Density–Viscosity Product of Small-Volume Ionic Liquid Samples Using Quartz Crystal Impedance Analysis

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Quartz crystal impedance analysis has been developed as a technique to assess whether room-temperature ionic liquids are Newtonian fluids and as a small-volume method for determining the values of their viscosity–density product, \( \eta \). Changes in the impedance spectrum of a 5-MHz fundamental frequency quartz crystal induced by a water-miscible room-temperature ionic liquid, 1-butyl-3-methylimidazolium trifluoromethylsulfonate ([C4mim][OTf]), were measured. From coupled frequency shift and bandwidth changes as the concentration was varied from 0 to 100% ionic liquid, it was determined that this liquid provided a Newtonian response. A second water-immiscible ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonylimide)imidide ([C4mim][NTf2]), with concentration varied using methanol, was tested and also found to provide a Newtonian response. In both cases, the values of the square root of the viscosity–density product deduced from the small-volume quartz crystal technique were consistent with those measured using a viscometer and density meter. The third harmonic of the crystal was found to provide the closest agreement between the two measurement methods; the pure ionic liquids had the largest difference of \( \sim 10\% \). In addition, 18 pure ionic liquids were tested, and for 11 of these, good-quality frequency shift and bandwidth data were obtained; these 11 all had a Newtonian response. The frequency shift of the third harmonic was found to vary linearly with square root of viscosity–density product of the pure ionic liquids up to a value of \( \sqrt{(\eta \rho)} \approx 18 \text{ kg m}^{-2} \text{ s}^{-1/2} \), but with a slope 10% smaller than that predicted by the Kanazawa and Gordon equation. It is envisaged that the quartz crystal technique could be used in a high-throughput microfluidic system for characterizing ionic liquids.

Over the past decade, the drive toward cleaner industrial processes has led to the development of ionic liquids as alternative, environmentally friendly, solvents.1,2 Ionic liquids provide good solvation with a range of compounds, have low volatility, are nonflammable, have a wide liquid range with temperature, and have tunable physical properties and a wide electrochemical window.3,4 They comprise solely ions that are liquid at room temperature and can be considered designer solvents with over 1 million simple ionic liquids alone. Their use with a range of reactions, such as Heck and Suzuki cross-coupling, hydrogenations, oxidations, Friedel–Crafts, Diels–Alder, and polymerization is favored because of the control of selectivity that can be achieved and the ease of recyclability of the catalysts.5–7 Ionic liquids have the potential for a wide range of applications including catalysis,3–7 organic synthesis,8 electrochemistry,9,10 separations and extractions,11,12 liquid crystals,13–15 and analytical solvents and coatings.16 However, the data on their physical properties as a function of chemical composition are limited, and extending the range of known data is difficult due to the expense and difficulty of producing large volumes of pure liquids for characterization.

Acoustic wave microsensors, such as the quartz crystal microbalance (QCM), are widely used for studying the properties of small-volume samples of liquids, the attachment of mass from the liquid phase and in situ determination of the properties of surface coatings, such as electrodeposited polymers, during the deposition process.17,18 A QCM operates by creating a high-frequency, typically 5 MHz, shear mode oscillation of the surface. When operated in a liquid environment, this surface oscillation entrains liquid and creates an oscillation, which for a Newtonian liquid decays within a penetration depth of the interface \( \delta = (\eta/ \)
and so some authors prefer to define a dissipation
is a measure of the loss of energy and of the damping of the shear
measured and are functions of the liquid properties. Bandwidth
trifluoroacetate; [OctSO₄]
the value of the viscosity
liquid is Newtonian, either the frequency change (the Kanazawa and
of whether an ionic liquid has a Newtonian response. If the ionic
are correlated, such that
Thus, by verifying that changes in resonant frequency and bandwidth
where the specific acoustic impedance of quartz is

\[
\frac{\Delta f}{f_0} = -\frac{1}{Z_0} \left( f_0 \eta \rho \right)^{1/2} \text{ and } \frac{\Delta B}{f_0} = \frac{2}{Z_0} \left( f_0 \eta \rho \right)^{1/2}
\]  

(1)

where the specific acoustic impedance of quartz is \( Z_0 = (\mu \rho_0)^{1/2} \approx 8.84 \times 10^{-6} \text{ kg m}^{-2} \text{s}^{-1} \), \( f_0 \) is the fundamental frequency and \( f_s = \frac{1}{2} f_0 \) is the overtone frequency at which the response is measured.\(^{21,22}\)

Thus, by verifying that changes in resonant frequency and bandwidth are correlated, such that \( \Delta f = -\Delta B / 2 \), eq 1 allows a determination of whether an ionic liquid has a Newtonian response. If the ionic liquid is Newtonian, either the frequency change (the Kanazawa and Gordon equation) or the bandwidth change can be used to determine the value of the viscosity–density product and from knowledge of the density, the viscosity can be deduced.

