responses for the PS-coated QCRs exposed to various concentrations of analytes in aqueous solution. The determination of the shear moduli was conducted using an iteration process with the initial values of the shear moduli and density in air.

Using the calculated values of the shear moduli for the various polymer films in water, Δf_s versus the viscoelastic film thickness were simulated for the TLM, LEM, and Sauerbrey equation. The results for a PIB coating, indicate that, for film thickness less than l.5 μm, the PIB-coated QCRs will operate in the gravimetric regime where measured frequency shifts are approximately linear with thickness or mass changes. A small deviation (<3%) from the gravimetric regime is obtained for coating thickness around 1.2 and 1.4 μm for PBdE and PS coatings, respectively. Beyond these thicknesses, calculated deviations increase, which indicate that viscoelastic effects must be accounted for in the total frequency shift. From the measured Δf_s, it is concluded that the investigated coatings are acoustically thin and that the coated devices are operating almost entirely in the gravimetric regime. Furthermore, the measured Δf_s due to analyte absorption indicate that changes in the film properties can be assigned to mass loading. This conclusion is further confirmed in the results of Figure 8, which show the TLM-predicted Δf_s as a function of TCE concentration in the PIB coating. The results are also compared to experimental data. It is noted that the TLM, LEM, and Sauerbrey models give essentially the same results (up to ∼2 μm of the coating thickness), thus confirming that the film mass loading is the dominant effect. For the investigated polymers, the measured admittance data were used to simulate frequency shifts corresponding to various concentrations of analytes in the coating.

Sensor Sensitivity. As known, most chemical sensing systems involve two types of sorption processes: chemisorption in which strong interactions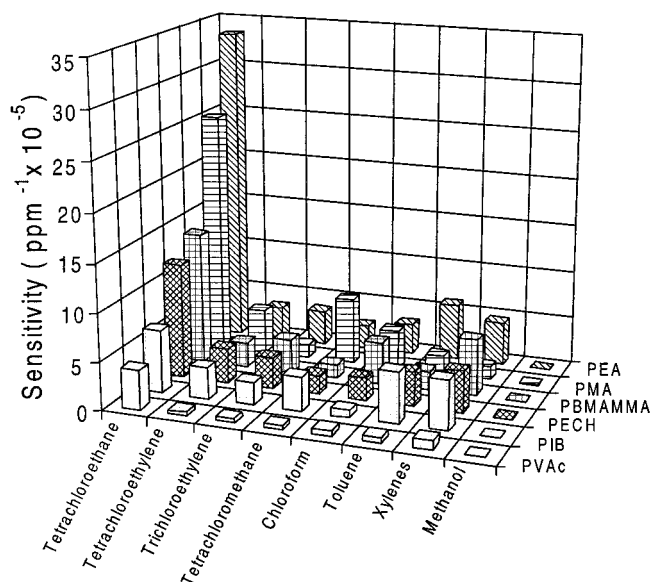, i.e., covalent or ionic bonds, occur between the coating and the analyte; and physisorption in which weak interactions occur. The most common physisorption mechanism is the van der Waals forces, which include dispersion, polar, polarizability, and Lewis acid−base interactions.[1,3,28] In aqueous environments, the organic analytes may escape from the water by sorbing into the particulate sites of the coating due to the unfavorable free-energy costs of remaining in the aqueous solution. Additionally, the analyte molecules may displace water molecules from the region near the coating surface to some extent and thereby be associated with the surface via the various interaction forces mentioned above. Since all of these interaction mechanisms can operate simultaneously, a combination of the sorption due to the unfavorable free energy and competition between water and analyte molecules dictates the final sensor response. This combination mainly depends on the structural properties of the organic analyte and the coating investigated. Therefore, an understanding of the interactions between analytes and coatings will help in the selection and/or design of sensitive materials for sensors.[1,28,29]

Sensitivities of the polymer-coated QCRs to different analytes of the various coatings/analyte pairs are shown in Figure 9. Sensitivity is defined as[7,18]

$$S = \frac{1}{\Delta f_c}\left(\frac{\Delta f_i}{c_i}\right) \qquad (20)$$

where Δf_i is the frequency shift caused by the exposure of the sensor to a concentration of the organic analytes, c_i, and Δf_c is the shift in series-resonant frequency due to the coating. Note that the methanol responses are subtracted from all other

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responses except methanol itself. As mentioned earlier,[18] Δf_c, accounts for the thickness of the coating.

