Pressure-Temperature Phase Diagram of Ionic Liquid Dielectric DEME-TFSI

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Abstract
Ionic liquids have proven highly effective as dielectrics in Electric Double Layer (EDL) devices for electrostatic doping in a range of materials. DEME-TFSI in particular is a commonly used dielectric due to its high ionic conductivity and low glass transition temperature of 182 K. Application of pressure provides a dual tuning parameter in tandem with the electric field yet progress is hampered by the lack of an accurate pressure-temperature phase diagram for DEME-TFSI. We present results on expansivity and leakage current measurements of the ionic liquid dielectric DEME-TFSI to provide a phase diagram mapping the glass transition temperature up to 0.6 GPa. This should allow the effective operation of EDL devices using DEME-TFSI under pressure.

Keywords: DEME-TFSI, ionic liquid, pressure, phase, glass transition

1 Introduction
Ionic liquids are highly polar binary salts with low melting temperatures that have gained much attention in recent years for their use in Electric Double Layer (EDL) devices. EDL devices provide a means to electrostatically dope various materials and continuously tune through their phase diagrams permitting a dramatic switching between material properties by applying potentials of only a few volts. Ionic liquids exhibit high dielectric constants and chemical compatibility with many materials compared to most electrolytes thus making them an ideal dielectric for EDL devices[1]. As such they have been shown to maximise the achievable carrier densities in EDL's[2] in order to induce metal-insulator transitions [3] as well as superconductivity in a range of materials[4, 5].
N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI) in particular is a commonly used ionic liquid dielectric for EDL devices due to its large electrochemical potential window and a low glass transition at 182 K\(^6, 7, 8\) where the mobility of ions falls to zero\(^3\). No known crystal phase has been observed\(^6\). Tuning of material properties using an EDL device relies on ion mobility and thus it is important to ensure parameters are altered above any glass or solid phase transition.

Pressure is also a common tuning parameter for material properties and potentially could increase the versatility of EDL devices. To date there has been some research into the use of pressure with electrostatic doping\(^9\) and on DEME-TFSI’s structure\(^8\) yet no definitive mapping of the glass transition shift. Effective function of EDL devices under pressure will rely on accurate tracking of the glass transition to ensure parameters are always altered whilst the dielectric is in its liquid state. In this paper we aim to present results on the mapping of this glass transition with pressure through measurements of the expansivity of DEME-TFSI along with the leakage current across it when used as a dielectric.

2 Experimental Details

Measurements were carried out by filling a standard piston cylinder pressure cell (maximum pressure 1.1 GPa) with the ionic liquid DEME-TFSI as the pressure medium. DEME-TFSI is dried prior to use under a vacuum line pressure of \(\sim 5 \times 10^{-3}\) mbar at \(\sim 120^\circ C\) for 24 hours to reduce water content and prevent electrolysis under voltage application\(^6, 7\). As ionic liquid dielectric properties cannot be measured by conventional means due to their high ionic conductivity\(^10\) we instead opted to measure the expansivity of the liquid as it undergoes the glass transition and the leakage current between fixed plates immersed within it. Many materials upon undergoing a liquid-glass transition experience a sudden change in their expansivity\(^11\) which should be detectable with a sensitive pressure gauge. A thermally cycled manganin gauge, primarily used to track the pressure\(^12\), is employed in conjunction with a sensitive KYOWA KFL-02-120-C1-11 strain gauge in the piston cell as a means of detecting this change associated with the glass transition. Platinum plates of area 50 mm\(^2\), separated \(\sim 100 \mu m\) apart by insulating plastic spacers, were chosen for immersion in the ionic liquid in order to avoid electrochemical reaction on application of voltage. A constant 2 V are applied between the plates whilst the small leakage current through the ionic liquid is measured by a Keithley 6517A Electrometer. A low voltage must be applied in order to remain within the potential window for DEME-TFSI and prevent oxidation/reduction reactions\(^6, 7\). Measurements are taken at each applied pressure whilst the cell is cooled and warmed on a cold finger closed cycle cryostat.

3 Results & Discussion

3.1 Expansivity Measurements

The change in expansivity of DEME-TFSI is measured by monitoring the temperature dependent resistance of a manganin gauge and sensitive strain gauge immersed in the ionic liquid within the pressure cell. At ambient pressure a small discontinuity in the manganin gauges resistance is detected as it is cooled or warmed within the cryostat at 176.4 \(\pm 2.0\) K. Strain gauges are specially designed to measure the stress and strain of a material as it undergoes expansion or contraction with temperature change, as such it also exhibits a similar, but more
greatly pronounced, discontinuity at $179.0 \pm 3.1$ K visible in Figure 1. These values are approximately consistent with the observed glass transition temperature of DEME-TFSI at 182 K [6, 7, 8] indicating that these discontinuities are indeed associated with this phase change.

