Density and Viscosity Measurements of Room Temperature Ionic Liquids Using Patterned Quartz Crystal Microbalances

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***Abstract*— Ionic liquids are becoming of increasing interest for an extensive range of applications. Small scale characterization processes are being continually researched to find cheap and efficient methods for processing ever smaller sample volumes. This work presents a dual Quartz Crystal Microbalance (QCM) setup with one smooth, and one patterned surface using chemically compatible materials allowing separate viscosity and density measurements of room temperature ionic liquids. Measurements were corroborated with standard measurement techniques and show good agreement, demonstrating the merit of the dual QCM setup in determining the physical properties of these exciting new solvents.**

I. INTRODUCTION

In a previous report[1] we demonstrated that the viscosity-density product of small quantities of ionic liquids could be obtained using a QCM up to a limit of 18 kg m^{-2} $s^{-1/2}$ by applying the Kanazawa & Gordan equation. To separate these parameters, the method described by Martin *et al.*[2] is used whereby measurements of frequency changes using a dual QCM setup allows separate determination of viscosity and density.

II. THEORY

A surface is considered smooth if the trapped liquid thickness is small compared to the liquid decay length[3] ensuring the liquid trapping response is negligible. The vertically patterned surface constrains a quantity of liquid within its structure in excess of the liquid which would be entrained by a smooth surface. This trapping effect restricts the liquid, allowing it to move only with the oscillating crystal surface. This results in the trapped liquid behaving as an ideal mass layer. For separate viscosity and density measurements, the height of the traps must be larger than the penetration depth (1) to cause an additional frequency change dependent only on the density. A dual device set-up containing one smooth and one textured QCM (Fig.1) allows viscosity and density to be resolved by comparison of these resonant frequency changes (2,3).

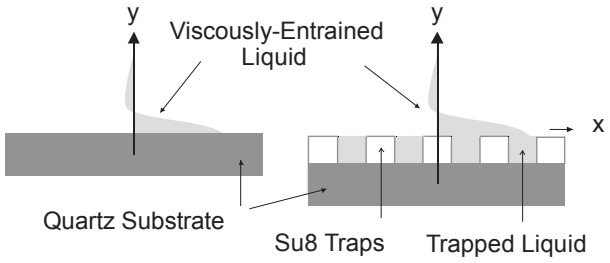

Figure 1 Diagram of (left) a smooth and (right) a patterned quartz crystal microbalance

$$\delta = (2\eta / \omega\rho)^{1/2} \tag{1}$$

$$\rho = \frac{N(\mu_q \rho_q)^{1/2}}{2 f_s^{\,2} h} \left| \Delta f_t - \Delta f_s \right| \tag{2}$$

$$\eta = \frac{2\pi h N(\mu_q \rho_q)^{1/2} (\Delta f_s)^2}{f_s \left| \Delta f_t - \Delta f_s \right|} \tag{3}$$

Where ρ is the density of liquid to be measured, η the viscosity of the liquid to be measured, *N the crystal* overtone number, h the effective height of traps, f_s the smooth crystal frequency, f_t trap bearing crystal frequency, Δf_t the change in trap bearing crystal frequency, Δf_s the change in the smooth crystal

frequency, ρ_q is the density of quartz (ρ_q = 2650kg/m^3) μ_q is the shear stiffness of quartz (μ_q = 2.95 x 10^{10}N/m^2).

III. Experimental

A. Photolithography

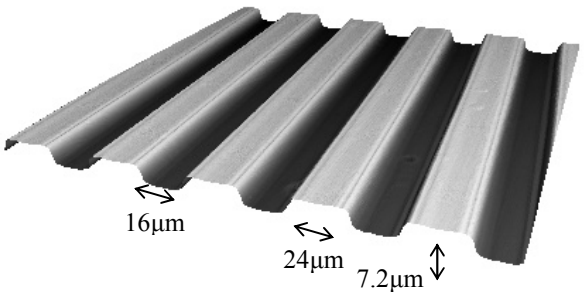

Figure 2 Optical profilometer image of textured surface

Crystals were first cleaned via sonication in a bath of Decon90 (Decon Laboratories LTD, Hove, UK) and deionised water heated to 80^{o}C for 20min. This removes any dust particles from the surface of the crystals. The reflective surface of the gold electrode causes problems with thick photoresists, leading to uneven exposure. To overcome this, an anti-reflective coating XHRIC-16 (Brewer Science, MO, USA) was applied by spinning at 3000RPM, and heating to 230^{o}C for 2 minutes before cooling slowly. This successfully prevents any unwanted reflections.

SU8-10 was applied to the surface of the QCM using a standard protocol. The traps are direction specific, and need to be placed perpendicular to the X direction of the crystal. Trap dimensions were checked for uniformity under a microscope, and measured using a Xyris 4000 WL (TaiCaan Technologies, Southampton, UK) optical profilometer (Fig. 2).

Due to the chemical reactivity of the ionic liquids there are limited materials which are compatible. To test the chemical resistance of the traps 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([C_6mim][NTf_2]) was left on the trap surface for 48 hours. Comparison of profiles before and after show no damage and the traps were then coated with titanium and gold.

B. Methodology

The dual QCM arrangement consists of two standard 1" polished quartz crystals operating at fundamental frequency of 5MHz. One crystal is left blank as a reference crystal, the other patterned with a resist over the electrode surface creating liquid traps (fig. 1).

A Quartz Crystal Microbalance holder made from PTFE was used to clamp the crystals. An Agilent E5062 network analyser was used to record the resonant frequency changes. Each measurement on each crystal requires only 60µl of liquid, allowing one viscosity and one density measurement to be obtained using only 120µl of ionic liquid.