The sensitivities of poly(epichlorohydrin) (PECH) for the investigated analytes are in general lower than those of poly(butyl methacrylate-*co*-methyl methacrylate) (PBMA−MMA). The lower sensitivity of the PVAc coating may be caused by the strong hydrogen bond between the methanol and ester groups of the PVAc coating. The polymers with relatively high polarities such as PMA, PEA, PBMA−MMA, and PECH, in general, show high sensitivities toward chlorinated hydrocarbon analytes. The acrylate groups of polyacrylate coatings (i.e., PMA, PEA, and PBMA−MMA) and the ether groups of the PECH coating can also form hydrogen bonds with methanol molecules. However, these hydrogen bonds are weaker than those of methanol/ester groups of the PVAc coating. This is due to the differences in their molecular structures and conformations. These weaker interactions result in the retention of the small amount of methanol molecules in polymer coatings. This may, in turn, enhance the solubility of the organic analytes and, hence, the sensitivity. PIB coating material usually cannot form hydrogen bonds with methanol molecules due to its structure and configuration. Therefore, only a bulk absorption process occurs for all of the investigated analytes. This, in turn, results in relatively lower sensitivity than those of PEA, PMA, PBMA−MMA, and PECH.

It is also observed that the PIB-coated QCR for tetrachloromethane exposure shows a higher sensitivity than trichloroethylene, tetrachloroethylene, and chloroform. It is also noted that a PVAc-coated QCR exhibits higher sensitivity toward chloroform than for the other investigated chlorinated hydrocarbons except tetrachloroethane. This may be caused by the higher polarities of the PVAc and chloroform molecules.

The results also indicate that the nonpolar coatings, i.e., PIB, show higher sensitivity toward toluene than xylenes. This may also be due to the relatively high water solubility of toluene. Moreover, relatively high polar coatings, i.e., PEA and PMA, also show higher sensitivity toward toluene than xylenes. However, relatively low polar coatings, i.e., PBMA−MMA and PECH, show higher sensitivity toward xylenes than toluene. This may be due to the polarity of the coating and weak hydrogen bond formation of methanol/polyacrylate groups and methanol/ether groups of the coatings, water solubility of the analytes, and some other related factors that can perturb the interaction between analytes and coatings. However, in general, PIB- and PEA-coated QCRs show higher sensitivity toward both toluene and xylenes compared to other polymer-coated QCRs exposed to these analytes.

Partition Coefficients. In chemical sensing, the sorption process in liquid environments can also be described by the partition coefficient, K_L, which is the thermodynamic parameter that measures the distribution of organic analytes between the coating and the aqueous solution. K_L helps define the inherent selectivity of a sensor coating material. In our context the aqueous solution is water. K_L can be defined as[18]

$$K_L = c_c/c_w \qquad (21)$$

where c_c is the concentration of the organic analyte in the coating and c_w is the concentration of the analyte in water.

Equation 21 can also be expressed in terms of the partition coefficient in gas phase, $K_g = c_c/c_g$, and the Henry's law constant, K_H, as follows:[18]

$$K_L = \frac{c_c}{c_w} = \frac{c_c}{c_g}\frac{c_g}{c_w} = K_g K_H \qquad (22)$$

where c_g is the analyte concentration in gas phase, $K_g = c_c/c_g$, and $K_g = c_g/c_w$. K_g is mainly controlled by the dispersion interaction of the coating/analyte pair with variations contributed by the polar interaction and Lewis acid−base interaction.[1,28] K_g allows the classification of the coatings and also determines the inherent selectivity of the coating.[1,28] Therefore, the interaction mechanisms that are used in gas sensing can still be applied to the sensing process in aqueous phase. However, it is expected that these interaction mechanisms will be modified by the analyte solubility in water. Indeed, It is known that the Henry's law constant, K_H, is directly proportional to both the activity coefficient of the compounds in water and the organic analyte vapor concentration of the pure organic liquid.[30,31]

To access and quantify the various dominant interaction mechanisms, a linear solvation equation can be used to separate the various components that contribute to the solvation process of analyte molecules in polymer coatings.[32,33] However, this will not be the case in the present paper, which will only focus on the overall value of K_L. The determination of the partition coefficients is only accurate if all contributions to the measured Δf_s can be established. As discussed earlier Δf_s are mainly due to mass loading and, therefore, can directly be used to estimate K_L for all coating/analyte pairs investigated. Combining eqs 20 and 22 and the Sauerbrey equation, the partition coefficient can be rewritten as

$$K_L = \frac{\Delta f_i}{\Delta f_c c_i}\rho_c = S\rho_c \qquad (23)$$

where ρ_c is the density of the coating. Note that eq 23 is only suitable for cases where changes due to viscoelastic effects are insignificant to the total sensor response, as it is here. It is also assumed that the analyte partition is so small as not to perturb the coating density. Equation 23 indicates that values of the sensitivity, however modulated by the density of coating, are still the primary determinant of K_L.

