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Characterising Ionic Liquids using the Quartz Crystal Microbalance

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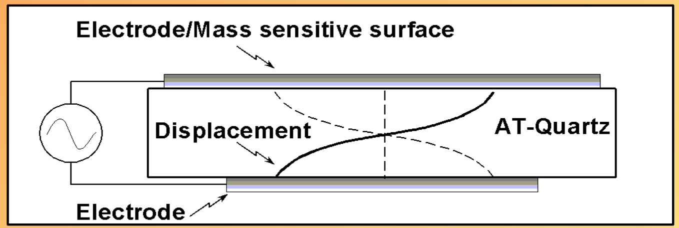
Introduction

- 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

Stored Room temperature Ionic Liquids

Quartz Crystal Microbalance QCM



Thickness Shear Mode Vibration

Piezoelectric crystal

Frequency given by quartz thickness

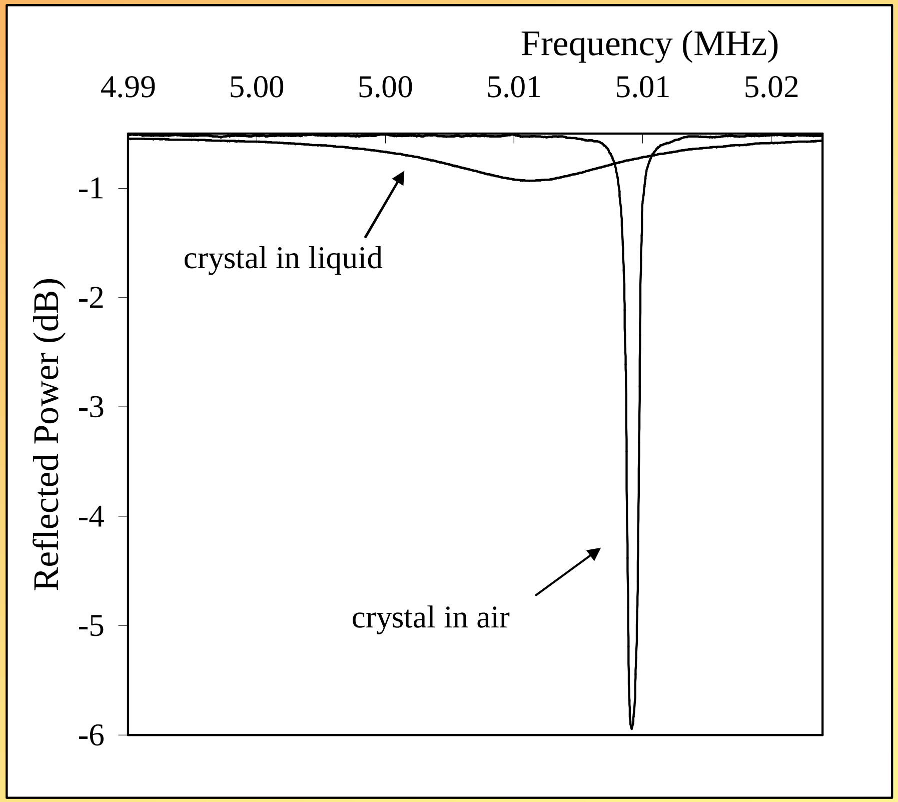
Sharp resonance

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

$\delta = 2\eta_{liq}/(\rho_{liq}\omega)$ 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