In this work, concentrations of a water-miscible room-
temperature ionic liquid, 1-butyl-3-methylimidazolium trifluoro-
methylsulfonate, [C₄mim][OTf], and a water-immiscible room
liquid is 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [C₄mim][NTf₂], are shown to be Newtonian according to impedance spectra for a 5-MHz quartz
crystal for concentrations from pure to 100% water or methanol,
respectively. Results for the density–viscosity values obtained
using the small-volume impedance spectra method are shown
to be consistent with those obtained using a viscometer. Finally,
data for 18 pure ionic liquids are presented, with Newtonian
behavior being confirmed for 12 of these and the validity of a linear relationship between frequency shift and square root of viscosity–density product being confirmed up to a limit of \( \sqrt{\rho d} \approx 18 \text{ kg m}^{-2} \text{s}^{-1/2} \).

**EXPERIMENTAL SECTION**

**Ionic Liquids.** 1-Butyl-1-methylpyrrolidinium trifluorotrifluoro-
ethyl methylphosphonium ([C₄mim][FAP]), 1-butyl-3-methylimidazolium trifluoracetate ([C₄mim][TFA]), 1-butyl-3-methylimidazolium dicyanamide ([C₄mim][DCA]), 1-butyl-1-methylpyrrolidinium dicyanamide ([C₄mim][DCA]), 1-ethyl-3-methylimidazolium thiocyanate ([C₄mim][SCN]), 1-butyl-3-methylimidazolium
methylsulfate ([C₄mim][MeSO₄]), 1-butyl-3-methylimidazolium
octysulfate ([C₄mim][OctSO₄]), and methyl-triethylammonium trifluoracetate ([N₅,8,8,8][TFA]) were obtained from Merck (98%)
1-Ethyl-3-methylimidazolium ethyl sulfate ([C₂mim][EtSO₄]) was
prepared by reacting 1-methylimidazole with diethyl sulfate according
to previously reported procedures.\(^{23}\) All other ionic liquids were
prepared in-house using standard literature methods from the
appropriate organic halide salt.\(^{24,25}\) The halide content of each ionic
liquid was measured by using suppressed ion chromatography\(^{26}\)
and the characterization of each ionic liquid used is shown in Table 1.

**Table 1. Halide Content, Water Content in Mass Fractions, Viscosity, and Density of Ionic Liquids Measured Using a Viscometer and Density Meter in This Study (at 25 °C)**

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Viscosity (cP)</th>
<th>Density (g cm⁻³)</th>
<th>[H₂O] (wt %)</th>
<th>Halide (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₄mim][SCN]</td>
<td>23.6</td>
<td>1.118</td>
<td>0.0307</td>
<td>&lt;5</td>
</tr>
<tr>
<td>[C₄mim][DCA]</td>
<td>28.8</td>
<td>1.059</td>
<td>0.0256</td>
<td>1830</td>
</tr>
<tr>
<td>[C₄mim][DCA]</td>
<td>36.5</td>
<td>1.013</td>
<td>0.0235</td>
<td>1790</td>
</tr>
<tr>
<td>[C₄mim][NTf₂]</td>
<td>36.5</td>
<td>1.520</td>
<td>0.0100</td>
<td>&lt;5</td>
</tr>
<tr>
<td>[C₄mim][NTf₂]</td>
<td>50.5</td>
<td>1.436</td>
<td>0.0986</td>
<td>&lt;5</td>
</tr>
<tr>
<td>[C₄mim][OTf]</td>
<td>83.2</td>
<td>1.292</td>
<td>0.0681</td>
<td>&lt;5</td>
</tr>
<tr>
<td>[C₄mim][NTf₂]</td>
<td>79.3</td>
<td>1.305</td>
<td>0.0101</td>
<td>&lt;5</td>
</tr>
<tr>
<td>[C₄mim][NTf₂]</td>
<td>80.1</td>
<td>1.357</td>
<td>0.0013</td>
<td>&lt;5</td>
</tr>
<tr>
<td>[C₄mim][OctSO₄]</td>
<td>98.4</td>
<td>1.237</td>
<td>0.0279</td>
<td>-a</td>
</tr>
<tr>
<td>[C₄mim][NTf₂]</td>
<td>95.0</td>
<td>1.321</td>
<td>0.0032</td>
<td>&lt;5</td>
</tr>
<tr>
<td>[C₄mim][NTf₂]</td>
<td>120.2</td>
<td>1.279</td>
<td>0.0652</td>
<td>&lt;5</td>
</tr>
<tr>
<td>[C₄mim][AcO]</td>
<td>139.7</td>
<td>1.243</td>
<td>0.0746</td>
<td>&lt;10</td>
</tr>
<tr>
<td>[C₄mim][MeSO₄]</td>
<td>188.0</td>
<td>1.208</td>
<td>0.0067</td>
<td>&lt;5</td>
</tr>
<tr>
<td>[C₄mim][FAP]</td>
<td>221.0</td>
<td>1.580</td>
<td>0.0132</td>
<td>&lt;100</td>
</tr>
<tr>
<td>[P₅,6,6,6,14][NTf₂]</td>
<td>335.9</td>
<td>1.065</td>
<td>0.0095</td>
<td>&lt;5</td>
</tr>
<tr>
<td>[C₄mim][TFA]</td>
<td>418.5</td>
<td>1.068</td>
<td>0.0744</td>
<td>&lt;5</td>
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<tr>
<td>[C₄mim][OctSO₄]</td>
<td>888.6</td>
<td>1.072</td>
<td>0.0113</td>
<td>&lt;7</td>
</tr>
<tr>
<td>[N₁,₈,₈,₈][TFA]</td>
<td>1708</td>
<td>0.966</td>
<td>0.0108</td>
<td>&lt;5</td>
</tr>
<tr>
<td>[C₄mim][SCN]</td>
<td>683.7</td>
<td>1.011</td>
<td>0.0307</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

