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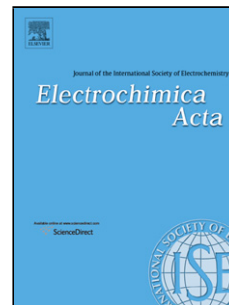
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Pulsed-Field Gradient NMR Self Diffusion and Ionic Conductivity Measurements for Liquid Electrolytes Containing LiBF₄ and Propylene Carbonate

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Abstract

Liquid electrolytes have been prepared using lithium tetrafluoroborate (LiBF₄) and propylene carbonate (PC). Pulsed-field gradient nuclear magnetic resonance (PFG-NMR) measurements were taken for the cation, anion and solvent molecules using lithium (⁷Li), fluorine (¹⁹F) and hydrogen (¹H) nuclei, respectively. It was found that lithium diffusion was slow compared to the much larger fluorinated BF₄ anion likely resulting from a large solvation shell of the lithium. Ionic conductivity and viscosity have also been measured for a range of salt concentrations and temperatures. By comparing the measured conductivity with a ideal predicted conductivity derived from the Nernst-Einstein equation and self diffusion coefficients the degree of ionic association of the anion and cation was determined and was observed to increase with salt concentration and temperature. Using the measured viscosity and self diffusion coefficients the effective radius of each of the species was determined for various salt concentrations.

Keywords: NMR, liquid electrolyte, conductivity, ionic association

1. Introduction

Liquid electrolytes are of scientific interest due to their use in electrochemical devices, they consist of an ionic salt dissolved in a solvent. The choices of these materials play a vital role in determining the dynamics of the ions in solution. Usually lithium based

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6 salts are chosen due to the high charge density that the lithium ions possess. The anion
7 is usually chosen to be relatively large in size to create an uneven charge distribution,
8 which promotes ionic dissociation. Since the primary application of liquid electrolytes
9 is in electrochemical devices it is important for the ions to be relatively mobile and free
10 to conduct, therefore a low ionic association is desired in these systems. In this study
11 lithium tetrafluoroborate (LiBF_4) was dissolved in propylene carbonate (PC) at molar
12 concentrations between 0.1-1.5M (mol dm^{-3}), which corresponded to molal concentrations
13 between 0.08-1.37 mol kg^{-1} . The aim of this current research is to probe the motion of the
14 ions in solution as a function of both temperature and salt concentration. A secondary
15 aim of this paper is to pave the way for future publications on polymer gel electrolytes;
16 which involve adding polymer to a liquid electrolyte at high temperatures to form a
17 porous polymer network filled with liquid electrolyte.
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20 Following the pioneering research of Wright [1] and Armand [2] into solid polymer
21 electrolytes and their potential for use in lithium batteries, thermo-reversible polymer
22 gel electrolytes (PGEs)[3, 4] have been studied at the University of Leeds with the in-
23 troduction of solvents [5, 6]. These gel electrolytes combine the high ionic mobility of
24 conventional liquid electrolytes with the mechanical advantage of incorporating a poly-
25 mer. Typical PGEs comprise of poly(vinylidene) fluoride (PVDF), propylene carbonate
26 (PC) and lithium salts[7, 8]. A first stage in developing a fundamental understanding of
27 these gel electrolytes has been to study the behaviour of model liquid electrolyte solu-
28 tions. Understanding the transport properties of these liquid electrolytes is important to
29 use as a basis of comparison. Therefore in this paper the pure liquid electrolyte system
30 is reported which will aid in the understanding of future papers concerning polymer gel
31 electrolytes.
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34 The experimental techniques which have been used to understand the dynamics of
35 the current system are pulsed-field gradient NMR, dielectric spectroscopy and viscos-
36 ity measurements. NMR has been proven to be a valuable tool for understanding the
37 dynamics of liquid solutions via different techniques. In a previous publication it has
38 been shown that the use of NMR relaxation times yield valuable information about the
39 rotational and translational motion of the ions in solution [9]. In this paper pulsed-field
40 gradient NMR was used in order to measure the translational self diffusion constants.
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6 It is possible to isolate individual nuclei using the corresponding resonant frequency. In
7 this paper results for ^1H , ^7Li and ^{19}F nuclei have been measured which corresponds to
8 the solvent molecules, lithium cation and fluorinated BF_4 anions, respectively. Therefore
9 measuring the diffusion constant in this manner can yield information about the dynam-
10 ics of each constituent within the liquid electrolytes; and these have been observed with
11 changing temperature and salt concentration. Pulsed-field gradient NMR measurements
12 have been carried out elsewhere on LiBF_4/PC systems for both liquids and polymer
13 gel electrolytes[10, 11]; however usually covering many samples over a small number of
14 concentrations and temperatures.
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20 Dielectric spectroscopy has been employed to measure the ionic conductivity of the
21 liquid electrolytes. The ionic conductivity of an electrolyte is of scientific interest due
22 to the primary application of these solutions as electrochemical devices; which require
23 high conductivities to adequately perform. Detailed research into liquid electrolytes con-
24 taining LiBF_4 have been measured elsewhere with carbonated solvents such as propylene
25 carbonate and their mixtures [12, 13, 14, 15]. In these papers many salt concentrations
26 and temperatures have been probed and have a main emphasis on covering a large range
27 of solvent mixtures. In the research presented here a single salt and solvent system was
28 chosen in order to understand the core principals of the dynamics of the individual con-
29 stituents. It should also be noted that in this research a conductivity cell was used which
30 are commonly used in solid or gel research. The reason for choosing such a technique was
31 in order to later compare the polymer gel electrolyte conductivity which were measured
32 using the same conductivity cell. This paper will not only consider the conductivity at
33 many different temperatures and salt concentrations, but will compare these results with
34 the diffusion constants which allow a more in depth study of the dynamics and solvation
35 of the ions in solution than previously reported.
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45 Viscosity measurements were also taken at various temperatures and salt concen-
46 trations. The viscosity of a liquid electrolyte directly affects the mobility of the ions
47 and therefore the conductivity. The viscosity was measured using a standard Ostwald
48 viscometer which relies on a calibration sample and measured density. The density of
49 the liquid electrolytes was measured alongside the viscosity measurements using several
50 volumetric flasks, which were housed in the same water bath as the viscometer. The
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6 use of the viscosity in this research was to determine trends in the average radius of the
7 solvent molecules, lithium cations and fluorinated BF_4 anions. It is also suggested in
8 this research that by fitting a simple exponential to the viscosity and diffusion data as a
9 function of salt concentration that the trends in the effective radii can be determined.

