

Ionic Liquids: A New Class of Sensing Materials for Detection of Organic Vapors Based on the Use of a Quartz Crystal Microbalance

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A QCM device employing ionic liquids as the sensing materials for organic vapors has been developed and evaluated. The sensing mechanism is based on the fact that the viscosity of the ionic liquid membrane decreases rapidly due to solubilization of analytes in the ionic liquids. This change in viscosity, which varies with the chemical species of the vapors and the types of ionic liquids, results in a frequency shift of the corresponding quartz crystal. The QCM sensor demonstrated a rapid response (average response time of less than 2 s) to organic vapors with an excellent reversibility because of the fast diffusion of analytes in ionic liquids. Furthermore, the ionic liquids, with zero vapor pressure and stable chemical properties, ensure a long-term shelf life for the sensor.

Since Sauerbrey¹ published the pioneering article on experimental verification of the mass-frequency shift relation for quartz crystal resonators, the quartz crystal microbalance (QCM) has been widely used to measure mass loadings in the nanogram region.^{2–5} Chemical sensing with QCM devices depends on two key elements.⁶ The first is a probe device to generate and detect minimal frequency shifts. The second is a chemically sensitive coating that absorbs the chemical species and produces a change in the oscillating frequency that is detectable by the probe device. So far, a variety of materials have been employed as coatings on the surfaces of QCM devices in an effort to modify the sensitivity and selectivity for chemical analytes. These materials have included ceramics, organic polymers, organic dendrimers, self-assembled monolayers, and organic oils and waxes. Several reviews of these types of films have appeared in the literature.^{3,4}

Here, we report the use of room-temperature ionic liquids as sensing materials for a QCM device.

Ionic systems consisting of salts that are liquid at ambient temperatures can act as solvents for a broad spectrum of chemical species.^{7–13} These ionic liquids are attracting increased attention worldwide because they promise significant environmental benefits.¹¹ Unlike the conventional solvents currently in use, they are nonvolatile and therefore do not emit noxious vapors, which can contribute to air pollution and health problems for process workers. The very unusual intrinsic property of these melts is that they consist *only of ions* and that they can be made *hydrophobic*.^{14,15} The use of such ionic liquids to carry out separations of mixtures of organic molecules and inorganic ions was recently reported.^{16–19} Their strong affinities for selected chemical species prompted us to consider the fabrication of vapor-sensing devices based on ionic liquids. As with polymeric films, the vapor pressures of these liquids are essentially undetectable. Accordingly, no loss of the ionic liquids can be induced by vaporization. The salts are usually liquids from ~ -100 °C and are thermally stable to ~ 200 °C, depending on the specific structures of the anions and cations. In contrast to solid polymeric

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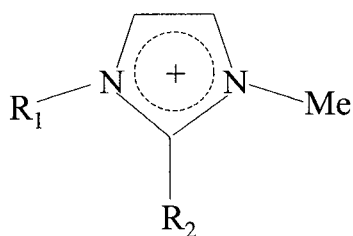
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Chart 1



films, they are liquids at ambient temperature, thus implying that fast diffusion can be achieved. To our knowledge, no QCM devices based on ionic liquids were reported previously.

EXPERIMENTAL SECTION

Materials. Toluene, methanol, ethanol, 2-propanol, 1-butanol, acetone, acetonitrile, chloroform, tetrahydrofuran, and ethyl acetate were obtained from Aldrich. All chemicals were used as received. The cations of the room-temperature ionic liquids used in this work were 1- R_1 -2- R_2 -3-methylimidazolium ($R_1R_2\text{MeIm}^+\text{TF}_2\text{N}^-$), where R_1 = ethyl, propyl, or butyl and R_2 = H or methyl (see structure in Chart 1). The conjugate anions are bis[(trifluoromethyl)sulfonyl]amide (TF_2N^-) and tetrafluoroborate (BF_4^-), respectively. These ionic liquids were synthesized as described in the literature.^{14,15,19} The water contents in as-synthesized ionic liquids vary with the type of the ionic liquids. The water impurity can be further removed from the ionic liquids through rotary evaporation under vacuum. A dry-air supply was generated by passing an in-house air supply through a gas purifier unit made by Domnick Hunter Ltd. for spectroscopy applications. This operation removed not only the water vapor impurity but also the carbon dioxide. Our QCM-based sensors using ionic liquids were used in ambient conditions. Hence, the ionic liquids were equilibrated with the dry air for 24 h. This protocol ensures the equilibrium partition of any residue impurities between the dry air and ionic liquids. The response of QCM coated with such ionic liquids can only be attributed to the uptake of organic vapors. The exact contents of water in these ionic liquids can be measured by Karl Fischer titration. For example, the water content for PrMeImBF_4 is 54 ppm while the corresponding content for $\text{PrMeIm}(\text{TF}_2\text{N})$ is 10 ppm. This is consistent with the difference of hydrophobicity between two melts. The Karl Fischer titrator used in these experiments is 652 KF-Coulometer (Brinkmann). The QCM devices coated by the ionic liquids described here are insensitive to the water impurity. A negligible effect of the water impurity in the samples on the frequency responses was observed.