* Halide-free preparation. \([C₄mim]^{+} = 1\text{-alkyl-3-methylimidazolium; [C₄mim]} +) = \text{trihexyltridecyphosphonium; [SCN]} = \text{thiocyanate; [DCA]} = \text{dicyanamide; [NTf₂]} = \text{bis(trifluoromethylsulfonyl)imide; [OTf]} = \text{trifluoromethanesulfonate; [AcO]} = \text{acetate; [MeSO₄]} = \text{methylsulfate; [FAP]} = \text{trifluorotris(perfluoroethyl)phosphosphate; [TFA]} = \text{trifluoroacetate; [OctSO₄]} = \text{octylsulfate.}
and density were made using a Brookfield DV-II programmable viscometer, and a DMA 4500 density/specific gravity/concentration meter; these methods require 1.5 and 0.5 mL of liquid, respectively. Before use, all the ionic liquids were dried using a heated oil bath at 60 °C while subjected to a vacuum (1 Torr) and left overnight to facilitate maximum water removal; water content of the ionic liquid was measured using a Karl Fischer titrator. A series of poly(dimethylsiloxane) (PDMS) oils (Aldrich) covering viscosities from 1 to 100 000 cP were used to give a comparison fluid that is known to deviate from a Newtonian behavior at high molecular weight. The temperature for both density and viscosity measurements could be controlled using a water bath and were set to 25 °C, which was the value recorded at the time the QCM measurements were made (Table 2).

**RESULTS AND DISCUSSION**

**Determination of Newtonian Liquid Behavior.** The change in bandwidth or change in frequency of the QCM allows the viscosity—density product of the liquid under test to be calculated using the linear relationships given by eq 1 provided the liquid is a Newtonian fluid. To test this linearity, Figure 2a shows the change in fundamental frequency and Figure 2b the corresponding change in bandwidth as a function of square root of the density—viscosity product obtained using the viscometer and density meter for a range of concentrations of two ionic liquids (water-miscible [C₄mim][OTf] diluted in water, squares, and water-immiscible [C₄mim][NTf₂] diluted in methanol, triangles). These data suggest that the QCM could be used to determine the square root of the viscosity—density product of an ionic liquid directly from small-volume samples. However, a linear response in Figure 2a or Figure 2b does not directly confirm that the liquid is Newtonian and, hence, that eq 1 can be applied.