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12 It is commonly known that the ionic conductivity will be affected by the number
13 of charge carriers that form neutral pairs. It is possible by using the Nernst-Einstein
14 equation along with the translational diffusion constants to predict the conductivity; with
15 the assumption that all charge carriers are unpaired and contributing to the conductivity.
16 Therefore by comparing the predicted and measured conductivities it was possible to give
17 an estimation of the degree of ionic association in the liquid electrolytes. Other methods
18 have been employed to probe the ion-ion interactions such as Raman spectroscopy as well
19 as using the Walden product and limiting molar conductivities [16, 17], however the use of
20 the Nernst-Einstein equation to predict conductivity was proven to be effective for
21 both liquid electrolytes [18, 19, 20, 21, 22, 23] and polymer gel electrolytes [24, 25, 26, 27]
22 and has been shown to yield a good approximation of the ionic interactions.
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31 **2. Experimental**

32 *2.1. Sample Preparation*

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35 All samples were prepared in an oxygen-free nitrogen filled glove box. The liquid elec-
36 trolytes were prepared by mixing LiBF_4 salt with PC solvent at molar concentrations of
37 0.1-1.5M at room temperature with magnetic stirrer bars. In this study the salt concen-
38 tration is expressed as salt molality rather than molarity; as molality is independent of
39 temperature. The molar concentrations of 0.1-1.5M corresponds to molal concentrations
40 in the range of 0.08-1.37 mol kg^{-1} . The PC used was 99.7% anhydrous, both the PC and
41 LiBF_4 were vacuum sealed from Sigma-Adrich. The liquid electrolyte samples for the
42 NMR diffusion measurements were sealed into 10 mm glass tubes for the ^{19}F and ^7Li
43 measurements and 5 mm glass tubes for the ^1H measurements. The tubes were sealed
44 in the nitrogen atmosphere of the glovebox to avoid any moisture in the samples.
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51 The conductivity samples were also sealed inside the cell while in the glovebox, to
52 reduce the chance of any moisture entering the system. While inside the Novocontrol
53 BS1200 conductivity rig there was a constant supply of nitrogen gas which kept the
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6 sample in a nitrogen atmosphere during measurements. Some preliminary measurements
7 were taken for liquid samples that were left in the cell for extended periods of time
8 before being measured; these measurements yielded the same results and therefore it was
9 assumed that moisture in the atmosphere was not affecting the sample.
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12 2.2. NMR Diffusion