Preparation of Ionic Liquid Films. A 6-MHz AT-cut quartz crystal (12.5-mm diameter) with gold electrodes (6-mm diameter) on each side was used as the QCM resonator. A spin coater (Chemat Technology, Inc.) was used to coat the ionic liquids on the surfaces of QCM devices. Briefly, a 6-MHz quartz crystal wafer was loaded on to the spin coater. Two drops of the ionic liquid were applied to the center of the gold electrode and then spread over the surface of the electrode by rotating the sensor at a speed of 2000 rpm for 2 min. Only excess ionic liquid located on the edge of the quartz wafer was wiped off by using an acetonitrile-soaked cotton swab. The acetonitrile impurity introduced in this process can be easily removed by vacuum or purging with the

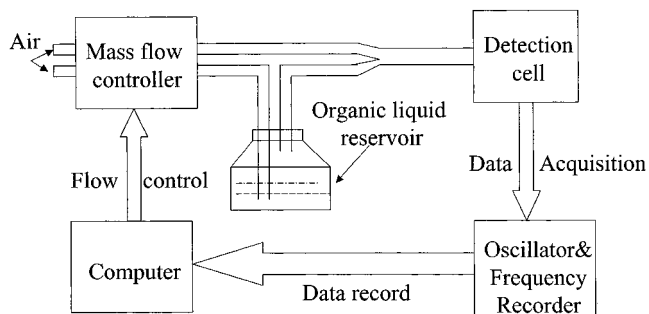


Figure 1. Experimental setup.

dry air. Rinsing with acetonitrile is also an easy means for recycling the used quartz crystal. This situation is very different from that for ceramic or polymeric films, where the recycle of quartz crystals is always difficult.

QCM Measurement. A schematic diagram of the detection system employed in this work is illustrated in Figure 1. The system was operated at a constant temperature of 25 °C. A saturated organic vapor stream was obtained by passing dry air through an organic liquid reservoir at a specific flow rate. Various concentrations of an organic vapor can be achieved by diluting the resulting saturated vapor with another stream of the dry air. Precise control of the mixing ratio of the dry air to the saturated organic vapor stream was maintained by using MKS mass flow controllers (MKS Instruments, Inc., Methuen, MA). An ICM laboratory oscillator (model 035360) was employed to supply the QCM circuit.²⁰ A Hewlett-Packard (HP) 53131A universal frequency counter was used for data acquisition. Both the MKS mass flow controllers and the HP frequency counter were connected to a personal computer, which was used to control the mass flow and to record experimental data simultaneously. The detection cell was purged with a steady flow of the dry air for 10 min after all of the modified QCM sensors were mounted. The initial frequency response was recorded at the end of the purge. An organic vapor stream with a specific flow rate was then introduced into the detection cell. Meanwhile, the frequency counter recorded the temporal resonance frequency of the QCM sensor. A rapid initial frequency increase followed by a plateau was observed after the organic vapor flowed through the detection cell. A steady response signal was typically observed within 2 s. The frequencies quickly reversed to the initial value when the organic vapor flow was replaced with the dry air. The frequency responses to the vapor streams with various concentrations of the organic vapor were measured by maintaining the total flow rate of 1 mL/s with different mixing ratios of the dry air to the saturated stream.²¹ By alternating organic species in the organic liquid reservoir, different organic vapors were thus sensed by the QCM detection system.

