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Small volume lab on a chip measurements incorporating the quartz crystal microbalance to measure the viscosity-density product of room temperature ionic liquids

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Abstract

A microfluidic glass chip system incorporating a quartz crystal microbalance (QCM) to measure the square root of the viscosity-density product of Room Temperature Ionic Liquids (RTIL) is presented. The QCM covers a central recess on a glass chip, with a seal formed by tightly clamping from above outside the sensing region. The change in resonant frequency of the QCM allows for the determination of the square root viscosity-density product of RTILs to a limit of ~10 kg m^{-2} s$^{-0.5}$. This method has reduced the sample size needed for characterisation from 1.5 ml to only 30 μL and allows the measurement to be made in an enclosed system.

I. INTRODUCTION

Room temperature ionic liquids (RTILs) are increasingly finding novel applications to chemical engineering problems for which they can be specifically tailored. RTILs are liquid at ambient temperature and comprise solely of ions. There are over 1×10^6 simple RTILs that need to be characterized to optimise their potential uses. Extending the available data on these pure liquids is difficult due to the expense of the large volumes required for traditional characterization methods. To advance quickly in this area it is necessary to develop a method for characterizing the physical properties of the liquids quickly and efficiently using as small a volume as possible. Possible applications for RTILs include separation techniques,[1] catalysis,[2] organic synthesis,[3] pharmaceutical solvents,[4] fuels cells[5,6] and many more. Some techniques for characterizing the RTILs have already been developed on chip including solution phase synthesis[7] and halide content[8].

It has previously been shown that the Quartz Crystal Microbalance (QCM) can be used to measure properties of RTILs [9,10] which include the square root of the viscosity-density product ($\sqrt{\rho\eta}$) using a small volume method requiring only 40 μL. The viscosity of small volumes is often measured using cantilevers with a volume of only 1 ml.[11] The frequency response of a 5 MHz quartz crystal with single sided liquid contact was characterised by the Kanazawa and Gordan equation (1),[12] which relates the change in frequency to the square root of the viscosity-density product,

$$\frac{\Delta f}{f_o} = -\frac{1}{Z_q}\left(\frac{f_s\eta\rho}{\pi}\right)^{1/2}, \tag{1}$$

where Δf is the change in resonant frequency, f_o is the fundamental frequency, the specific acoustic impedance of quartz: $Z_q = (\mu_q\rho_q)^{1/2} = 8.84 \times 10^6$ kg m^{-2} s^{-1}, $f_s = nf_o$ is the overtone frequency at which the response is measured, ρ and η are the density and viscosity of the liquid respectively.

In this work we extend the previous study to incorporate the QCM on a glass micro-fluidic chip so reducing the required volume, allowing the measurement to be made in a sealed system, reducing the risk of water contamination, and giving the possibility of integrating other measurements onto the same chip.

II. EXPERIMENTAL

A. Microfluidic device setup

The custom designed microfluidic glass chip (3 cm × 3 cm × 1mm) was fabricated by Micronit Microfluidics BV (The Netherlands) using two layers of glass. The chip consists of an open top circular cell of radius 5 mm and depth 300 μm with flow passages to and from the cell formed by wet etching (depth 125μm), the QCM covers the open top circular cell, see Fig. 1. To connect to the flow system, standard Upchurch (WA, USA) microfluidic connectors were used, consisting of polyether ether ketone (PEEK) capillary tubing (inner diameter of 150 μm and outer diameter of 360 μm, stock 1572) with headless nuts and ferrules (outer diameter of 360 μm, stock F-123Hx and N-123–03x). To minimise risk of blockage a 2 μm filter capsule assembly (stock M-542) was used.
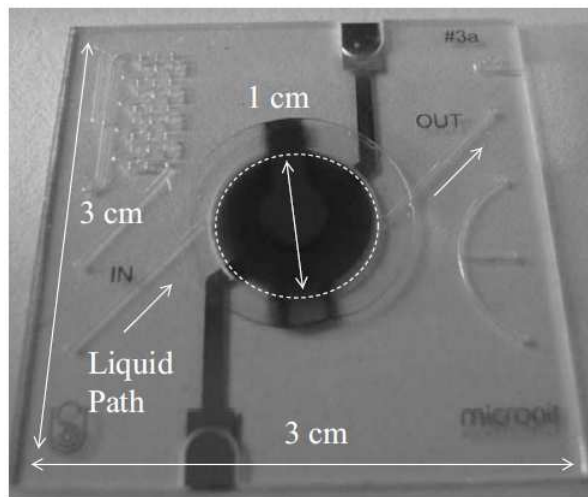

Fig. 1 Image of microfluidic glass chip; the QCM sits over the open top circular cell.