[1] 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

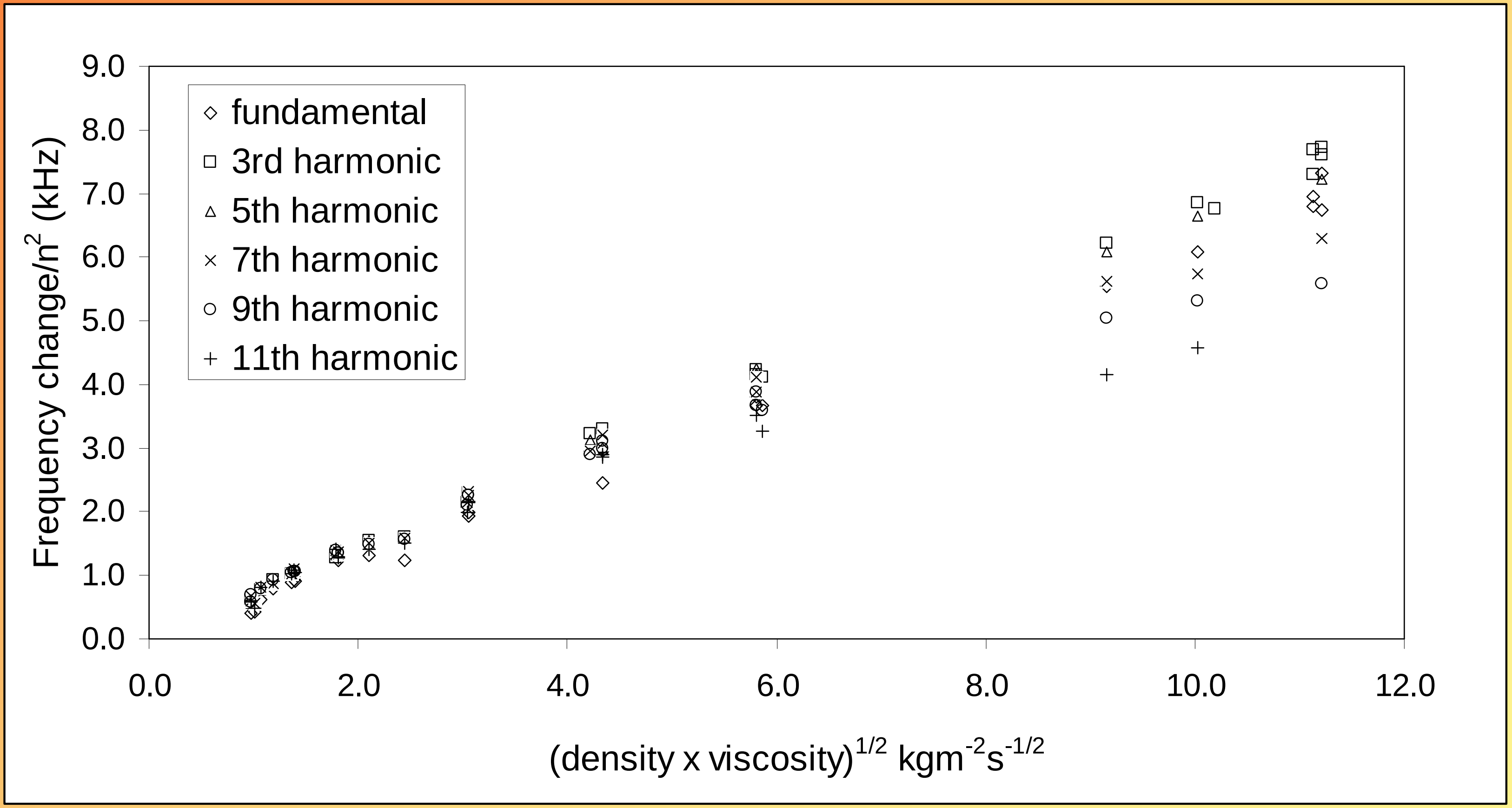
- 5MHz Polished Crystal in a PTFE QCM holder
- Measurements made on 1st, 3rd, 5th, 7th, 9th & 11th harmonic
- 40µl liquid under argon
- Brookfield (MA, USA) DV-II+ Programmable viscometer (1.5ml), and a DMA 4500 Density meter (0.5ml). Karl-Fischer titration for water content measurements

Results: Harmonic data

Kanazawa & Gordon Equation: $[C_4mim][OTf]$

$$\frac{\Delta f}{f_o} = -\left(\frac{n f_o \rho_l \eta_l}{\pi \rho_q \eta_q}\right)^{1/2} \qquad \frac{\Delta f}{\sqrt{n}} = -c f_o^{\,3/2} \sqrt{\rho \eta}$$

