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Physical and Electrochemical Investigations into Blended Electrolytes Containing a Glyme Solvent and Two Bis{(trifluoromethyl)sulfonyl}imide-Based Ionic Liquids

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In this paper, we report on thermophysical and electrochemical investigations of a series of molecular solvent/ionic liquid (IL) binary mixture electrolytes. Tetracycyle glycol dimethyl ether (TEGDME) is utilized as the molecular solvent component in separate mixtures with two bis{(trifluoromethyl)sulfonyl}imide anion based ILs paired with similarly sized cyclic and acyclic alkylammonium cations; 1-butyl-1-methylpyrrolidinium bis{(trifluoromethyl)sulfonyl}imide, [Pyrr14][TFSI] or N-butyl-N,N-dimethyl-N-ethalammonium bis{(trifluoromethyl)sulfonyl}imide, [N112][TFSI]. The blending of ILs with select molecular solvents is an important strategy for the improvement of the typically sluggish transport capabilities of these interesting electrolytic solvents. Bulk volumetric and transport properties are reported as a function of temperature and binary mixture formulation; demonstrating the capacity for enhancing desired properties of the IL. Micro-disk electrode voltammetry and chronoamperometry in O2 saturated binary mixture electrolytes was used to assess the effect of formulation on the solubility and diffusivity of the dissolved gas. In addition, further investigations of the behavior of the O2 redox couple at a GC macro-disk electrode are discussed.

The exploration of ionic liquids (ILs) as alternatives to conventional molecular solvents in electrolyte formulations is continually growing for a variety of electrochemical applications. These low melting organic salts can be tailored to exhibit a variety of properties, including hydrophobicity and thermal, chemical, and electrochemical stability, which make them attractive candidate electrolyte solvents. Composed solely of ionic components, ILs consequently possess intrinsic electrolytic conductivity and are additionally non-volatile. These properties have encouraged the use of ILs as (complete or partial) substitutions of the volatile components of commercial Li-ion batteries, electrochemical double layer capacitors (EDLCs), and other prospective battery technologies (e.g. Na-ion, Mg-ion and metal-air batteries) for the development of potentially safer devices.1–15 Furthermore, the high (electro)chemical stabilities and non-voltalities exhibited by many IL structures provides interesting electrolytic media for electrochemical gas sensors (e.g. for O2, CO2, NO2) where traditional solvents are prone to evaporation leading to device failure, and also for electromechanical actuator,23–25 and electrodeposition applications.26–28

Nevertheless, while the properties of ILs are dependent on the virtually unlimited combinations of different cation and anion structures, the attractive features are generally coupled with sluggish transport properties relative to conventional electrolytes based on either aqueous or organic solvents. In turn, electrochemical devices constructed with neat IL electrolytes are likely to suffer transport limitations on useable current rates for the given application, for example restricting power capabilities of storage devices and response times for electrochemical sensors.

In the scope of addressing the shortcomings of IL materials for electrolyte applications, structural modifications of the constituent ions may be utilized to fine-tune the properties of the resulting IL. However, present state-of-the-art developments of novel IL materials have yet to yield sufficient promotions in transport properties without the sacrifice of other vital features. For example, we recently reported the characterization of newly synthesized ILs based around ethereal/alkyl-functionalized sulfonium cations paired with the bis{(trifluoromethyl)sulfonyl}imide, [TFSI]–, anion.29 Such anion/cation combinations yielded ILs with comparatively low viscosities/good conductivities but lower thermal and electrochemical stabilities when compared with ILs based on analogous alkyl-functionalized ammonium or phosphonium aprotic cations.30,31 Alternatively, ILs may be blended with appropriate, lower viscosity organic molecular solvents with the goal of exploiting the positive aspects of the respective components. Therein, these aspects primarily relate to improved transport properties of the molecular solvent component and the potential to improve safety and stability issues with the IL. The mutual solubility between many ILs and common non-aqueous electrochemical solvents enable the consideration of a wide range of formulations in a given mixture with the prospect of balancing the desired properties. As such, investigating the application of IL/molecular solvent blends as electrolytes for Li-ion batteries,1–4 Na-ion batteries,13 Li-O2 chemistry,32–34 and EDLCs,7–10 has continually revealed material benefits relating to electrolyte stability and device safety.

Herein, this work details the thermophysical characterization and electrochemical investigations of a series of IL binary mixtures with tetraethylglycol dimethyl ether (TEGDME) for potential electrolyte applications. As part of the dipolar aprotic family of glyme solvents, TEGDME exhibits intermediate associative strength and good (electro)chemical stabilities. However, the longer chain structure affords this glyme solvent with lower vapor pressure and volatility than the shorter chain glyme analogues. Physical characterization of (X)[Pyrr14][TFSI] – (1-X)TEGDME binary mixtures, where [Pyrr14]+ is 1-butyl-1-methylpyrrolidinium, reported as a function of formulation and select comparisons are made wherein this IL is replaced with an acyclic ammonium cation analogue IL, N-butyl-N,N-dimethyl-N-
ethylammonium; [N\textsubscript{1413}][TFSI]. Furthermore, as a function of the binary mixture formulation, electrochemical measurements were utilized to investigate electrochemical stability windows, solubilities and diffusivities of dissolved O\textsubscript{2} and characteristics of the electroreduction of dissolved O\textsubscript{2}.

**Experimental**

**Materials and syntheses.**—1-Bromobutane (98%), N,N-dimethyl-N-ethylamine (99%), N-methylpyrrolidine (99%), tetraethylglycol dimethyl ether (>99%), acetonitrile (99.8%), dichloromethane (99.5%), diethyl ether (>99%) and ferrocene (98%) were purchased from Sigma-Aldrich. Lithium bis(trifluoromethyl)sulfonyl imide (battery grade) was purchased from 3 M. All reagents used for synthesis were used as received. \(^{1}H\) and \(^{13}C\) NMR spectra were recorded at 293.15 K on a Bruker Avance DPX spectrometer at 300 MHz and 75 MHz, respectively. Lithium content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on an Agilent 5100 ICP-OES. The determination of lithium content and CHNS Microanalysis was performed by Analytical Services at Queen’s University Belfast. The full description of the IL synthetic procedures for [Pyrr\textsubscript{1}][TFSI] and [N\textsubscript{1413}][TFSI] is provided in the electronic supporting information (ESI) along with NMR characterization and spectra and the results of Microanalysis and lithium and water content.