Figure 3 presents the data for the various concentrations of ionic liquids as a change in fundamental frequency against change in bandwidth. The frequency shift and bandwidth increase data are well-described by a linear relationship. To illustrate typical results for a non-Newtonian liquid, Figure 2 and Figure 3 also present data for a range of poly(dimethylsiloxane) oils (circles), which are known to deviate significantly from Newtonian behavior at higher molecular weight; this deviation can be clearly observed above a change in frequency of 3 kHz corresponding to a viscosity of 10 cP. For the ionic liquids, the majority of data in Figure 3 follow the solid line with a slope of 0.5, which is the prediction for a Newtonian liquid; the inset confirms this for concentrations up to 90%. At concentrations of ionic liquid above 90%, there is a small deviation with a slightly larger bandwidth than predicted for a given frequency shift. This is probably due to the increased difficulty in accurately fitting the resonant curves for the bandwidth for the pure ionic liquids with high viscosity (high damping), making the identification of the resonant frequency more reliable than the determination of the bandwidth. In addition, although the samples were measured in a glovebag, the high hygroscopicity of the ionic liquids and the high sensitivity of viscosity on the water content for the pure ionic liquids may also contribute to the slight variance observed.

**Third Harmonic Data for Viscosity-Density Product.** The frequency change can be converted to square root of viscosity—density product using the Kanazawa and Gordon equation (eq 1). Figure 4 shows the square root of the density—viscosity product plotted as a function of concentration of the water-miscible [C₄mim][OTf] using the QCM frequency shift measured at the third harmonic (diamonds) and the corresponding product calculated from the independent viscometer and density meter measurements (squares).

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The inset in Figure 4 shows the corresponding square root of the density–viscosity product for the QCM and non-QCM techniques; the straight line is a best fit with a slope of 0.96. The inset also provides a comparison of the density–viscosity product calculated from the third harmonic (diamonds) and from the fundamental (circles) of the quartz crystal. Both the fundamental and the third harmonic data agree within experimental error with the non-QCM measurements at lower viscosities, but at the highest viscosity, the data from the fundamental mode slightly underestimate the viscosity–density product. In contrast, the third harmonic data remain in agreement with viscometer and density meter data over the full concentration range up to pure ionic liquid. We found that the third harmonic gave better agreement with the non-QCM measurements than all the other harmonics measured. The data for the water-immiscible ionic liquid [C\text{4mim}][NTf_2] also resulted in the same conclusions with the third harmonic data providing a low-volume sample measurement of density–viscosity product consistent with the results using the larger volumes in the viscometer and density meter; the data are shown in Figure 5. In both cases, the largest error from repeated measurements (~±10%) occurs for the pure liquids, which given the hygroscopic nature of these room-temperature ionic liquids and sensitive dependence on liquid composition of the viscosity, is not surprising.

### Pure Ionic Liquids

A set of 18 pure ionic liquids was tested using both the small-volume quartz crystal impedance technique and the large-volume viscometer. Figure 6a shows a linear correlation between changes in resonant frequency, \( \Delta f \), and bandwidth, \( \Delta B \), for 11 of the ionic liquids for which reliable fits of the bandwidth were obtained at the fundamental frequency (the first 11 ionic liquids in Table 1); replicate measurements have been included. All of these ionic liquids are reasonably described by the test for Newtonian behavior, \( \Delta f \approx -\Delta B/2 \), although the best fit to the data gives a gradient of 0.439 (solid line). Figure 6b shows the change in resonant frequency as a function of the square root of viscosity–density product measured using the viscometer and density meter for all 18 ionic liquids. There is a clear threshold at around \( \sqrt{\rho \eta} \approx 18.7 \text{ kg m}^{-2} \text{ s}^{-1/2} \) after which two ionic liquids, [P\text{6,6,6,14}][NTf_2] and [C\text{4mim}][TFA], deviate slightly from the linear prediction and a further two, [C\text{4mim}][OctSO_4] and [N\text{1,8,8,8}][TFA], deviate significantly from the linear prediction. At these high levels of viscosity where resonant curves are very broad and difficult to fit accurately, however, it was possible to fit the full resonant curve for one of these, [C\text{4mim}][OctSO_4], and it did satisfy the Newtonian criteria given by, \( \Delta f = -\Delta B/2 \). This would indicate that all ionic liquids tested for which the quartz crystal method was able to provide accurate results (i.e., up to \( \sqrt{\rho \eta} \approx 18 \text{ kg m}^{-2} \text{ s}^{-1/2} \))
were Newtonian. Figure 7 shows the correlation of the square root of viscosity-density product estimated using the third harmonic frequency shift of the quartz crystal with the data from the viscometer and density meter for the 16 pure ionic liquids satisfying the linear prediction or having a slight deviation from the linear prediction; Table 1 gives the average values measured for all 18 liquids measured. For data points up to $\sqrt{\rho \eta} \approx 18 \text{ kg m}^{-2} \text{s}^{-1/2}$, the data can be fitted by $\sqrt{\rho \eta}_{\text{QCM}} = 0.92 \sqrt{\rho \eta}_{\text{viscometer}}$, thus indicating around a 10% underestimate by the quartz crystal impedance method compared to the viscometer. However, in a high-throughput application of the technique, such an underestimate could be corrected by using a calibrated value for the numerical coefficient in eq 1 rather than the theoretical value from the Kanazawa and Gordon equation.