Experimental values for K_L, denoted as $K_{L(exp)}$, are compared with calculated values of $K_{L(calc)}$ using eq 22, and the partition coefficients in gas phase, K_g. The results for PEA-coated QCRs are shown in Table 1. Note that the K_g values are obtained from the measurement data in ref 34 and the K_H values are calculated using the ratio of organic vapor concentration of the pure organic liquid and the concentration of organic analyte in water.[30,31] It is observed that the partition coefficients of the analytes in the

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(32) Grate, Jay; Abraham, M. H.; McGill, R. A. *J. Eng. Appl. Sci.* **1996**, *2*, 2075−2079.
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Table 1. Logarithms of the Partition Coefficients of the Different Organic Analytes and a Poly(ethyl acrylate)-Coated QCR

analyte	$\log K_g{}^a$	$\log K_{L(calc)}{}^b$	$\log K_{L(exp)}{}^c$
tetrachloroethane	5.07	3.25	2.49
tetrachloroethylene	3.54	3.56	1.50
trichloroethylene	3.14	2.78	1.52
tetrachloromethane	2.98	2.97	1.36
chloroform	3.43	2.64	1.48
toluene	3.58	3.01	1.74

[a] K_g represents the known partition coefficients of the organic analytes in gas phase. [b] $K_{L(calc)}$ represents the partition coefficients of the organic analytes calculated from eq 22. [c] $K_{L(exp)}$ represents the partition coefficients of the organic solvents in water as calculated from the measured frequency shifts, Δf_s.

polymers are higher in gas phase than in water. This may be due to the competition between water and analyte molecules which decreases the amount of the analyte molecules in the polymer coating and K_H. The difference between $K_{L(exp)}$ and $K_{L(calc)}$ may be due to the addition of methanol in the analyte solution which changes the solublity, hence K_H. As mentioned earlier, K_L is inversely related to the water solubility of the analytes. Hence, the added methanol will result in a reduction of the value of K_L. However, the effects of methanol on sensor response are additive and linear within the measured concentration range. Additionally, the sensitivities to methanol for all of the investigated coatings are very small (see Figure 9), and their concentrations in the working solutions are also small (~0.39 wt %). Thus, the trends of the value of $K_{L(exp)}$ should be similar to that of the actual K_L. Therefore, $K_{L(exp)}$ can still be used as a model to determine the various coating sensitivities. In addition, a significant drop in Q of the crystal under liquid loading may contribute to the observed drop in sensitivity in liquid, hence the partition coefficients. Moreover, the results also show that the $K_{L(calc)}$ values are higher than the $K_{L(exp)}$ values. In the present case, the cumulative load (coating and water) may have been large enough to lead to a reduction in sensitivity. In fact, this is the case if one observes the denominator $L' = L_q + L_m + L_f + L_l$ in eq 16. For gas sensing, L_l is nonexistent, which makes the value of L' smaller, resulting in larger values of Δf_s for the same added mass, i.e., ΔL. Thus, changes in mass caused by trace analytes added to water will result in a relatively smaller frequency shift, hence lower values of $K_{L(exp)}$. Although eq 22 cannot accurately predict the K_L values, the results of Figure 9 still can be used to select sensitive coatings for direct sensing in liquid.

In general, the results also show that the extracted values of K_L decrease with increasing K_H for a given analyte. However, the deviations from linearity were observed, probably due to the addition of methanol in the analyte solution. The added methanol, which improves the water solubility of the analyte and hence changes the values of K_H, will result in variations in K_L values.

CONCLUSION

Quartz crystal resonators coated with polymers have been investigated for the direct detection of organic compounds in aqueous environments as opposed to headspace vapor detection. The objective has been to contribute to the understanding of both the sorption process in liquid environments and the sensor response and, hence, the selection of the sensitive coatings for the implementation of sensors. The effects of both the viscoelastic properties of the coating and the added mass on the sensor responses have been characterized. It has been shown that while mass loading remains the primary detection mechanism, especially for acoustically thin coatings, changes in the viscoelastic properties of the polymer coatings may also affect the sensor responses for a given analyte.

To further the understanding of the viscoelastic and added mass effects, the measured admittance data have been analyzed by utilizing both the lumped-element model and transmission line model (TLM)[1,12−15] to extract all contributions to the sensor response. In studies that involve relatively low concentrations of organic compounds and acoustically thin coatings, the subsequent changes in viscoelastic properties of the coatings are still such that the sensors operate in the gravimetric regime. For most applications involving the detection of relatively low concentrations of organic compounds and the use of acoustically thin viscoelastic films, changes in the complex shear modulus of the coatings contribute less than 5% of the total shift in the series resonant frequency. Therefore, the measured Δf_s, assumed to be totally due to mass loading, can be used to approximately calculate partition coefficients, which are needed for the selection of the coatings and, hence, the identification of analytes through the implementation of sensor arrays. However, it is observed that the partition coefficients of the analytes in the polymers are higher in gas phase than in water, due in part to the competition between water and analyte molecules, to the water solubility of the given organic analyte, and to the added methanol used to improve the solubility of analytes in water. The addition of methanol to the analyte solution changes the solubility, hence K_H, and decreases the coating sensitivity to the analyte. All of the above, together with the decrease in the device sensitivity in water (low Q) contribute to the reduction in partition coefficients. The competition in the ternary system of molecules (water, methanol, analyte) probably results in decreasing the amount of analyte molecules that can be absorbed by the polymer coating. Despite the observed decrease in sensitivity, and the change in the water solubility of the analyte due to added methanol, the calculated sensitivity/partition coefficients can still be used to select coatings for the implementation of sensor arrays.