**Sample preparation.**—Prior to any physical or electrochemical measurements, the synthesized ILs were dried in a two-step procedure. The ILs were firstly dried under vacuum (ca. 10\textsuperscript{-3} mbar) using a rotary-vane vacuum pump (RV3, Edwards) at elevated temperatures (363 K – 373 K) with stirring to remove the majority of water over a period of two days. Without exposing the IL sample to ambient atmosphere, these were further dried under high-vacuum (ca. 10\textsuperscript{-5} – 10\textsuperscript{-6} mbar) using a turbomolecular vacuum pump (HiCube 80 Eco, Pfeiffer Vacuum) with heating (363 – 373 K) and stirring over a further period of one or two days. The ILs were then immediately stored in an Ar-filled glove box (<2 ppm, H\textsubscript{2}O) without exposure to external atmosphere. The water content of samples was analyzed by Karl Fischer Coulometric titration (899 Coulometer, Metrohm) where the resolution of the measurements was 0.001 wt% (or 10 ppm) and the measurements were conducted in triplicate. This drying process of the ILs was found to effectively reduce water content below 10 ppm (i.e. below the measurable range for the device).

Furthermore, prior to any physical or electrochemical measurements, the TEGDME solvent was purified by vacuum distillation over freshly activated molecular sieves (4 Å). Approximately 10% of the starting mass was discarded in the initial and final fractions and the middle fraction was collected and stored over molecular sieves (4 Å) inside the Ar filled glove box.

Binary and ternary mixtures were prepared by mass under the Ar atmosphere of the glove box using a BP 110 S balance (Sartorius, ±0.1 mg) at a temperature of ca. 305.15 K. For all binary mixtures of IL and TEGDME, both liquids were mutually miscible and a homogeneous solution was readily achieved.

**Physical measurements.**—The density measurements of the liquid samples were completed using a DMA40 oscillating tube density meter (Mettler Toledo, ±1 \times 10\textsuperscript{-4} g \cdot cm\textsuperscript{-3}) in the range of 293.15–333.15 K (±0.01 K). Prior to any measurements, the instrument was cleaned with acetone and dried with dehumidified air. The viscosity of the samples was measured using an AMVn falling/rolling ball viscometer (Anton Paar) with a 1.8 mm capillary (2.5–70 mPa\textsuperscript{s} range) in the range of 293.15–333.15 K (±0.01 K) at atmospheric pressure.

The conductivity measurements were completed using a sensION+ EC71 benchtop meter with a 3-plate platinum sensION-5670 conductivity probe (<0.5% of range) with an in-built Pt1000 temperature probe (Hach Lange). The conductivity probe was calibrated using aqueous KCl standard conductivity solutions (147 \textmu S cm\textsuperscript{-1}, 1413 \textmu S cm\textsuperscript{-1}, and 12.88 mS cm\textsuperscript{-1} at 298.15 K). Measurements of the binary mixture conductivity as a function of formulation were completed inside the Ar-filled glove box at ca. 305 K ± 1 K. This temperature was dictated by the internal atmosphere of the glove box. To complete these measurements a fixed mass of one component was weighed accurately into a custom-built 2 necked glass flask. A small stirrer bar was added to the bottom of the flask and the conductivity probe was inserted into the liquid sample via one glass neck and the conductivity and temperature of the pure component was recorded. Small amounts of the second component were then added directly to the liquid sample via the second neck and the mass of the addition was accurately recorded by difference. The solution was then mixed well to ensure homogeneity and the conductivity and temperature of the binary mixture was recorded, without stirring, once a stable reading was attained. The measurement was repeated, using only weighed amounts of the second component and measuring conductivity and temperature was repeated continuously on the same sample to provide conductivity data for a wide range of compositions of the binary mixtures. For conductivity measurements on fixed compositions as a function of temperature, the samples were prepared inside the glove box by immersion of the conductivity probe into a glass test tube containing the liquid sample and a small magnetic stirrer. The probe was sealed inside the tube using an O-ring seal and Parafilm. The conductivities of the samples were then measured as a function of temperature within a range of 293.15–363.15 K (±0.2 K) and the sample was heated using a small oil bath. The conductivity and temperature of the sample were recorded, without stirring, once a stable reading (ca. one minute) was observed.

**Computational methods.**—Calculation of the IL free volume was conducted using the COSMOTHERM\textsuperscript{X} software (version C30 15.01) with COSMO files computed with the DFT/B3LYP/TZVP level of theory as described by our group previously.\textsuperscript{35,36} As demonstrated previously, an estimation of IL free volume can be straightforwardly acquired using the COSMO-RS (Conductor-like Screening MOdel for Real Solvents) computational method.\textsuperscript{37} In short, the free volume is calculated as the difference between the molar volume (calculated using the ratio between the molecular weight and the density at 303 K predicted by the COSMOTHERM\textsuperscript{X} software) and the COSMO volume of each IL. Herein the COSMO volume, i.e. the total volume encompassed by the computed COSMO surface, of the IL is the sum of COSMO volumes of each anion and cation.