Clearly the product of the density and viscosity only has limited application and usually the individual values are required, for example, in process design. Recently, predictive modeling of density data based on molar volume calculations of the constituent ions has been reported by a number of groups.30–33 Jacquemin et al. showed using >2000 data points that the density could be predicted with an uncertainty of 0.48% as a function of temperature.34 This level of predictability may be used in conjunction with the QCM-derived value for the $\rho \eta$ and therefore provide a predicted viscosity for a given ionic liquid. This is a significant advance given that conventional measurements of $\eta$ require >1.5 mL of ionic liquid whereas by this method the sample size may be reduced to 40 $\mu$L.

The measurements reported herein are in good agreement with previously reported data on the effect of shear rate on viscosity for ionic liquids. Seddon et al. studied the viscosity of $[C_n\text{mim}][BF_4]$ (n = 4 to n = 12) and $[C_n\text{mim}][PF_6]$ (n = 4 to n = 12) ionic liquids and found that for all except $[C_{12}\text{mim}][BF_4]$ the viscosity for independent of shear rate was indicative of Newtonian behavior.35 While for $[C_{12}\text{mim}][BF_4]$ above 65 °C this was also true, below this temperature non-Newtonian behavior was observed due to the phase transition from the isotropic liquid phase into the liquid crystalline region. Non-Newtonian behavior has also been reported for benzy-functionalized imidazolium-based

ionic liquids by Kulkarni et al. as well as a number of 
[C10mim][CF3COO], [C10mim][NTf2], and [C10mim][SCN].
Interestingly, this is not found in the QCM data where 
[C10mim][NTf2] fits the linear trend of eq 1. Although, the addition 
of solutes to ionic liquids has been shown to result in non-
Newtonian behavior, this has predominantly been for ionic liquids 
containing functionalized cations, for example, where strong 
hydrogen bonding can occur between the solute and ionic 
liquid.37–39 Li et al. showed that the plastic and then Newtonian 
behavior was observed as the shear rate increased for mixtures 
of [Me3NC2H4OH][Zn2Cl5] and ethanol.39 Herein, where the ionic 
liquid–water interaction may be considered as weaker, only 
Newtonian behavior was observed. Recent calculations have 
shown that non-Newtonian behavior may be expected for many 
ionic liquids, even those thought as showing Newtonian behavior 
on the macroscale, if the ionic liquid is confined in microchannels, 
for example.40 The QCM technique coupled with microchannel 
devices will enable this prediction to be studied in detail and is 
the subject of an ongoing study.

CONCLUSION

In this article, we have shown that quartz crystal impedance 
analysis can be used to determine whether mixtures of a water-
miscible and a water-immiscible ionic liquid with water and 
methanol, respectively, have Newtonian responses when subject 
to a high-frequency oscillation. For ionic liquids with a Newtonian 
response, it has been shown that viscosity–density products can 
be determined from small-volume samples without the need for 
calibration liquids. The results also demonstrate that the third 
harmonic of the crystal resonance provides the greatest consist-
tency over the full range of concentrations with results obtained 
using a viscometer and density meter. Data obtained for 12 pure 
ionic liquids were found to show Newtonian responses with 
correlated shifts in quartz crystal frequency and bandwidth. The 
change in frequency for pure ionic liquids was directly proportional 
to the square root of the viscosity–density product for values up 
until \(\sqrt{(\eta \rho)} \approx 18.7 \text{ kg m}^{-2} \text{s}^{-1/2}\).

Figure 6. Fundamental mode data for 19 pure ionic liquids. (a) Correlation between change in resonant frequency and change in bandwidth 
demonstrating Newtonian behavior, (b) change in resonant frequency as a function of viscosity–density product. The data are described by a 
linear relationship up to \(\sqrt{(\eta \rho)} \approx 18.7 \text{ kg m}^{-2} \text{s}^{-1/2}\).

Figure 7. Correlation between density–viscosity product for 17 pure 
ionic liquids determined using viscometer and density meter and by 
using the change in resonant frequency of the quartz crystal at the 
third harmonic. The solid line has a slope of unity. The linear 
correlation breaks down for the highest viscosity ionic liquids at around 
\(\sqrt{(\eta \rho)} \approx 18 \text{ kg m}^{-2} \text{s}^{-1/2}\).

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