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15 NMR diffusion previously measured at Leeds [25] used a Stejskal-Tanner pulse se-
16 quence. Here the NMR pulse sequence used was a complex bipolar stimulated echo
17 pulsed-field gradient (BPStE-PFG) originally designed by Cotts [28]. Cotts sequence
18 was an adapted form of a Stejskal-Tanner pulse sequence which eliminates background
19 magnetic fields and has been used here at Leeds in previous studies [8].
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23 Background magnetic field gradients manifest due to inhomogeneities in the magnetic
24 field. The use of bipolar pulses removes these background magnetic field gradients. This
25 introduces the relation for intensity of signal in the form of;
26

$$27 \quad I = I_0 \exp \left(-4\pi^2 \gamma^2 \delta^2 G^2 D \left(\Delta - \frac{\delta}{3} \right) \right) \quad (1)$$

28
29 where G is the gradient field strength, Δ is the time between subsequent gradient pulses, δ
30 is the gradient pulse duration and D is the self diffusion coefficient. The NMR parameters
31 used were $\Delta=40$ ms, $\delta=10$ ms and the time between radio frequency (rf) and gradient
32 pulses was 1 ms [25]; these values were unchanged throughout the experiments. The
33 diffusion experiments are two dimensional as they are performed multiple times each with
34 a different value for the pulsed-field gradient strength G . As the gradient is increased the
35 intensity would decrease and therefore by fitting equation 1 to the decay of intensity as a
36 function of gradient strength the diffusion constants were determined. The software that
37 was used was Bruker Topspin 1.5, this software contains a function that calculates the
38 maximum gradient strength to be used depending on the value of the diffusion constant
39 being measured. Between the application of each of the various gradient strengths a time
40 was left in order for the magnetisation from the previous run to dissipate. This delay is
41 known as the recycle delay and was set here to $5T_1$.
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51 The three different nuclei used here were ^1H , ^7Li and ^{19}F which correspond to the
52 solvent molecules, cations and anions, respectively. The diffusion coefficients were meas-
53 ured using a 400 MHz Bruker AVANCE II Ultrashield NMR spectrometer. All diffusion
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6 measurements were carried out using a Diff60 probe supplied by Bruker. Three resonant
7 frequencies used were 400 MHz, 155 MHz and 376 MHz for the ^1H , ^7Li and ^{19}F nuclei,
8 respectively. The 90° pulse durations were measured using an inbuilt software function
9 of Bruker Topspin 1.5 which was used as an interface for the diffusion measurements.
10 The pulse durations used were determined to be $6.6 \mu\text{s}$ at a power level of 0 dB, $15.4 \mu\text{s}$
11 and $19.6 \mu\text{s}$ at a power level of 3 dB for the ^1H , ^7Li and ^{19}F , respectively.
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15 The fitting of the equation 1 has been carried out using Bruker topspin1.5 software
16 which utilises an iterative process based on the Levenberg-Marquardt algorithm [29, 30],
17 in each case the integrated intensities were used.
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21 *2.3. Ionic Conductivity*

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23 Electrical conductivity has two contributing factors, the conductivity of the ions
24 within the liquid electrolytes (ionic conductivity) and the conductivity arising from the
25 movement of electrons (electronic conductivity). The liquid electrolytes are dominated
26 by the ionic conductivity here making the electronic conductivity negligible. Therefore
27 the term conductivity was synonymous with ionic conductivity in these liquid electro-
28 lytes. The conductivity is defined as the inverse of the resistivity of the sample and was
29 determined by using;
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$$34 \sigma = \frac{1}{\rho} = \frac{d}{AR_s} \quad (2)$$

35
36 where σ is the ionic conductivity, ρ is the resistivity of the solution, d is the thickness of
37 the sample, A is the cross-sectional area of the electrodes and R_s is the bulk resistance of
38 the sample. The bulk resistance was taken as the real impedance at the point where the
39 imaginary impedance was zero. The conductivity cell used had a cross sectional area of
40 $(0.975 \pm 0.009) \text{ cm}^2$ and a thickness of $(2.01 \pm 0.02) \text{ mm}$. Therefore the cell constant used
41 for all measurements was given by the ratio of d/A of $(0.22 \pm 0.01) \text{ cm}^{-1}$.
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46 Conductivity measurements were taken with a Novocontrol Alpha Beta frequency
47 analyser which was connected to a modified BDS1200 Novocontrol conductivity rig. The
48 conductivity cells were custom built and consisted of two stainless steel electrodes with
49 polytetrafluoroethylene (PTFE) spacers; PTFE was chosen as the spacer as it is inert
50 and has a very high melting temperature. The cells were made using inert stainless
51 steel blocking electrodes prohibiting the lithium ions from chemically reacting with the
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6 electrodes. An alternating current (AC) was applied to the cell by the Novocontrol
7 analyser in the frequency range of 1-10⁷ Hz. The total impedance of the conductivity
8 cell is given by;

$$Z_{Cell} = \left[\frac{R_s}{1 + (\omega C_s R_s)^2} \right] - i \left[\frac{\omega C_s R_s^2}{1 + (\omega C_s R_s)^2} + \frac{1}{\omega C_{dl}} \right] \quad (3)$$