**Electrochemical measurements.**—Electrochemical experiments where a macro working electrode is utilized were conducted using a VMP3 multichannel workstation (Biologic Science Instruments). Electrochemical experiments where the working electrode was a micro-electrode were conducted using either the VMP3 multichannel workstation equipped with a low-current module or an Autolab PGSTAT302 workstation (Metrohm). All electrochemical measurements were conducted in a custom-built 6 necked glass cell (two gas inlet/outlet ports and four electrode ports) designed to facilitate three-electrode electrochemical experiments with two different working electrodes in the same small volume (ca. 1–1.5 cm\textsuperscript{3}) of electrolyte solution. The gas inlet was fitted with a bubbler enabling the gas to be bubbled directly into the liquid electrolyte. The counter electrode was a Pt wire coil heat sealed into a glass capillary and the reference electrode was a Ag wire immersed in a 0.01 mol \cdot dm\textsuperscript{-3} solution of silver trifluoromethanesulfonate (Ag[OTf]) in [Pyrr\textsubscript{1}][TFSI] separated from the bulk solution by a glass frit (herein referred to as Ag[OTf]/Ag). The macro and micro working electrodes used were a glassy-carbon macro-disc (3 mm diameter, ALS Co. Ltd.) and a Pt micro-disc electrode (10 \mu m diameter, Model G0225, Princeton Applied Research), respectively. Prior to any measurements the two working electrodes were polished using alumina slurries of decreasing grain size (1.0 \mu m, 0.3 \mu m and 0.05 \mu m, Buehler) in ultra-pure water on microcloth soft lapping pads (Kenmet Ltd.). After polishing and rinsing with ultra-pure water, the electrodes were sonicated for 2 min in ultra-pure water to remove any residual alumina. The area of the Pt micro-disc electrode was calibrated by measuring the steady-state...
current of the single-electron oxidation of 2 mmol・dm$^{-3}$ ferrocene in a 0.1 mol・dm$^{-3}$ solution of tetrabutylammonium perchlorate in acetoneitrile. In this solution, the diffusion coefficient, $D$, is known to be 2.3・$10^{-9}$ m$^2$・s$^{-1}$ at 293.15 K. $\times\times$ (2.43・$10^{-9}$ m$^2$・s$^{-1}$ at 298.15 K) and is, in turn, used to calibrate the radius, $r_c$, of the micro-disk electrode using the equation

$$i_{ss} = 4nFDC^hr_c$$

where $i_{ss}$ is the steady-state oxidation current, $n$ is the number of electrons transferred ($n = 1$ for the oxidation of ferrocene), $F$ is the Faraday constant (96485 C・mol$^{-1}$) and $D$ and $C$ are the diffusion coefficient and concentration of ferrocene in the bulk acetoneitrile solution.

The 6-port electrochemical cell was prepared inside the Ar-filled glove box. The gas inlet and outlet ports were fitted with valves and the cell was completely sealed inside the glove box. Outside of the glove box, the sealed cell was placed inside an incubator (Genlab), holding the sample at 303 ± 1 K, which also acted as an effective Faraday cage. The gas inlet/outlet ports were connected to gas supply via Swagelok connections. High-purity O$_2$ (N5.0, BOC) was flowed via two CaSO$_4$ desiccant columns (Drierite) and a small tube containing P$_2$O$_5$ desiccant directly into the liquid electrolyte of the glass cell. Micro-disk electrode voltammetry was conducted periodically, while O$_2$ bubbling was paused, to determine when the solution had become saturated (typically 15–20 min). Micro-disk experiments were conducted prior to switching to the GC macro-disk electrode based on the consideration that any changes made to the electrolyte by unexpected side-reactions during voltammetry or chronamperometry would occur on a much smaller scale (for the micro-disk) and, therefore, have less significant effect on subsequent measurements.

Once the electrolyte was deemed saturated with O$_2$, micro-disk electrode cyclic voltammetry (CV) was conducted in the region of 0 to $\pm2.5$ V vs. Ag/OTf$^-$/Ag. Potential step chronoamperometry (CA) experiments at the micro-disk electrode were then conducted in the O$_2$ saturated electrolyte. The potential of the Pt micro-disk electrode was held at a potential of zero Faradaic current (0 V vs. Ag/OTf$^-$/Ag) and then stepped instantaneously to a potential at which the reduction of dissolved O$_2$ is diffusion controlled (ca. $\pm2.3$ to $\pm2.2$ V vs Ag/OTf$^-$/Ag; as determined from the current plateaus observed during CV experiments). The potential was held at the diffusion controlled reducing voltage for several seconds and the current was recorded with a sampling time $\leq 0.001$ s. CA potential step experiments were repeated multiple times for each sample with a minimum period of 15 min between each individual measurement. The 15 min resting period was employed to enable the distribution of dissolved O$_2$ to equilibrate following the perturbation caused by the potential step, i.e. so that the concentration of dissolved O$_2$ local to the electrode surface can relax to equal the concentration of O$_2$ dissolved in the bulk electrolyte.

The resulting chronoamperometric transients were then analyzed using the Shap and Szabo equation (Equation 2) to extract best-fit coefficients for concentration ($c$) and diffusion coefficient ($D$) of the analyte, dissolved O$_2$. The current ($i$) is fitted as a function of time ($t$) using the equation

$$i = 4nF CdF(t)$$

where $n$ is the number of electrons transferred; $F$ is the Faraday constant (96485 C・mol$^{-1}$) and $f(t)$ is given by Equation 3:

$$f(t) = 0.7854 + 0.8862 \sqrt{\frac{r^2}{4Dt}} + 0.2146 \exp \left(- \frac{0.7823 \sqrt{\frac{r^2}{4Dt}}}{0.5782} \right)$$

where $r$ is the radius of micro-disk electrode, fixed by the calibration described previously. Simulated CA transients were generated using a non-linear fitting function (OriginPro 8.1) of Equations 2 and 3 to attempt a best fit with the experimental data and, therefore, to attain best-fit values for the unknown variables, $c(O_2)$ and $D(O_2)$. Transients were typically analyzed over a period of 0.02 – 2 s; the current response within the first 20 ms is considered to be highly dependent on rapid non-Faradaic charging of the electrical double layer and is, therefore, not included in the analysis.

Following the CA experiments at the Pt micro-disk electrode, the working electrode was changed to the GC macro-disk electrode. Cyclic voltammetry was conducted within a voltage range of 0 to $\pm2$ V vs Ag/OTf$^-$/Ag at a range of scan rates. A period of approximately 5–8 min was utilized between each scan to allow the system to equilibrate. All CV experiments conducted at the GC electrode were completed with $iR$-compensation based on the ZIR-technique at 85% within the EC-Lab software (Biologic Science Instruments).

Following all CA and CV experiments at both working electrodes, a small mass of ferrocene was added into the liquid electrolyte. CV experiments at both electrodes were used to determine an estimation of the formal redox potential of the single electron oxidation of ferrocene to ferrocenium. The formal redox potential is utilized as an internal reference couple to normalize the measured potential at the Ag/OTf$^-$/Ag reference electrode versus the Fc$^+$/Fc potential.