The chip is clamped in a holder with a specially designed top clamping system (Figs. 2 and 3). This allows clamping of the QCM onto the glass chip outside the sensing region; the QCM is connected via spring contact pins.
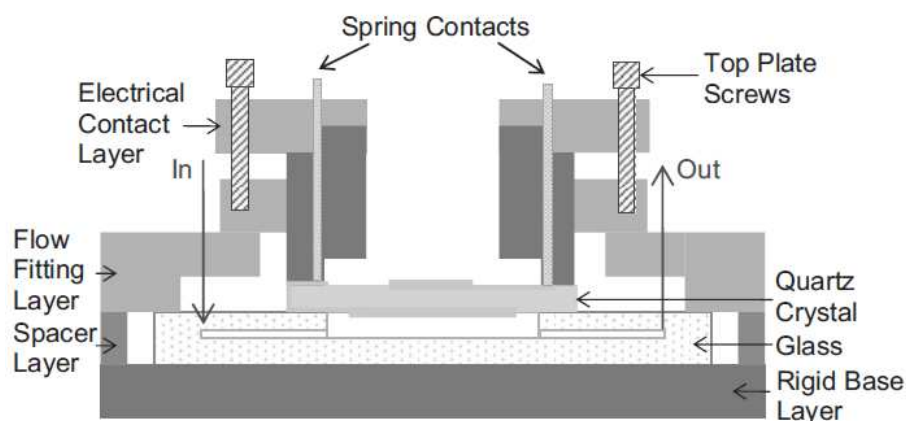

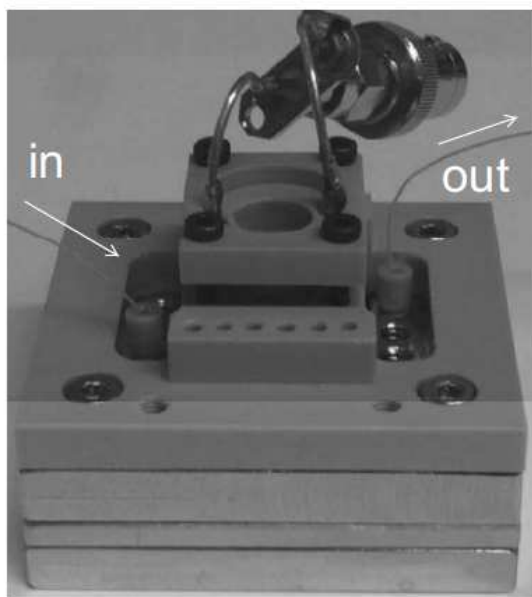**Fig. 2** Chip clamping system, including quartz crystal.

Fig. 3 Image of cell setup, with QCM clamped within the system.

Polished quartz discs (0.538 in. diameter) with a resonant frequency of 8 MHz were purchased from International Crystal Manufacturing (OK, USA). Wrap around electrodes with diameters: Top 8 mm and bottom 4 mm were fabricated with 10 nm titanium and 150 nm gold using an Emitech K575X sputter coater.

Due to the chemical nature of the RTILs it is important to use only chemically resistant materials. It has been found that by tightly clamping the PEEK against the QCM and the glass chip, a good seal is formed negating the need for any further sealing.

To ensure a stable temperature the chip was placed in an Octagon 10 incubator (Brinsea, UK) and all measurements made at 30°C. Liquid flow rate was controlled via a Nemesys syringe pump (Cetoni, Germany) with a gas tight syringe (Hamilton, Switzerland) volume dependent on the viscosity of the liquid. The chip requires a sample volume of only 30 μl and has been compared to measurements made with a Brookfield DVII+ Programmable viscometer (temperature controlled at 30°C via a water bath) and DMA4500 Density/specific gravity/concentration meter, which require a combined volume of 1.5 ml.