10
11 where C_s is the capacitance of the electrolyte, C_{dl} is the capacitive term from the elec-
12 trodes (or double layer), ω is the frequency of the AC signal and i denotes the imaginary
13 term of the impedance. When $\omega C_s \ll R_s$ the total impedance of the cell can be reduced
14 to;

$$Z_{Cell} \approx R_s - \frac{i}{\omega C_{dl}} \quad (4)$$

15 therefore the real part of the impedance was equal to the bulk resistance of the sample
16 when the imaginary impedance was zero. In order to determine the point at which this
17 occurs Cole-Cole (Nyquist) plots were used.

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19 The temperature of the sample was maintained by a flow of nitrogen gas through with
20 a 400 W heater. The heater was monitored and controlled by a Eurotherm thermostat.
21 In this research each sample was sealed inside the conductivity cell and all temperatures
22 were measured consecutively from low temperature (253 K) to high temperature (353 K).
23 Each sample was repeated a minimum of three times in order to obtain an average with
24 an uncertainty which indicates the reproducibility of the measurements. It was found
25 that between repeat readings the variance was no more than 2%.

26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 2.4. Viscosity

41 The viscosity of the liquid electrolytes were measured at different temperatures and
42 salt concentration using a standard Ostwald viscometer ('U' tube). The temperature
43 was controlled via a water bath placed on a hotplate operated by a thermocouple and
44 Eurotherm thermostat. This method limited the temperature range of 293-333 K. Two
45 thermocouples were placed inside the water bath in order to ensure there was no tem-
46 perature gradient. One was placed at the bottom of the bath and was connected to the
47 thermostat, the other at the top which was used as a reference temperature. In addition
48 a mechanical stirrer was placed in the bath in an attempt to keep the temperature of the
49 bath homogeneous. At all times the two thermocouples were within 0.5 K of each other.

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6 A calibration sample was used in order to to eliminate the need for geometrical
7 constants, the ratio of the viscosities is given by:
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$$\frac{\eta_{Sample}}{\eta_{Calibration}} = \frac{t_{Sample}\rho_{Sample}}{t_{Calibration}\rho_{Calibration}} \quad (5)$$

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11 where ρ_{Sample} and $\rho_{Calibration}$ are the densities of the sample solution and calibration
12 solution, respectively and t_{Sample} and $t_{Calibration}$ are the time taken to fall a given length
13 through the tube in each instance. Here pure PC was used as the calibration liquid as
14 it has been well characterised elsewhere [31]. Only the viscosity of pure PC was used
15 from Barthel et al [31]; the density of the pure PC was measured *in situ*. The density
16 was measured using 10 ml volumetric flasks, these flasks were housed in the same water
17 bath as the viscometer; this was to ensure a systematic temperature between the two
18 measurements. Two different volumetric flasks were placed in the water bath, both
19 containing the same solution; this was to achieve an average and an attempt to reduce
20 the error. In intervals of 10 K the flasks were set at the 10 ml line and weighed. It was
21 found that there was very little difference between the two flasks.
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31 **3. Results**