RESULTS AND DISCUSSION

A typical QCM sensor response curve toward repeated exposure to acetone vapor is shown in Figure 2. In general, the QCM sensor modified by the ionic liquids showed sharp responses to organic vapors. The solubility equilibrium of organic vapors in

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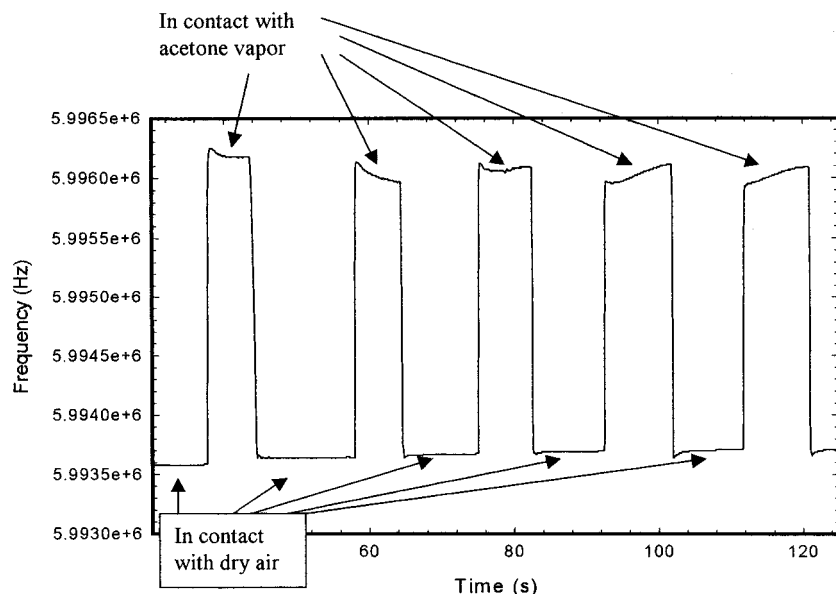


Figure 2. Response of QCM device to alternate flushing by saturated acetone vapor and air.

Table 1. Responses of QCM Sensors Coated with Ionic Liquids to Selected Organic Vapors (Ionic Liquids Listed Here Contain the Tf_2N^- Anion)

	ionic liquid, Δf_{mod}^a					
	EtMeImTf ₂ N (ethyl-)	PrMeImTf ₂ N (propyl-)	BuMeImTf ₂ N (butyl-)	HepMeImTf ₂ N (heptyl-)	UnMeImTf ₂ N (undecyl-)	PrMe2ImTf ₂ N
	-5740	-5701	-6345	-5392	-6171	-6215
toluene	2324	1680	3525	2065	3228	1532
methanol	1377	588	2341	112	567	429
ethanol	977	670	1565	53	459	250
2-propanol	1804	1422	3338	637	3839	553
1-butanol	1511	796	3991	1525	5378	653
acetone	2650	3372	4320	3212	3501	3461
acetonitrile	2886	2899	4939	2041	2925	3009
dichloromethane	1316	1124	1195	987	1121	1073
chloroform	1557	1021	1291	541	1342	1291
ethyl acetate	3654	3654	4289	4151	2781	4471
tetrahydrofuran	4150	4155	5054	4358	5164	4450

^a Δf_{mod} : frequency shift induced by coating ionic liquids on quartz crystals.

ionic liquids can be reached in a few seconds. The instability of the frequency shift in Figure 2 was caused primarily by the turbulence of sample introduction and poor sample mixing. Nine different ionic liquids were investigated in this work, with each ionic liquid membrane showing a distinct response for a particular vapor. Tables 1 and 2 list the responses of the QCM devices made from the nine ionic liquids toward selected saturated organic vapors at 25 °C. Because the actual concentration of a saturated organic vapor stream depends on the vapor pressure, these responses are not directly correlated to the sensitivities of the ionic liquids toward the organic vapors. The vapor pressure varies greatly from one organic solvent to another. As seen in Tables 1 and 2, the resonance frequencies of our QCM device modified by the ionic liquids increased sharply when in contact with organic vapors. This response is opposite to that of conventional QCM devices based on detection of mass loadings, where the sorption of organic vapors to a solid polymeric or metallic film decreases the frequency of the quartz crystal. Accordingly, we cannot rationalize our results based on the equation originally derived by Sauerbrey.¹

Table 2. Responses of QCM Sensors Coated with Ionic Liquids to Selected Organic Vapors (Ionic Liquids Listed Here Contain the BF_4^- Anion)

	ionic liquid, Δf_{mod}		
	EtMeImBF ₄ (ethyl-)	PrMeImBF ₄ (propyl-)	BuMeImBF ₄ (butyl-)
	-5504	-5559	-5697
toluene	578	765	1627
methanol	2598	431	1241
ethanol	818	447	769
2-propanol	1453	1406	1905
1-butanol	819	854	1645
acetone	2469	3319	4090
acetonitrile	2341	3996	4672
dichloromethane	435	918	1933
chloroform	747	1243	2372
ethyl acetate	1730	2988	4702
tetrahydrofuran	2381	3500	4777