The square root viscosity-density product is calculated by measuring frequency changes and applying the Kanazawa & Gordon equation.[12] Measurements of resonant frequency changes of the QCM were obtained by tracking the frequency of the minimum insertion loss using an

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Agilent E5061A network analyser for both the fundamental frequency and the third overtone. Liquid flow was stopped to allow the frequency measurements to be recorded.

Various concentrations of water glycerol solutions (0-85% v/v) were used as calibration liquids to ensure the QCM frequency changes were behaving according to the expected relationship.[12] Measurements of various concentrations of a water miscible RTIL [C_2mim][EtSO$_4$] (0-100% v/v) and a further eight RTILs were studied (Table I). The RTILs were dried under vacuum over night at 65 °C before use to ensure minimal water content. Immediately prior to QCM measurements, the viscosity and density were measured on a standard viscometer and densitometer ensuring that the water content for a given liquid was the same for both techniques; halide content was recorded using suppressed ion chromatography.[16]

Liquid flow rates ranged from 0.04 μl/s for highly viscous samples (>100 cP) to 2 μl/s for cleaning. Six fluid volume changes are used to ensure there is no residue remaining from previous samples. For this purpose, water and methanol are used until the resonant frequency of the crystal returns to its unloaded value. Liquid exchange is made without opening the cell; if the cell is opened, recalibration would be needed to ensure the QCM is operating as expected.

TABLE I. RTIL names and sources.

RTIL	Chemical name	Manufactured	Halide content (ppm)
[C_2mim][EtSO$_4$]	1-ethyl-3-methylimidazolium ethylsulfate	In house using standard literature methods[a]	Halide free
[C_2mim][NTf$_2$]	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide		<5
[C_4mim][NTf$_2$]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide		<5
[C_6mim][NTf$_2$]	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide		<5
[C_8mim][NTf$_2$]	1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide		<5
[C_{10}mim][NTf$_2$]	1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide		<5
[C_4dmim][NTf$_2$]	1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide		<5
[C_4mpyrr][NTf$_2$]	1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide		<5
[C_4mpyrr][DCA]	1-butyl-1-methylpyrrolidinium dicyanamide	Merck (98%)	1790

[a]References 13-15.

B. Seal Leakage Rate

The leakage rate of liquid out through the seal may be estimated using the model of radial flow in a gap of uniform height, as illustrated in Fig. 4. Determination of the velocity and pressure distribution (p) in the gap is relatively straightforward since the gap height is small in relation to radial position and the flow is necessarily in the Stokes flow regime. For these conditions one finds with approximation of order h/r the equation for radial pressure gradient in terms of leakage volume flow rate Q_L, gap height h, liquid viscosity μ, and radius r,

$$\frac{dp}{dr} = -\frac{6\mu Q_L}{\pi h^3 r}. \tag{2}$$

Integration from r_1 to r_2 then yields a relation between pressure differential and leakage flow rate,

$$Q_L = \frac{\pi h^3 (p_1 - p_2)}{6\mu \ln(r_2/r_1)}. \tag{3}$$

In practice, the gap is not uniform and varies according to the surface undulations in the glass and quartz surfaces. For the optical-quality surfaces involved in the experimental seal, the surface undulations are expected to be around 0.1 µm. Using this value for the height and a pressure difference of 1 bar, Eq. (3) gives a leakage flow rate of 1.5 pl/s in the case of a liquid with 0.1 Pas viscosity. For continuous operation for 1 day, it can be worked out that if the leaked liquid formed a quarter-circular fillet around the perimeter of the cover disk, the fillet radius would be about 100 µm. In fact very little liquid could be detected over similar periods of operation, which suggests that in fact the gap geometry corresponded to a yet smaller effective gap size than the 0.1 µm assumed above.
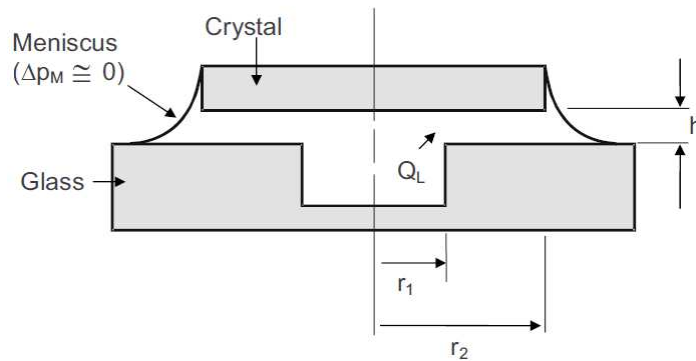

Fig. 4 Model geometry used to characterise the seal leakage rate.