Results and Discussion

Physical characteristics of electrolyte blends.—As discussed previously, a primary disadvantage typically associated with ILs for electrochemical energy storage systems relates to the sluggish transport properties commonly observed. High viscosities and moderate-to-poor conductivities exhibited by the ILs, which generally worsen upon the addition of Li-salts, inhibit the mobility of active species involved in charge/discharge processes and contribute to increased resistances. These factors are among the primary motivations for blending the IL component with a lower viscosity molecular solvent. The effect of formulation on the physical and electrochemical properties is described for the full range (i.e. from $X = 0$ to 1) for the (XI)Pyrr$_{14}$[TFSI] – (1-X)TEGDME binary mixtures. For comparison of structural effects, characterization of an acyclic cation analogue IL, [N$_{124}$][TFSI] and the respective xH$_x$ = 0.4 binary mixture with the TEGDME solvent, is also described. As is evidenced from the following discussion, despite being one carbon atom lighter than the cyclic IL, the transport properties of both ILs are very similar, allowing for good comparison of structural effects.

The measurements of viscosity of the binary mixture (XI)–(1-X)TEGDME were completed using a rolling ball viscometer as a function of temperature and the results are presented in Figure 1a. The numerical data is given in Tables S1 and S2 in the ESI for the [Pyrr$_{14}$][TFSI] and [N$_{124}$][TFSI] mixtures, respectively.

Firstly, the measured viscosities of the neat [Pyrr$_{14}$][TFSI] (77.7 mPa$\cdot$s at 298.15 K) and neat TEGDME (3.5 mPa$\cdot$s at 298.15 K) are in agreement with values previously reported in the literature. As would be expected, the viscosity of all studied mixtures is reduced with increased temperature. Furthermore, across all temperature ranges, continued addition of TEGDME to the IL affects a reduction in the measured viscosities wherein the greatest reduction in viscosity is observed at lower temperatures; i.e. the viscosities of the mixtures converge at higher temperatures. An additional benefit of mixing ionic liquids with lower viscosity molecular solvents is related to the promotion of electrolytic conductivity typically observed. Relatively strong prevalent Coulombic interaction between the counterions within the IL ultimately limit the ionic mobility and, in turn, the ability of the IL to rapidly conduct charge. Presented in Figure 1b is the measured conductivity of the binary mixture (XI)Pyrr$_{14}$[TFSI] – (1-X)TEGDME as a function of IL molar fraction, X[Pyrr$_{14}$][TFSI]. The measurement was completed under an inert, dry atmosphere of an Ar-filled glove box by periodically adding small, accurately weighed quantities of one component to a fixed mass of the second component. After each addition, the mixture is effectively mixed and the conductivity is recorded. The temperature of these measurements is 305 K ± 1 K, as dictated by the internal atmosphere of the glove box. Within IL systems, the observed bulk viscosity and conductivity are typically inversely linked. As such, in agreement with the aforementioned reduction in viscosity, the measured conductivity is increased upon addition of TEGDME. This observation primarily relates to the increased mobility of the...
The conductivity is plotted as a function of IL concentration in Figure S5 in the ESI. The conductivity maximum, observed at $x_{[\text{Pyrr}14][\text{TFSI}]} = 0.43$ corresponds to a concentration of ca. 1.66 mol·dm$^{-3}$. Although the vapor pressure of both components of the binary mixture are known to be very low (0.132 kPa at 373 K for TEGDME), having a higher ionic component within the formulation can effectively lower the vapor pressure of the mixture (according to Raoult’s Law). This consideration is important for the improvement of electrolyte safety by reducing the likelihood of forming combustible vapors in the event of device malfunction.

The temperature dependence of the conductivity was also measured for discrete formulations of the binary mixture, presented in Figure 1c. The numerical conductivity data as a function of formulation temperature is provided in Tables S3 and S4 in the ESI, the concentration of [Pyrr14][TFSI] and [N1124][TFSI] mixtures, respectively. As expected, increasing the sample temperature results in an increase in the observed conductivity relating to the increased mobility of the charge carrying ions. The inset graph in Figure 1c, representing a zoomed in plot of the lower end of the temperature scale, demonstrates that the same trend in conductivity as function of IL molar fraction is observed compared to the data presented in Figure 1b. Across the temperature range, the shapes of the curves highlight a change in behavior as the quantity of IL in the mixture decreases. The temperature dependence of the solvent rich formulation, wherein $X = 0.2$, is almost linear across the studied range while the formulations containing higher IL fractions increase more exponentially. As a result, at higher temperatures there is a shift in the observed maximum conductivity toward more IL rich formulations. This is related to the competition between the mobility of the charge carrying ionic species (which increases with temperature and at greater TEGDME fractions) and the concentration of these ions available to conduct the charge. As such, at higher temperatures the mobility of the ionic components in the IL rich formulations becomes sufficiently high (as inferred from the significant reduction in viscosities) that high ionic concentrations remain beneficial. This shift in the observed maxima is shown graphically in Figure S6 in the ESI. Additionally, further extrapolation of the observed temperature dependencies (using the Vogel-Tammann-Fulcher equation, discussed below) would suggest that, under a purely hypothetical scenario without the inevitable evaporation of the molecular solvent, at temperatures greater than ca. 420 K, the neat IL would exhibit the greatest conductivity. In this hypothetical scenario, the mobility of the charge carrying species (i.e. all components of the liquid) becomes sufficiently high so that addition of this solvent only serves to dilute the ions and, in turn, reduce the electrolytic conductivity.

The experimental viscosity, $\eta$, and conductivity, $\sigma$, of the mixtures were correlated as a function of the temperature, $T$, using the Vogel-Tammann-Fulcher (VTF) equations

$$\eta = \eta_o \exp \left( \frac{B^\eta}{T - T_o} \right)$$

and

$$\sigma = \sigma_o \exp \left( \frac{-B^\sigma}{T - T_o} \right)$$

where $\eta_o$ and $\sigma_o$ represent the limiting viscosity and limiting conductivity, respectively, and $B^\eta$ and $B^\sigma$ are correlation parameters relating to the pseudo activation energies and the glass transition temperatures of the mixtures, respectively. Excellent correlation is achieved for all data sets as a function of temperature allowing for accurate interpolation of properties at specific temperatures. The coefficients of the best-fits for the VTF equations for all mixtures are given in Tables S1 and S2 for viscosity and Tables S4 and S5 conductivity in the ESI.