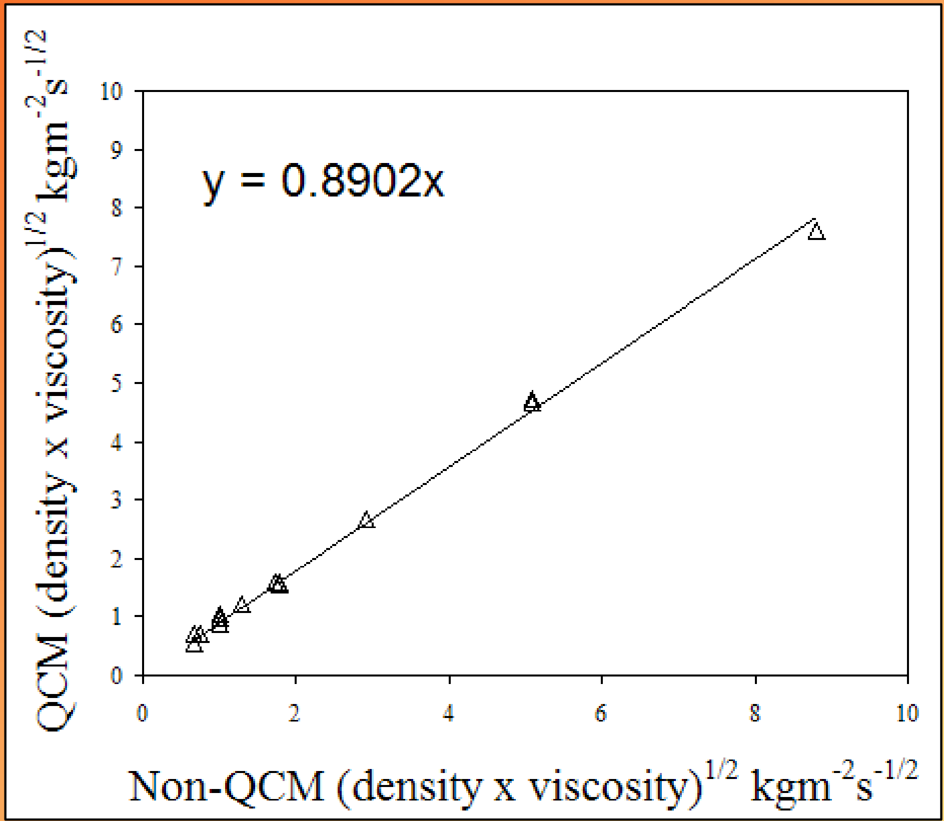
$c = 2.46 \times 10^{14}\ kg^2/m^4/s^2$

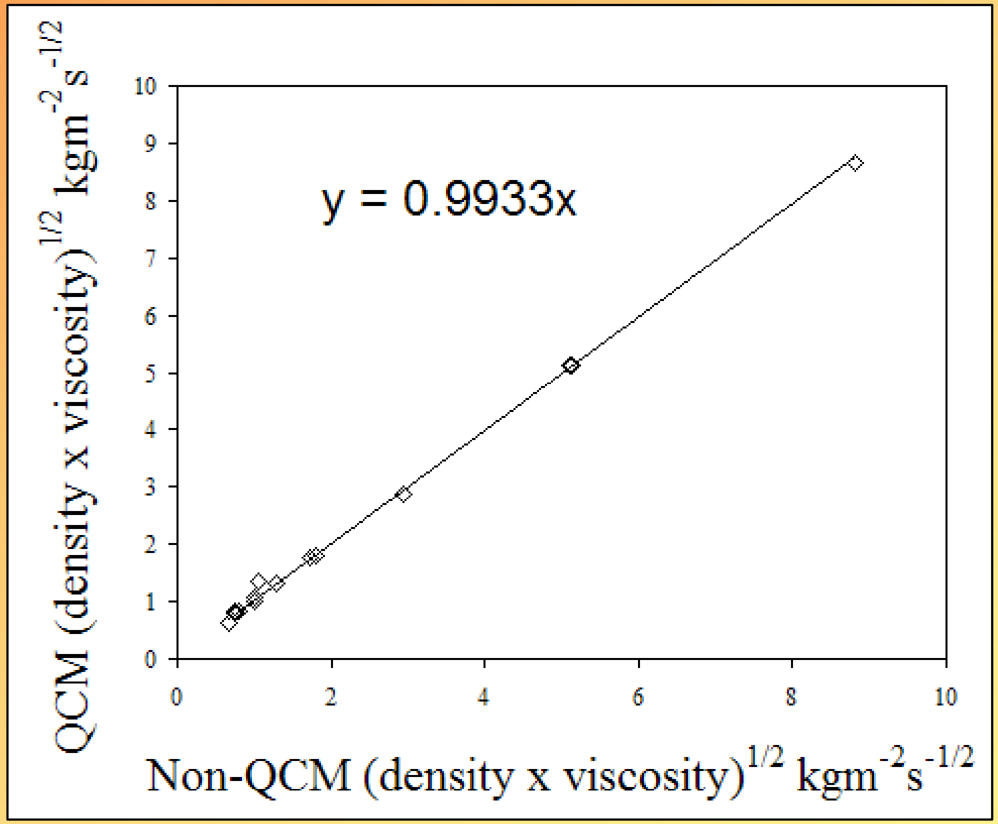


Harmonic data agreement

Water miscible – diluted with water

$[C_4mim][OTf]$





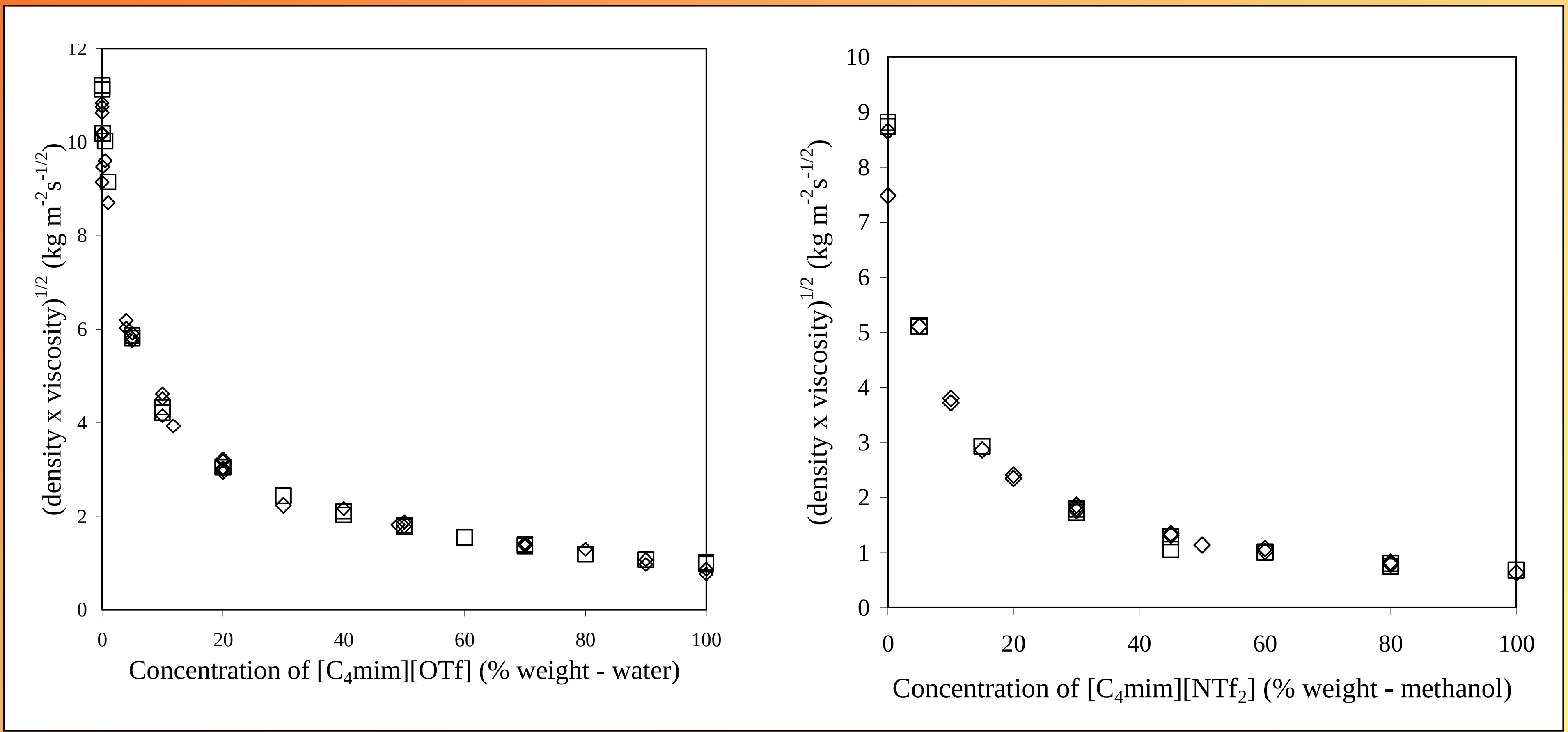
Better agreement with 3rd harmonic

Results – Varying concentration of ILs

3rd Harmonic data

Water miscible IL [C_4mim][OTf]

Water immiscible IL [C_4mim][NTf_2]



◇ QCM data   □ non-QCM data

Pure Ionic Liquids

Water Miscible

$[C_2mim][EtSO_4]$
$[C_4mim][OTf]$
$[C_2mim][SCN]$
$[C_4mim][MeSO_4]$
$[C_4mim][DCA]$
$[C_4mim][AcO]$
$[C_4mpyrr][DCA]$