III. RESULTS AND DISCUSSION

The QCM response for various concentrations of $[C_2mim][EtSO_4]$ are shown in Fig. 5. This figure shows the frequency and insertion loss changes as a function of time operating at the third harmonic frequency. The changes in resonant frequency and insertion loss are very repeatable, with the figure showing the same liquid tested on the chip three times. On each occasion the frequency response returns to its original frequency. This consistency demonstrates that the sample volume of liquid is sufficient to provide reliable results.
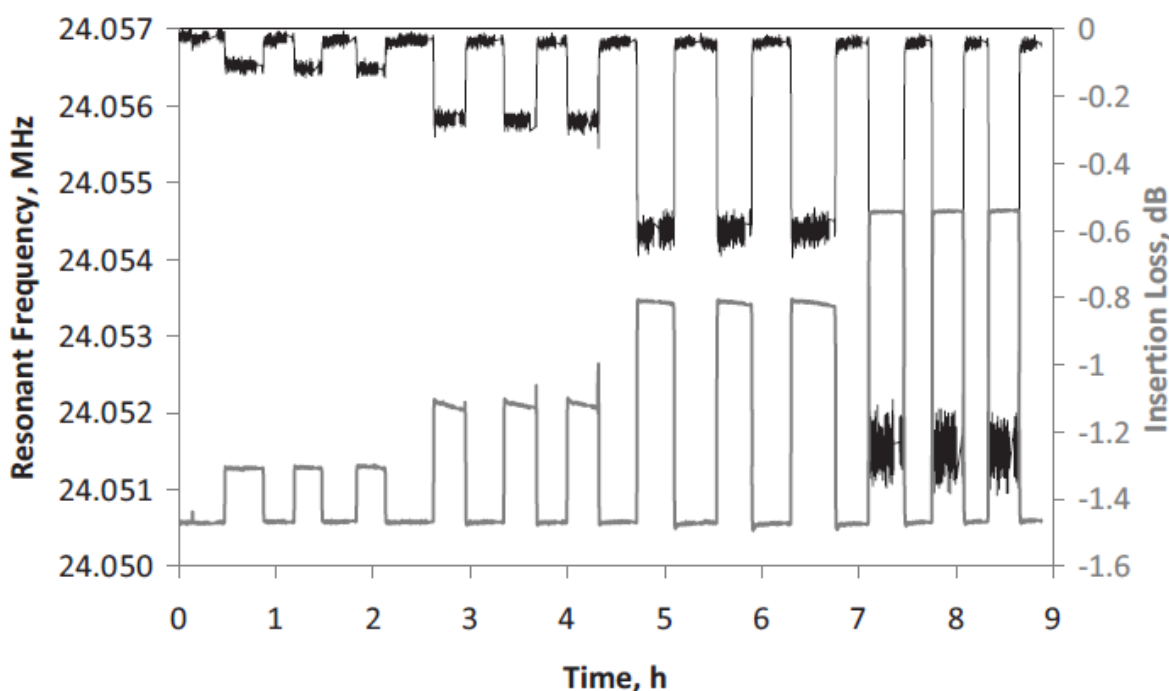

Fig. 5 A frequency and insertion loss time plot showing repeatability for the third overtone resonant frequency, sensing dilutions of $[C_2mim][EtSO_4]$.

