Characterising Ionic Liquids using the Quartz Crystal Microbalance

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Introduction

- Quartz Crystal Microbalance (QCM) to obtain Viscosity-density product
- Room Temperature Ionic Liquids
- Experimental Set-up
- Results
  - Fundamental vs. Harmonics
  - Two diluted ionic liquids
  - 19 Pure ionic liquids of varying viscosities
- Conclusions
Quartz Crystal Microbalance QCM

Thicknes Shear Mode Vibration

Piezoelectric crystal

Frequency given by quartz thickness

Sharp resonance

Frequency reduces and resonance broadens due to mass in interfacial layer.

\[ \delta = \frac{2\eta_{\text{liq}}}{\rho_{\text{liq}} \omega} \text{ where } \omega = 2\pi f \]

Kanazawa & Gordon\(^1\) \(\Rightarrow \Delta f \propto -\sqrt{(n \eta \rho)} f^{3/2} \)

*Frequency is sensitive to the viscosity density product for Newtonian liquids*

\[\text{[1]}\text{ KANAZAWA, K. K. & GORDON, J. G. (1985) FREQUENCY OF A QUARTZ MICROBALANCE IN CONTACT WITH LIQUID. Analytical Chemistry, 57, 1770-1771.}\]
Room Temperature Ionic Liquids

Liquids comprised solely of ions which are liquid at room temperature

Useful properties:-

• Low volatility
• Non flammable
• Good liquid range
Experimental Set-up

- 5MHz Polished Crystal in a PTFE QCM holder

- Measurements made on 1\textsuperscript{st}, 3\textsuperscript{rd}, 5\textsuperscript{th}, 7\textsuperscript{th}, 9\textsuperscript{th} & 11\textsuperscript{th} harmonic

- 40µl liquid under argon

- Brookfield (MA, USA) DV-II+ Programmable viscometer (1.5ml), and a DMA 4500 Density meter (0.5ml). Karl-Fischer titration for water content measurements
Results: Harmonic data

Kanazawa & Gordon Equation:

\[
\frac{\Delta f}{f_o} = -\left(\frac{n f_o \rho \eta_1}{\pi \rho_q \eta_q}\right)^{1/2} \quad \frac{\Delta f}{\sqrt{n}} = -c f_o^{3/2} \sqrt{\rho \eta}
\]

\[c = 2.46 \times 10^{14} \text{ kg}^2/\text{m}^4/\text{s}^2\]

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![Graph showing frequency change vs. (density x viscosity)^{1/2} kgm^{-2}s^{-1/2}](image)

- fundamental
- 3rd harmonic
- 5th harmonic
- 7th harmonic
- 9th harmonic
- 11th harmonic
Harmonic data agreement

Water miscible – diluted with water

\[ [\text{C}_4\text{mim}][\text{OTf}] \]

Better agreement with 3\textsuperscript{rd} harmonic
Results – Varying concentration of ILs

3rd Harmonic data

Water miscible IL $[\text{C}_4\text{mim}][\text{OTf}]$  
Water immiscible IL $[\text{C}_4\text{mim}][\text{NTf}_2]$
Pure Ionic Liquids

**Water Miscible**

- [C$_2$mim][EtSO$_4$]
- [C$_4$mim][OTf]
- [C$_2$mim][SCN]
- [C$_4$mim][MeSO$_4$]
- [C$_4$mim][DCA]
- [C$_4$mim][AcO]
- [C$_4$mpyrr][DCA]
- [C$_4$mim][TFA]
- [C$_6$mim][Cl]
- [C$_4$mpyrr][TFA]

**Water Immiscible**

- [C$_n$mim][NTf$_2$](n=2,4,6,8,10)
- [C$_4$mpyrr][NTf$_2$]
- [C$_4$mpyrr][FAP]
- [P$_{6,6,6,14}$][NTf$_2$]
- [C$_4$mim][OctSO$_4$]

$\sqrt{\eta \rho}$ ranges from 5 $\rightarrow$ 80 kgm$^{-2}$s$^{-1/2}$
Clear limit just below $20 \text{ kg m}^{-2} \text{ s}^{-1/2}$

Shows Newtonian behaviour
Conclusions

• QCM can be used to measure the $\sqrt{\eta \rho}$ of small volumes of RTILs
• Improved agreement on 3rd Harmonic
• A practical limit of just below 20 kg m$^{-2}$ s$^{-1/2}$
  – when using the Kanazawa & Gordon equation to measure 19 pure ionic liquids.
• Possible use for lab-on a chip: characterising ionic liquids

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