$[C_4mim][TFA]$
$[C_6mim]Cl$
$[C_4mpyrr][TFA]$

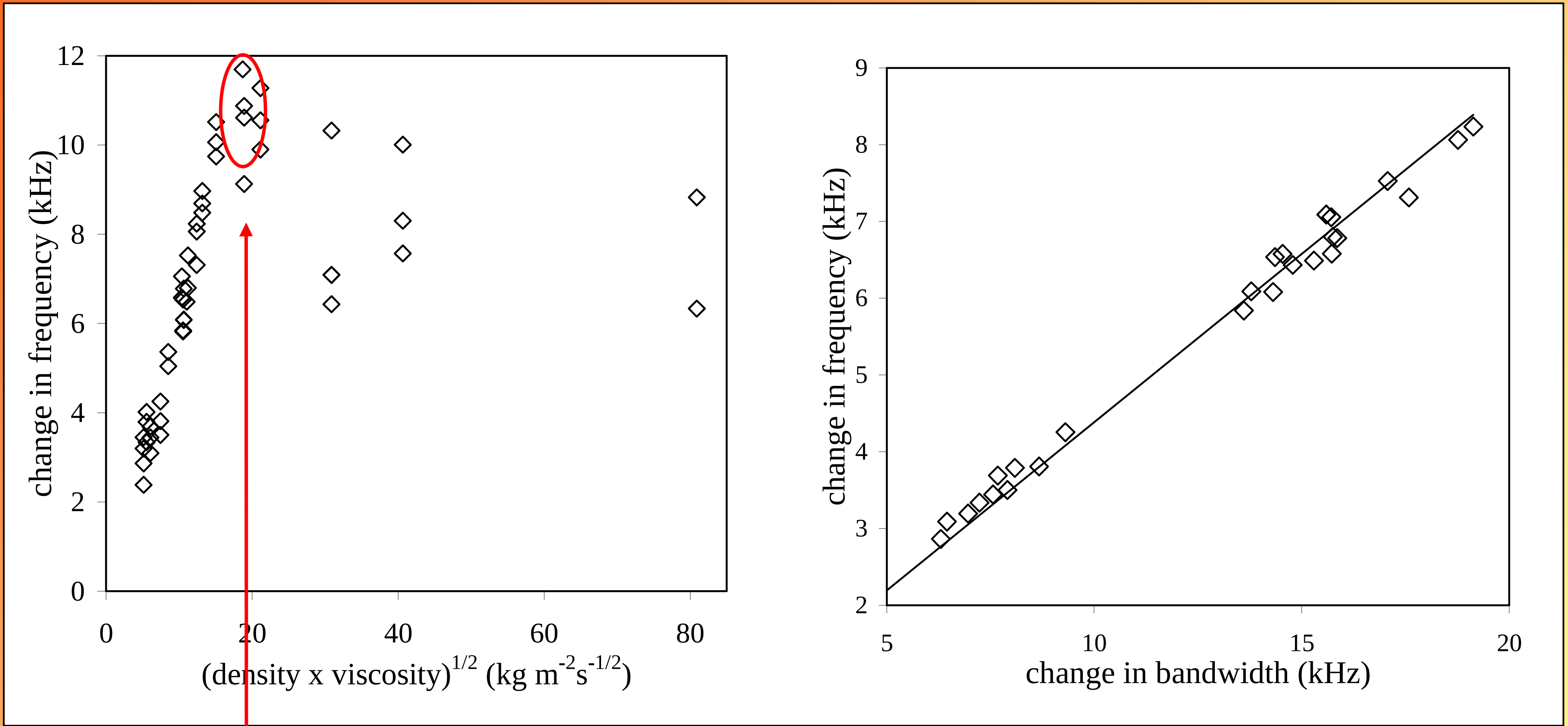
Water Immiscible

$[C_nmim][NTf_2]$(n=2,4,6,8,10)
$[C_4mpyrr][NTf_2]$
$[C_4mpyrr][FAP]$
$[P_{6,6,6,14}][NTf_2]$

$[C_4mim][OctSO_4]$

$\sqrt{(\eta\rho)}$ ranges from
5 → 80 $kgm^{-2}s^{-1/2}$

19 Pure Ionic Liquids



Clear limit just below 20 kg m^{-2} $s^{-1/2}$

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

Acknowledgements

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