Figures 6 and 7 show the calculated square root viscosity-density product from the frequency change of the QCM, operating on the fundamental and third harmonic, respectively, and compare them against the value obtained from the traditional measurements made on the viscometer and densitometer. The figures show values obtained for various concentrations of water glycerol solutions (0-85% v/v) confirming that the QCM behaves according to the Kanazawa and Gordon relationship. The response at the fundamental frequency (Fig. 6) shows reasonable agreement with some scatter in the water-glycerol solution data particularly at the lower viscosities. This scatter is significantly reduced when sensing on the third harmonic (Fig. 7). Both data sets follow the line of unity well. The RTILs present similar behavior with the scatter in the data for the fundamental significantly reduced when sensing on the third harmonic; the largest scatter is seen for the most viscous liquid measured ($\sqrt{\rho\eta}$ ~11 kg m^{-2} s$^{-1/2}$).
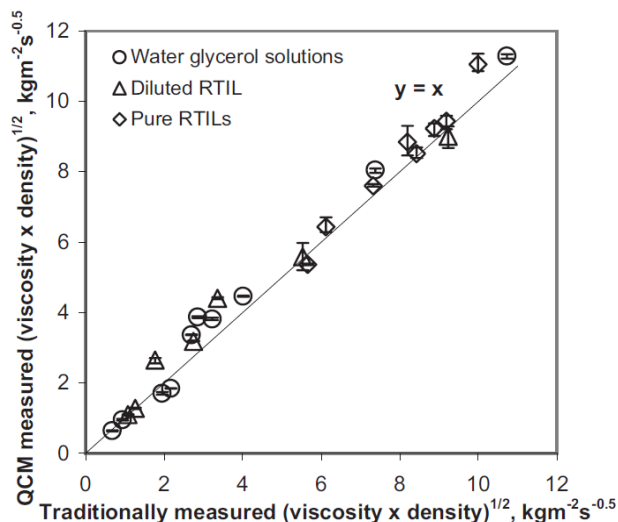
Fig. 6 Fundamental frequency data plot of the $(\text{viscosity} \times \text{density})^{1/2}$ for water glycerol solutions, dilutions of $[C_2mim][EtSO_4]$ and 8 pure RTILs (where traditional measurements refer to the value calculated from the viscometer and densitometer). A unity line is plotted to demonstrate linearity.

Fig. 7 Third overtone frequency data plot of the $(\text{viscosity} \times \text{density})^{1/2}$ for water glycerol solutions, dilutions of $[C_2mim][EtSO_4]$ and 8 pure RTILs (where traditional measurements refer to the value calculated from the viscometer and densitometer). A unity line is plotted to demonstrate linearity.
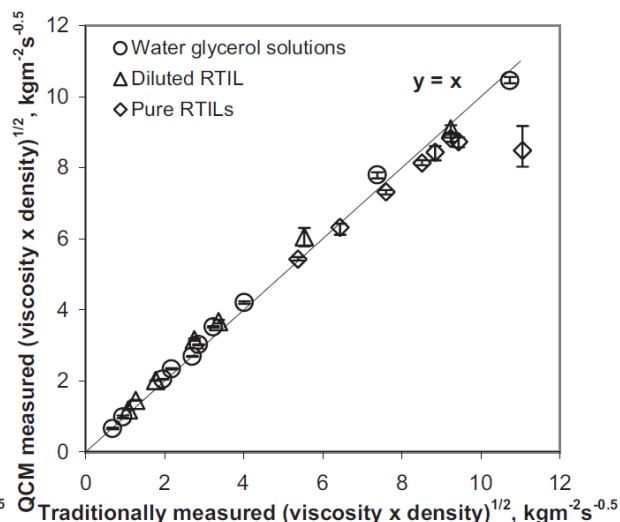
It has previously been reported that the third harmonic provides a more accurate frequency change measurement.[17] This is confirmed in Figs. 6 and 7. We have also seen this behavior experimentally when working with 9 MHz quartz crystals although these data have not been included. At the frequencies used, standing (compressional) waves were not a problem; however at other frequencies, this may become a problem but could be overcome with use of a spoiler.[18] For high viscosity liquids ($\sqrt{\rho\eta} > 10$ kg m^{-2} s$^{-1/2}$), this behavior begins to break down and we believe we have reached the limit of detection for the 8 MHz QCM in the system. The agreement between the traditional viscosity-density measurements and QCM measurements is excellent despite several orders of magnitude difference in shear rates.

IV. CONCLUSION

By using the laboratory on a chip system detailed above, we have measured the viscosity-density product of room temperature ionic liquids using volumes as low as 30 μl, which can be further reduced by optimising the tubing lengths. This compares well with commercially available hardware with typical volumes around 150 μl.[19] The QCM offers an excellent alternative to larger volume techniques and is particularly advantageous when characterizing hygroscopic liquids, whereby the viscosity decreases exponentially with water contamination. Ideally this method would be combined with a simulation study such as those described by *J. Jacquemin et al.*,[20] allowing us to extract viscosity and density as separate components for RTILs.

ACKNOWLEDGMENTS

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