The relationship between viscosity and conductivity in ILs is commonly observed in terms of ionicity by plotting a variation of the Walden plot; a plot of $\log_{10}(\eta^{-1})$ vs. $\log_{10}(\Lambda)$ where $\eta^{-1}$ and $\Lambda$ represent the reciprocal viscosity (or fluidity, in units of Poise$^{-1}$) and the molar conductivity (in units of S·cm$^{-2}$·mol$^{-1}$), respectively. The molar conductivity, $\Lambda$, is calculated from the specific conductivity, $\sigma$, and

Figure 1. (a) Measured viscosity of the (X)IL – (1-X)TEGDME binary mixtures as a function of temperature. (b) Conductivity of the (X)[Pyrr14][TFSI] – (1-X)TEGDME binary mixture as a function of a semi-continuous range of formulations at a single isotherm of 305 ± 1 K. (c) Conductivity of a set of discreet formulations of the (X)IL – (1-X)TEGDME binary mixture as a function of temperature. The inset graph represents a zoomed in section of the data at lower temperatures. The circle and diamond symbols represent data for the [Pyrr14][TFSI] and [N1124][TFSI] based mixtures, respectively. Solid and dashed lines (a and c) represent VTF correlation of the [Pyrr14][TFSI] and [N1124][TFSI] based mixtures, respectively.
Figure 2. Walden plot of the (X)IL – (1-X)TEGDME binary mixtures as a function of the temperature and composition. The different symbols represent individual compositions with a range of temperatures while the solid connecting lines represent the isothermal behavior as a function of composition. The dashed line and dash-dot line represent the so-called ideal KCl line and the respective Walden behavior with respect to temperature quite commonly is not equal to 1. In fact, the gradient of the reported binary mixtures ranges from 0.868 to 0.948 and the respective Walden intercepts (Log10(ρα)) unless CC License in place (see abstract).
where \( x \) and \( M_i \) are the molar fraction and molecular weight of components 1 and 2, respectively, \( \rho_{\text{exp}} \) is the experimentally measured density of the mixture and \( \rho_i \) is the density of the pure components 1 and 2. The calculated \( V_m^E \) values for the \((X)\)\(\text{[Pyr}_{14}\)\(\text{][TFSI]} \) – \((1-X)\)TEGDME are presented for a range of temperatures as a function of the composition in Figure 3. The solid lines represent correlation of the data by a third order Redlich-Kister polynomial expansion

\[
V_m^{E,\text{calc}} = x_1 x_2 \sum_{k=0}^{3} A_k (x_1 - x_2)^k
\]

where \( A_k \) is the coefficient of the polynomial expansion of the order \( k \). The coefficients of the Redlich-Kister correlation are presented in Table S7 in the ESI along with the standard deviation, \( \sigma_{SD} \), as calculated by the equation

\[
\sigma_{SD} = \left[ \frac{\sum (V_{m,\text{Exp}}^E - V_{m,\text{Calc}}^E)^2}{n - p} \right]^{0.5}
\]

where \( V_{m,\text{Exp}}^E \) represents the experimentally determined excess molar volumes, \( V_{m,\text{Calc}}^E \) represents the excess molar volume as calculated by Equation 13, and \( n \) and \( p \) represent the number of experimental data points and the number of coefficients used in the correlation, respectively.

The sign and magnitude of deviations in molar volumes shift as a function of the composition. In general, deviations from ideal \( V_m^E \) may be caused by cohesive or repulsive intermolecular interactions between the components of the mixture and/or by reorganization of the molecular packing within the solution depending on size and shape contributions. The sign of the \( V_m^E \) of the \((X)\)\(\text{[Pyr}_{14}\)\(\text{][TFSI]} \) – \((1-X)\)TEGDME binary mixtures takes the form of a S-shaped curve wherein the value is positive in IL rich formulations and shifts to larger, negative deviations in the solvent rich formulations. Furthermore, across the entire composition range the calculated excess molar volumes decrease (i.e. become more negative) with increasing temperature. In addition, the calculated excess molar volume for the \( X = 0.4 \) \([\text{N}_{1124}\text{][TFSI]} \) mixture corresponds to slightly larger negative deviations (ca. \(-1.67 \text{ cm}^3 \text{ mol}^{-1} \) at 298.15 K), albeit of a similar magnitude to the equivalent \([\text{Pyr}_{14}\text{][TFSI]} \) formulation.

Positive deviations in the IL rich compositions of the studied mixtures are indicative of expansion of the occupied volume relative to the molar volumes of the pure components. This could be attributed to the disruption of associative forces between constituent ions of the IL or the result of inefficient packing of the reasonably long chain oligoether in the IL structure. Conversely, upon further dilution with TEGDME the excess molar volume shifts to larger negative deviations indicative of contraction of the molar volumes. With \([\text{TFSI]}^{-} \)–based salts paired with small, charge dense alkali metal cations (i.e. \( \text{Li}^+ \) ions), the long flexible glyme chains are able to effectively coordinate the positive charge via the ethereal oxygen lone pairs. However, in mixtures with a bulky organic, more sterically hindered, weak Lewis acidic pyrroldinium cation, any such interaction would be expected to be weaker and significantly more complex. In the TEGDME rich formulations (wherein \( X_{\text{IL}} = 0.4, 0.2 \)) significant drops in the % ionocity (Table 1, Figure 2) are indicative of a reduction in the proportion of free ions available for the conduction of charge. This observation was supported by the strong, negative deviations in \( V_m^E \) shown in Figure 3. In the binary mixtures, the oxygen atoms in the glyme solvent chain will preferentially exist closer to areas of partial positive charge on the cation (in competition with the anion). For both cations, the reasonably distributed positive charge lies most accessibly on the alpha hydrogens of the four methyl/methylene carbons surrounding the nitrogen heteroatom center. As the quantity of TEGDME increases to equal and exceed a 1:1 mole ratio, the TEGDME may preferentially occupy the majority of these partially positive sites and, hence, restrict the available positioning of the negatively coordinating sulfonyl oxygens of the \([\text{TFSI]}^{-} \) anion within the first shell surrounding the IL cation. In effect, this spatial restriction may increase the probability of ion pair formation within the solvation core shell.