Further measurements are conducted at a range of pressures after the pressure cell has been sealed and loaded. The discontinuity previously seen in the manganin gauge became indistinguishable from noise at the following pressure steps and thus we were unable to determine the glass transition temperature using this gauge. However due to the sensitive nature of the strain gauge we were still able to observe and track the glass transition temperature which shows steady increase with pressure as can be seen in Figure 1. Interestingly under pressure the change in expansivity detected by the strain gauge is no longer a sharp discontinuity but rather a broad peak disrupting the approximate linearity of the resistance with temperature. Potentially this feature could be due to the pressure within the cell falling with temperature, as...
is often seen with the slow contraction of any pressure medium, essentially resulting in the glass transition being shifted across a larger temperature regime thereby spreading out the sharp discontinuity. Another possibility is that upon transitioning into the glass phase the pressure application is no longer hydrostatic resulting in a pressure gradient across the DEME-TFSI. If large enough not all of the DEME-TFSI may remain in the glass phase until lower temperatures are reached thus resulting in a less defined transition zone. Regardless of the loss of the sharp discontinuity the onset of this broad peak is still indicative of a change in expansivity thus we take this to be our estimate for onset of the glass phase transition as shown by the dashed vertical lines in Figure 1.

Figure 2: Leakage current across platinum plates immersed in DEME-TFSI at various pressures. Vertical dashed lines indicate proposed onset of glass transition, arrows the weak minimum for rubber phase extent and approximate room temperature applied pressures are listed.
3.2 Leakage Current Measurements

The ionic conductivity of DEME-TFSI quickly falls as it is cooled which can be observed by the rapidly decreasing leakage current between plates immersed within it[3]. As shown in Figure 2 at approximately 0.3 GPa of pressure we see just such an exponential decrease until it plateaus at a stable value. This plateau is consistent with previous measurements of the leakage current where DEME-TFSI experiences a rubber phase between its liquid-glass transition and ion mobility begins to slow[3]. There appears to be a weak minimum of the leakage current at the edge of this plateau, indicated by arrows in Figure 2, that could be taken to correspond to the limit of the rubber phase. At 204 K there is a sharp cutoff where it is believed the ion mobility suddenly slows to such an extent on approaching the glass phase that measurements exceed the limits of our instrumentation (I < 1 x 10^{-12} A) and as such we have taken this to be our measure of the glass transition.

Figure 2 illustrates how the cutoff, weak minimum and plateau region are all shifted to higher temperatures as the pressure is increased indicating the glass transition and rubber phase migration is consistent with the expansivity shifts observed in section 3.1. Dashed lines indicate extrapolation of stable high temperature data down to the plateau as measurements in this intermediate region were too erratic to provide meaningful data due to the temperature falling too quickly. Interestingly the leakage current in the rubber phase remains constant at approximately 1 x 10^{-10} A implying that ion mobility is independent of pressure.

![Figure 3: DEME-TFSI temperature-pressure phase diagram as determined from leakage current and expansivity measurements under pressure. Pressure at each temperature determined using manganin gauge[12]. Dashed line indicates proposed onset of rubber phase between liquid-glass transition. Included is ambient pressure glass transition from literature[6, 7].](image)
3.3 Phase Diagram

Figure 3 shows the glass transition temperatures determined by averaging multiple thermal cycles of expansivity and leakage current measurements at each pressure. Rather than using room temperature applied pressures, as in Figures 1 & 2, values at each observed glass transition temperature were determined using the manganin gauge\cite{12} to provide the most accurate pressure experienced by DEME-TFSI at this point.

The estimate of the glass transition temperature from leakage current measurements appears to be consistently higher than that determined from the strain gauge. In all likelihood this is due to the fact that ion mobility slows whilst DEME-TFSI is in the rubber phase\cite{3}. Thus the expansivity measure from the strain gauge provides the most accurate estimate of the glass transition temperature whilst the leakage current cutoff helps indicate the lower regime of the rubber phase immediately above it rising in tandem with increased pressure.

Previous measurements of the leakage current in an EDL device have suggested that this rubber phase is present at room temperature for pressures in excess of 0.59 GPa\cite{9}. Considering the weak minimum in our leakage current measurements to mark the extent of the rubber phase we have plotted this on our phase diagram and would estimate a value of around 255 K at 0.6 GPa, which is nearing room temperature.

4 Conclusions

Through expansivity and leakage current measurements we have mapped the glass transition and shift of the rubber phase of DEME-TFSI up to applied pressures of 0.6 GPa to create a pressure-temperature phase diagram. Effective application of EDL devices at ambient pressure generally requires change of bias at 40 - 60 K above the glass temperature to ensure ion mobility and a set wait time for equilibrium to be established\cite{3}. Our data shows that this should be done at increasing temperature with pressure. We also note that the leakage current measured in the rubber phase is almost independent of pressure. Thus mobility of the ions appears to remain unchanged with pressure implying that the same wait time for equilibrium on change of bias at ambient pressure can be applied at other pressures.

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References