Frequency shifts of QCM devices result from a comprehensive change in the physicochemical properties of a surrounding

medium. In addition to the change of film density on the QCM electrode, the variation of viscosity of a surrounding medium can also give rise to a frequency shift of the resonator. Kanazawa and Gordon²² derived the following equations, which express the frequency shift (Δf) of the quartz crystal in contact with a fluid and the decay length (δ) of the shear wave:

$$\Delta f = -f_0^{3/2}(\eta_L \rho_L / \pi \mu_Q \rho_Q)^{1/2} \quad (1)$$

$$\delta = (\eta_L / \pi f_0 \rho_L)^{1/2} \quad (2)$$

where f_0 is the oscillation frequency of the free (dry) crystal, η_L and ρ_L are the absolute viscosity and density of the liquid, respectively, and μ_Q and ρ_Q are the elastic modulus and the density of the quartz, respectively. In general, the solubilities of organic vapors in imidazolium-based ionic liquids are known to be high as compared with those of organic polymers. The dissolution of organic vapors in ionic liquids can induce changes in many physical properties of the ionic liquids.^{23–25} The two factors that are relevant to our present discussion are the changes in viscosity and density upon addition of organic cosolvents. Both Hussey's and Seddon's groups have carried out systematic measurements^{23,26} of kinematic viscosity and density as a function of selected cosolvent concentrations for AlCl_3 -EMIC (EMIC = 1-ethyl-3-methylimidazolium chloride) and air-stable alkylmethylimidazolium tetrafluoroborate melts, respectively. Their studies have shown that both the viscosity and the density of the AlCl_3 -EMIC and the air-stable ionic liquids greatly decrease with the addition of low-viscosity cosolvents. The reduction of viscosity is more pronounced than that of density. The origin of the strong dependence of viscosity on the cosolvent concentration in ionic liquids is not completely understood. The addition of low-viscosity organic compounds in ionic liquids is believed to decrease ion-pairing or ion aggregation by solvating interacting anions and cations. For example, the addition of 4.4 wt % acetonitrile into a basic AlCl_3 -EMIC ionic liquid results in a decrease in the viscosity from 26.90 to 13.60 $\text{cm}^2 \cdot \text{s}^{-1}$ and a decrease in the density from 1.2713 to 1.2373 $\text{g} \cdot \text{cm}^{-3}$. Assuming that a QCM device is coated with this basic AlCl_3 -EMIC and 4.4 wt % acetonitrile is adsorbed by the ionic liquid on the QCM device, a frequency shift would occur according to eq 1. Insertion of the known values of density and viscosity in eq 1 gives a positive frequency shift of 1640 Hz induced for this hypothetical QCM device using the ionic liquid membrane. If 4.4 wt % acetonitrile were adsorbed on a QCM device coated with a solid film, the corresponding negative frequency shift would be less than 250 Hz based on Sauerbrey's equation. The general physical properties of the stable ionic liquids used in the present application should be very similar to those of AlCl_3 -EMIC, with the exception of specific affinities toward different organic vapors. Therefore, our observed large, positive frequency

shifts can be rationalized by the decrease in viscosity and density upon sorption of organic vapors. The independence of the observed frequency shifts on the weight of an ionic liquid membrane further confirmed that these shifts could be attributed mainly to the viscosity and density changes because these latter values are intrinsic properties. As seen from Tables 1 and 2, the frequency response of the QCM device coated with ionic liquids is exceptionally large for a number of the organic vapors. Accordingly, the QCM vapor sensor using ionic liquids can be made to be quite sensitive to certain chemicals. This QCM frequency response results primarily from the strong dependence of viscosity on the concentration of organic vapors in the ionic liquids on QCM devices.