**Electrochemical measurements of IL/TEGDME blends.**—One attractive feature commonly exhibited by ILs is their wide electrochemical stability windows. Defined by the potential range between the cathodic and anodic potential limits of bulk reductive and oxidative decomposition of the electrolyte, respectively, large electrochemical stability windows have enabled access to previously inaccessible voltage ranges in electroanalytical and electrodeposition techniques. For electrochemical energy storage devices, the wide electrochemical window provides an electrochemically unreactive medium for supporting the electroactive faradaic processes in battery technologies and the electrostatic charge separation which underpins the energy storage mechanism in EDLCs. Given the direct proportionality between EDLC energy and power densities and the square of the cell operative voltage,\(^{31}\) increasing the stable voltage ranges of the materials is one of the main attractions of utilizing highly electrochemically stable ILs in this field. The electrochemical window of the studied IL/TEGDME mixtures was measured by cyclic voltammetry (CV) at a glassy carbon macro-disk working electrode (3 mm diameter) under an inert, dry atmosphere of an Ar-filled glove box. The CVs of the studied mixtures are shown in Figure 4. The onset potentials for reductive decomposition \( (E_{\text{r}}) \) and oxidative decomposition \( (E_{\text{o}}) \) of the electrolyte are approximated by a graphical method to estimate the potential at which a tangent to the main oxidation/reduction wall crosses the flat electrochemical baseline wherein no significant faradaic current is observed. The magnitude of the electrochemical stability windows, \( \Delta E \) (defined by the equation

\[ j \text{ -- } \text{mA cm}^{-2} \]

\[ E / V \text{ vs. } \text{Fc}^+ / \text{Fc}^- \]

**Figure 4.** Electrochemical stability window of the \((X)\)\(\text{[Pyr}_{14}\)\(\text{][TFSI]} \) – \((1-X)\)TEGDME binary mixtures at a glassy carbon macro-disk working electrode. All cycles were completed at a scan rate of 2 mV s\(^{-1}\). The electrochemical stability window of the pure acyclic alkylammonium IL, \([\text{N}_{1124}\text{][TFSI]} \), is also shown.
$\Delta E = E_a - E_c$ of the two ILs, [Pyr$_{14}$][TFSI] and [N$_{1124}$][TFSI], are almost identical at ca. (5.8–5.9) V. However, upon addition of the TEGDME solvent to the mixture, a significant reduction in the apparent anodic stability (ca. 1 V) of the electrolyte is observed irrespective of the solvent quantity. As such, while the onset potential for electrolyte oxidation increases by several tenths of millivolts with increased IL proportions, the anodic potential limit of the electrolyte mixtures is limited by the TEGDME solvent. This potential limit for the oxidative decomposition of TEGDME, 1.4–1.5 V vs. $\text{Fc}^+/\text{Fc}$, is in good agreement with previously reported values (i.e. $E_a = 4.7$–4.9 V vs. Li$^+$/Li based on the experimental approximation of $E(\text{Fc}^+/\text{Fc}) = 3.25$ V vs. $E(Li^+/Li)$ in this medium).$^{33}$

An investigation of the effect of binary mixture formulation of the transport, solubility, and electrochemistry of dissolved O$_2$ was conducted using voltammetric techniques at macro- and micro-disk electrodes in tandem. This has potentially interesting outcomes for the application of these formulations as IL-based electrolytes for amperometric O$_2$ sensors and non-aqueous metal-air batteries. Firstly, the application of these formulations as IL-based electrolytes for ampero-electrodes in tandem. This has potentially interesting outcomes for the conducted using voltammetric techniques at macro- and micro-disk electrodes. The measured CV traces for the $(x)$[Pyr$_{14}$][TFSI] – (1-$x$)TEGDME mixtures were completed under a sealed, static environment at 303 K. Cyclic voltammetry (CV) was first utilized to observed the O$_2$ re-duction/oxidation and, consequently, determine the potential step for each measurement was in the range of $-2.2$ to $-2.3$ V vs. Ag[OTf]/Ag over a period of 2 s. The solvent and diffusion coefficient of dissolved O$_2$ ($D(O_2)$), derived from correlation of CA transients using Equation 2, is shown as a function of the binary mixture formulation in Figure 6a. The numerical values are presented in Table S8 in the ESI. The O$_2$ solubility in neat [Pyr$_{14}$][TFSI] (10.21 mmol·dm$^{-3}$) is in reasonable agreement with our previously reported value under slightly different conditions (9.15 mmol·dm$^{-3}$ at 297 K).$^{36}$ The acyclic IL, [N$_{1124}$][TFSI], exhibits a slightly reduced solubility (8.09 mmol·dm$^{-3}$) compared to

![Figure 5](https://ecsd.org/site/terms_use) unless CC License in place (see abstract).
its cyclic analogue. However, dilution of both ILs with the TEGDME solvent yields reduction in the uptake of dissolved O2. This behavior is expected considering the lower solubility of O2 in pure TEGDME; reported previously, using non-electrochemical measurements, as 4.43 mmol·dm⁻³ at 298 K. Nevertheless, more interesting is the seemingly steep drop in O2 solubility moving from xIL = 1 to 0.9/0.8 which appears to level out at higher TEGDME fractions; indicating that even small quantities of the solvent reduce the desirable higher solubility in the pure IL. Considering the highly structured nature of many ILs, the TEGDME may be affecting disruptions in the IL structure and potentially removing free holes in which the small O2 molecule could occupy.