The viscosity and density measurements have been corroborated using a Brookfield DV-II+ Programmable viscometer requiring 0.5ml and an Anton Paar DMA 4500 Density meter requiring a volume of 1ml giving a total volume requirement of 1.5ml.

Measurements were made with water-glycerol solutions for calibration, and then on a room temperature ionic liquid 1-butyl-3-methylimidazolium trifluoromethylsulfonyl ([C_4mim][OTf]) diluted with water. The room temperature ionic liquid was dried before use ensuring minimal water content. Measurements were recorded with the crystals in a glove box under argon.

IV. Results

A. Water-glycerol

Fig. 3 and 4, show separately determined viscosity and density for water-glycerol solutions. These act as a calibration for future measurements. Results from the dual QCM setup are compared to traditional methods. Each point shows an individual measurement repeated three times.

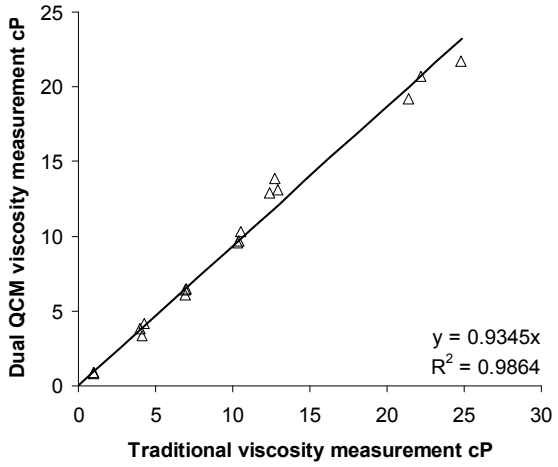

Figure 3 Water-glycerol calibration plots for viscosity measurements

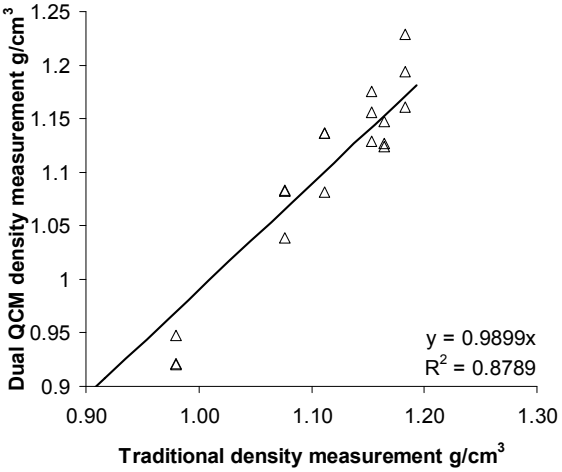

Figure 4 Water-glycerol calibration plots for density measurements

B. Room Temperatue Ionic Liquid

Fig. 5 and 6, show measurements made with diluted [C_4mim][OTf]. Results from the dual QCM setup are compared to traditional methods and show good agreement.

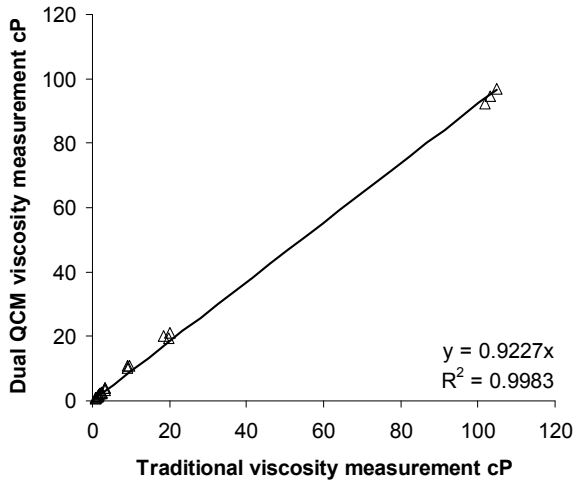

Figure 5 Varying the viscosity & density of [C_4mim][OTf] by dilutions with water: viscosity measurements

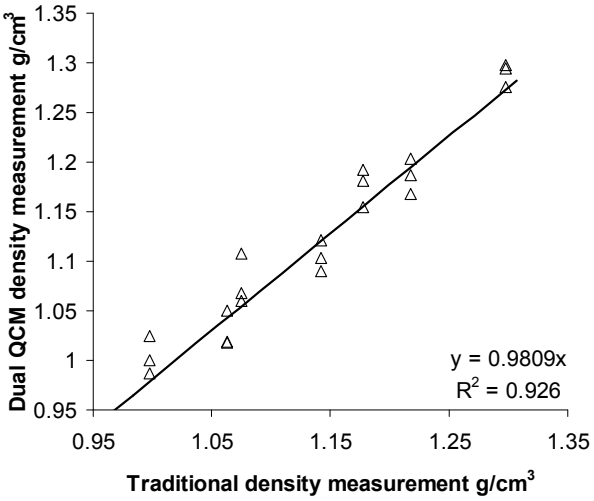

Figure 6 Varying the viscosity & density of [C_4mim][OTf] by dilutions with water: density measurements

V. CONCLUSION

We have presented an experimental technique demonstrating separate viscosity and density measurements of Room Temperature Ionic Liquids. These have been resolved from frequency measurements made on a dual QCM set-up. The agreement between these two measurement methods demonstrates the merit of the dual QCM setup in determining the physical properties of these exciting new solvents with an order of magnitude reduction in required sample volume.

REFERENCES

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