As seen from Tables 1 and 2, the responses of the ionic liquid-based QCM device toward a specific vapor depend on the types of cations and anions present. For example, the $\text{PrMe}_2\text{ImTf}_2\text{N}$ -based QCM device has a frequency shift of 429 Hz when in contact with saturated methanol, while the frequency shift is 1377 Hz for the $\text{EtMeImTf}_2\text{N}$ -based QCM device. This difference can be attributed to that of the corresponding cations. The hydrophobicity of PrMe_2Im^+ is greater than that of EtMeIm^+ , thereby resulting in a difference in the solubilities of the hydrophilic methanol vapor in the two ionic liquids. This interpretation can be also used to rationalize the responses of these two devices toward acetone. Since acetone is more hydrophobic than methanol, its affinity for PrMe_2Im^+ would be slightly stronger than that for EtMeIm^+ . Accordingly, the frequency shift of the $\text{PrMe}_2\text{ImTf}_2\text{N}$ -based QCM device should be greater than that of the $\text{EtMeImTf}_2\text{N}$ -based QCM device. As seen from Table 1, our experimental results are consistent with this assertion. Further support for the difference in hydrophobicity between the two ionic liquids is from the direct measurement of the QCM devices made of the ionic liquids for response induced by water sorption. The response (425 Hz) of the $\text{EtMeImTf}_2\text{N}$ -based QCM device is much more than that (49 Hz) of the $\text{PrMe}_2\text{ImTf}_2\text{N}$ -based QCM device. The fact that the affinities of ionic liquids toward certain organic vapors can be tailored through the functional modification of cations or anions further highlights the superior properties of ionic liquids for sensor applications. Although it is impossible to detect a specific vapor using a single QCM device, the array of such devices made of different ionic liquids can be used to selectively monitor organic vapors. The response spectrum recorded by the array device can be coupled with chemometric methods, such as the neural network, to identify the content of a specific target vapor.^{3–5} Even though hydrophobicity plays an important role in determining the affinity of a specific ionic liquid toward a chemical vapor, the interactions responsible for the solubility of a specific vapor in an ionic liquid are extremely complex and are affected by many other structural factors, such as stereochemistry and polarity. Accordingly, the results listed in Tables 1 and 2 cannot be fully explained using the simple model of hydrophobicity.

The sensitivity of the QCM sensors coated with the ionic liquids toward a specific organic vapor can be calculated from the slope of the calibration line.²⁷ Figure 3 gives the calibration curve of the frequency shift versus acetone concentration for the $\text{PrMeImTf}_2\text{N}$ -modified sensor. A linear response zone was found in the concentration range from 2.3×10^4 to 3.8×10^5 ppm (Figure

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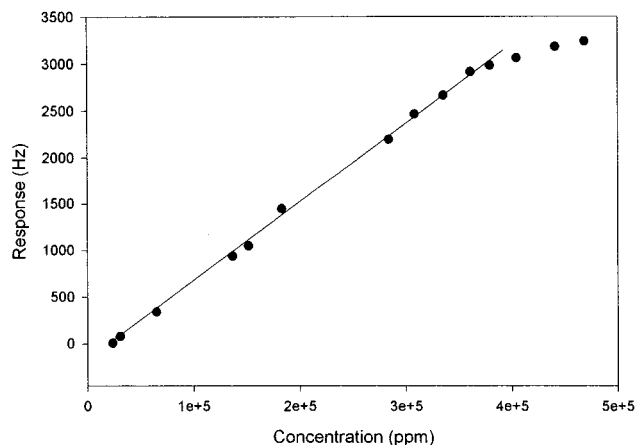


Figure 3. Calibration curve of frequency shift vs acetone for PrMelmTf₂N-modified sensor.

3). The slope of this linear zone is 8.58×10^{-3} Hz/ppm, which could be viewed as the sensitivity of the QCM device in this linear zone. An intercept of -183 Hz was determined by linear regression. This finding indicates that the above linearity of frequency versus concentration could not be extended to low concentrations. This linearity also fails at high concentrations (Figure 3). The background noise of our QCM sensors results primarily from the

nonsteady flow of the vapor stream. A slow flow rate could result in a lower background noise.

In conclusion, we have successfully developed and tested a QCM sensor for selected organic vapors using ionic liquids as sensing materials. The frequency shifts result from the plasticization of the ionic liquids induced by sorption of the organic vapors. The general phenomena²⁸ of plasticization have been previously used in electrochemical detection of solutes in polymers and other molten salt systems.^{29,30} The QCM device has been previously used to measure chemical processes that can result in significant changes of viscosities in the corresponding reaction media.^{31–33} The essentially zero vapor pressure of the ionic liquids eliminates the possibility of loss of these liquids due to vaporization. In addition, our data show that the mass transport rates of analytes in ionic liquids are much faster than those observed for solid inorganic or organic coatings.³ The short response time and excellent reversibility make the QCM devices based on ionic liquids good candidates for the development of new detection systems for gas chromatography and industrial volatile organic vapors.

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