With regards to the transport of the dissolved gas, the O2 diffusivity is, as expected, lowest in the two neat ILs (i.e. the most viscous media). Dilution of the ILs with the TEGDME solvents yield significant promotions in the mobility of O2. Since viscosity is a measure of the materials resistance to flow, a logical inverse proportionality generally exists between the transport rate of solutes and the electrolyte viscosity. This relationship, i.e. \( D \propto \eta^{-1} \), where \( \eta^{-1} \) (the reciprocal viscosity) is known as the fluidity, is commonly discussed in terms of some variation of the Stokes-Einstein equation

\[
D = \frac{k_B T}{6\pi \eta a}
\]  

where \( k_B \), \( T \) and \( a \) represent the Boltzmann constant, the temperature, and the hydrodynamic radius of the solute in question, respectively. We recently reported that within a family of closely related cyclic alkylammonium [TFSI]⁺, based (including [Pyrr14][TFSI]), such a relationship is followed to a degree. Conversely, where a significant variety of IL structures are used, Einstein-Stokes type dependencies are typically not observed for O2, and other small solute molecules like H₂ and H₂S, suggesting that alternate solvent-solute interactions play an important role. Additionally, a lower dependence on the IL viscosity may be expected for a non-coordinating solute like O2, given the order of magnitude difference between measured values for \( D(O_2) \) and the previously reported self-diffusion coefficients for pure [Pyrr14][TFSI] (where \( D([Pyrr14]⁺) \) and \( D([TFSI]⁻) \) = 0.25 × 10⁻¹⁰ and 0.2 × 10⁻¹⁰ m²·s⁻¹, respectively, at 305 K). This relationship is explored for the IL/TEGDME binary mixtures in Figure 6b. For the [Pyrr14][TFSI]-based mixtures studied as a function of formulation, this relationship is non-linear across the studied range and, thus, inadequately described by Equation 15. Incidentally, the self-diffusion coefficient of neat TEGDME solvent at 303 K is 2–3 × 10⁻¹⁰ m²·s⁻¹. Though the diffusivity of the O2 analyte cannot be measured using these electrochemical techniques in a neat (and, therefore, electronically insulating) organic solvent, approximate extrapolation of the trend shown in Figure 6a for the [Pyrr14][TFSI]/TEGDME mixture would suggest this value (i.e. \( D(O_2) \) in neat TEGDME) would lie in the range of 13–16 × 10⁻¹⁰ m²·s⁻¹. Again, this is nearly an order of magnitude higher than the solvent molecule owing to the nonassociative nature of neutral O2 in TEGDME.

Interestingly, despite exhibiting lower O2 solubilities and slightly higher viscosities at both \( X = 1 \) and 0.4 than the equivalent [Pyrr14][TFSI] electrolytes, the [N1124][TFSI] based electrolytes affords improved O2 transport compared to the cyclic cation analogue. For the two neat ILs, the measured diffusion coefficients of the dissolved gas are within approximate experimental error but the higher O2 solubility in [Pyrr14][TFSI] may be related to the higher free volume (\( V_f \)) within this IL (where \( V_f = 41.38 \text{ cm}^3\cdot\text{mol}^{-1} \) and 40.42 cm³·mol⁻¹ at 303 K for [Pyrr14][TFSI] and [N1124][TFSI], respectively, as calculated using the COSMO-RS computational method). This would allow a greater quantity of cavities or holes within [Pyrr14][TFSI] which the small neutral O2 molecule can occupy. Within the two blended electrolytes, the O2 solubility/diffusivity will be affected by IL-solvent interactions. As previously discussed in the concluding paragraph of the Physical characteristics of electrolyte blends section, solvent coordination with the partially positive alpha hydrogens of each cation may consequently restrict the available sites for cation-anion interaction within the first shell surrounding IL cations. This, in turn, can increase the tendency for the formation of ion-pairs. Affect appearing most significant for the [N1124][TFSI] which the small neutral O2 molecule can occupy. Increasing the probability of TEGDME coordination with the -CH₂- or -CH₃ groups of the butyl and methyl groups, respectively. The acrylic [N1124][TFSI], however, is not constrained by a ring structure and, therefore, TEGDME-cation interaction may more readily occur at any of the four alpha hydrogen sites, allowing more effective solvation of the complete ion pair in this case. The resulting lower ion-pair solubility of [N1124][TFSI] will reduce probability of IL-O2 interactions and, it is speculated that, this allows greater mobility of the dissolved gas within the TEGDME rich pockets of these apparently non-homogenous mixtures. Further investigations, however, of the structural ordering and interactions in these IL-solvent mixtures are needed.

Following completion of micro-electrode measurements, the working electrode connection was moved to the glassy carbon macrodisk electrode where CV experiments were performed on the equivalent O2-saturated binary mixtures. The respective voltammograms for these mixtures are shown in Figures 7a and 7b. Multiple scan rates (\( \nu \)) were utilized between 5 and 500 mV·s⁻¹ within a voltage window of 0 to −2 V vs. Ag/AgOTf/Ag. A summary of the peak potentials, \( E_{pc} \) and \( E_{pa} \), peak current densities, \( j_{pc} \) and \( j_{pa} \), and peak charges, \( Q_p \) and \( Q_a \) (where subscript c or a refers to cathodic or anodic processes, respectively) for the 20 mV·s⁻¹ scans is shown in Table II. For the neat ILs, charge and current ratios for the redox processes exist very close to unity at these modest scan rates while these ratios are found to decrease by 10% and more at scan rates of 100 mV·s⁻¹ and greater. While this is a good indication of good
chemical reversibility (stability) on these timescales, peak-to-peak potential separations (i.e. $\Delta E_p$), however, exceed 59 mV (where $n$ is the number of electrons transferred). Further, both $\Delta E_p$ and $E_{p^-} - E_{pc^+}$ (where $E_{pc^+}$ represents the cathodic potential at half peak height) are found to increase consistently with increasing scan rates. This feature is commonplace within neat IL electrolytes wherein the process kinetics and mass transport may be mutually sluggish and the overall O2 reduction process is quasi-reversible.64-65 Plots of the cathodic reduction peak current density, $j_p$ vs. $\nu^{1/2}$ revealed mostly linear dependencies on the current magnitude with significant deviations occurring only at the higher scan rates. Plots of $j_p$ vs. $\nu^{1/2}$ for each studied electrolyte are shown in Figure S7 in the ESI along with the respective CV traces. Within each of these plots, the experimental current density peaks are compared with theoretical values based on the Randles-Ševčík equations for reversible systems

$$j_{p,rev} = -0.446nFC(nFDv/RT)^{0.5}$$  \[16\]

where $n = 1$ or 2 and for quasi-reversible systems

$$j_{p,\text{quasi}} = -0.496nFC(anFDv/RT)^{0.5}$$  \[17\]

where $j$ represents the current density in A·cm$^{-2}$, $F$ is the Faraday constant, $C$ and $D$ represent the analyte concentration (in units of mol·cm$^{-3}$) and diffusion coefficient (in units of cm$^2$·s$^{-1}$), respectively, $\alpha$ represents an approximation of the transfer coefficient, $\nu$ represents the scan rate (in units of V·s$^{-1}$) and $R$ and $T$ represent the molar gas constant (8.3145 J·mol·K$^{-1}$) and the absolute temperature, respectively. The value utilized for $\alpha$ was estimated, from the shape of the O2 reduction curve, using the equation proposed by Lavagnini et al.66

$$E_p - E_{p/2} = 1.857RT/anF$$  \[18\]

where all symbols are as defined previously and $E_p - E_{pc}$ is given in volts. These plots show that, particularly for the for the cathodic peaks, a general linear dependence in agreement with Equations 16 and 17 where $n = 1$, indicative of a single electron transfer process, as expected. However, deviations below $j_{p,rev}$ are consistently observed at higher scan rates.

For the two neat IL electrolytes, where the O$_2$/O$_2^+$ couple appears chemically reversible, treatment of the derived CV data by the Nicholson method affords an approximation of the heterogeneous electron transfer rate constant, $k_{st}$, by application of the relationship

$$\psi = k_{st}(\pi nD F v/RT)^{0.5}$$  \[19\]

where the symbols within the brackets are as defined previously and $\psi$ represents the kinetic parameter dependent on the peak potential separations, $\Delta E_p$.66 Values for $\psi$, applicable where $\Delta E_p < ca. 500$ mV, were estimated using Equation 20 proposed by Lavagnini et al.66 as a correlation of the original working curves constructed by Nicholson.66

The slope of the $\psi$ vs. $[\pi n D F v/RT]^{-0.5}$ plots, shown in Figure S8 in the ESI, provides an approximation of $0.7 \times 10^{-3}$ cm$^{-1}·s^{-1}$ and $1.2 \times 10^{-3}$ cm$^{-1}·s^{-1}$ for the $k_{st}$ value of O2 reduction in [Pyr14][TFSI] and [N1124][TFSI], respectively. However, a pre-requisite of this methodology is complete compensation for any iR-drop within the experiment which, qualitatively, appears insufficient for the [Pyr14][TFSI] IL and, thus, would yield an under-estimation for $k_{st}$. In support of this, by simulation of the CV traces at $50$ mV·s$^{-1}$ using the EC-Lab software, and a simple E-mechanism only, good agreement between simulation and experiment is only achieved when an additional ca. 500 mV is introduced (Figure S9 in the ESI). Post-processing of $E_p$ values for [Pyr14][TFSI] using $E_p(\text{corr}) = E_p + iR$ and $R = 500$ $\Omega$ followed by Nicholson treatment using the corrected $E_p(\text{corr})$ values affords a crude approximation of $k_{st} = 1.1 \times 10^{-3}$ cm$^{-1}·s^{-1}$.

Peak information relating to the $20$ mV·s$^{-1}$ CV traces shown in Figure 7a and 7b is provided in Table II as a function of the mole fraction of IL. As the proportion of TEGDME is increased, the reductive charge passed decreases initially but increases significantly

![Figure 7. iR-compensated cyclic voltammograms of O2-saturated (a) (X)[Pyr14][TFSI] – (1-X)TEGDME binary mixtures and (b) the [N1124][TFSI] IL and (0.4)[N1124][TFSI] – TEGDME binary mixtures at a 3 mm diameter glassy carbon macro-disk electrode at 303 K. All cycles were completed at a scan rate of 20 mV·s$^{-1}$.](image)

<table>
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<th>X$_{IL}$</th>
<th>$E_p$ / V vs. Fe$^{3+}$/Fe</th>
<th>$E_{pa}$ / V vs. Fe$^{3+}$/Fe</th>
<th>$\Delta E_p$ / V</th>
<th>$E_{1/2}$ / V vs. Fe$^{3+}$/Fe</th>
<th>$j_p$ / mA·cm$^{-2}$</th>
<th>$j_{pa}$ / $j_p$</th>
<th>$Q_p/Q_a$</th>
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for the higher TEGDME fractions (where $X_{\text{H}} = 0.6$ and 0.4). This trend is simply attributed to a trade-off between $O_2$ solubility, which is highest at low TEGDME fractions, and $O_2$ diffusivity which compensates the $O_2$ supply capability at higher TEGDME fractions. Further, as shown in Table II, $\Delta E_p$ tends to decrease with the addition of TEGDME solvent. However, more critically is the uniform reduction in the oxidative peak magnitude on the return sweep. As highlighted by the ratios between the peak current densities ($i_{\text{pc}}/i_{\text{pa}}$) and the oxidative and reductive charges ($Q_{\text{p}}/Q_{\text{a}}$), which decrease almost linearly as a function of the TEGDME mole fraction, the presence of the glyme solvent appears to drastically affect the chemical stability of the $O_2/O_2^*$ couple in these mixtures. This is indicative of a coupled irreversible homogeneous chemical reaction following the electroreduction of the superoxide to the TEGDME solvent. Additionally, peak current ratios $i_{\text{pc}}/i_{\text{pa}}$ (where $i_{\text{pa}}$ represents the peak currents estimated from a $y(t) = 0$ Ampere baseline) in the high TEGDME fraction blends were found to increase at increasing scan rates. Using Nicholson’s semi-empirical relationship between reactions. However, any such proton abstraction or ether hydroperoxides enhances the O$_2$ supply capability at higher TEGDME fractions. Further, the two neat ILs, differing in molecular structure and temperatures firstly highlights the important potential for thermal and electrochemical properties of the ILs, the results further highlight the importance of the pursuit for new, highly stable, electrolyte solvent materials.

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