32 *3.1. NMR Self Diffusion*

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35 Pulsed-field gradient stimulated echo NMR diffusion measurements of liquid electro-
36 lytes containing PC/LiBF₄ were measured for samples with salt concentration in the
37 range of 0.1-1.5M, which corresponds to molal concentrations in the range 0.08-1.37 mol
38 kg⁻¹. This upper limit was chosen due to the salt reaching saturation. It has been shown
39 that the stimulated echo pulse sequence is a more reliable method of measuring self dif-
40 fusion than a standard gradient echo sequence [32]. The three resonant frequencies used
41 were for the ¹H, ⁷Li and ¹⁹F nuclei in order to track the diffusion of the PC molecules,
42 cation and anion, respectively. When choosing the diffusion time Δ for the self-diffusion
43 measurements the longitudinal relaxation times (T_1) have to be considered. The diffu-
44 sion times are usually set so that the T_1 values are much longer than the diffusion time.
45 This is to ensure that there is no decay of the signal during the diffusion measurement.
46 However since the pulsed-field gradient stimulated echo pulse sequence was a constant
47 time experiment the value the diffusion time did not have to be much smaller than T_1 .
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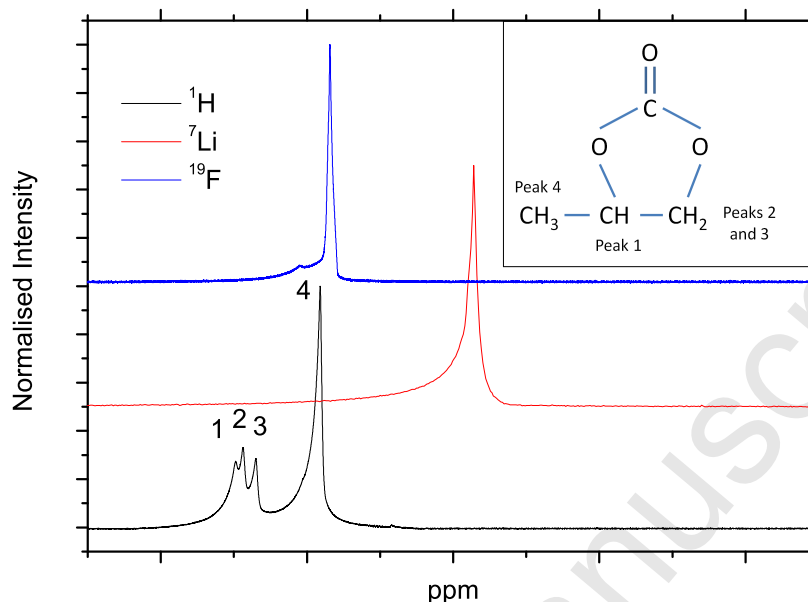


Figure 1: NMR spectra for PC/LiBF₄ liquid electrolytes using ¹H, ⁷Li and ¹⁹F. The ¹H and ⁷Li spectra are for PC/LiBF₄ (0.89 mol kg⁻¹) and PC/LiBF₄ (0.61 mol kg⁻¹) for the ¹⁹F spectrum. The ¹H, ⁷Li and ¹⁹F nuclei were used to measure diffusion of PC molecules, lithium cation and fluorinated anion respectively. All spectra taken at 303 K. Arbitrary chemical shift reference was used. Inset shows structure of propylene carbonate (PC).

If the diffusion time was too long (i.e. $2-3T_1$) then the signal would decay too much and therefore the signal to noise ratio (SNR) would be too large. The longitudinal relaxation times were measured for this system elsewhere[9] and found to be of the order of seconds. The diffusion time used here was 40 ms, which is two orders of magnitude smaller, therefore no decay occurred during the diffusion measurements and the SNR was observed to be very good.

Typical spectra for each nuclei are displayed in figure 1 which shows the NMR spectra for PC/LiBF₄ (0.89 mol kg⁻¹) for the hydrogen and lithium nuclei and PC/LiBF₄ (0.61 mol kg⁻¹) for the fluorine nucleus. The fluorine and lithium spectra exhibited a single peak in the NMR spectra. There was a slight shoulder to some of the fluorine spectra however this was attributed to the shimming. The hydrogen spectrum which was essentially the NMR spectrum for the propylene carbonate molecule exhibited four peaks. The four peaks were attributed to the various hydrogen sites on the molecule. The inset to figure

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6 1 shows the structure of the propylene carbonate molecule which has a C-H, a C-H₂ and
7 a C-H₃ bond attached the the ring. The four peaks of the NMR spectra are attributed to
8 these different hydrogen sites. The peaks have been denoted 1-4 where peak 1 represents
9 the C-H bond, peaks 2 and 3 represent the C-H₂ and peak 4 represents the C-H₃ bond.
10 Peak 4 exhibited a much higher intensity than the other peaks, this was attributed to
11 the C-H₃ bond having three times the number of hydrogen atoms than the other sites.
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15 The diffusion for the hydrogen nucleus was determined from the area of the spectrum
16 as a function of gradient strength (G), the entire spectrum was used. However clearly it
17 is possible to also determine the diffusion of each of the peaks of the hydrogen spectrum.
18 The diffusion measurements of each peak were found to be very similar within error of
19 each other. Taking for example a PC/LiBF₄ (0.89 mol kg⁻¹) liquid electrolyte at 293
20 K the values of diffusion were (2.07±0.02), (2.06±0.02), (2.06±0.02) and (2.06±0.01)
21 (10⁻¹⁰ m² s⁻¹) for peaks 1-4 of the PC molecule, respectively. The largest deviance
22 between peaks was observed at higher temperatures, however, the deviance was around
23 0.5% at maximum. The intensity was used to fit the peaks as there was some overlap of
24 peaks 1-3 and therefore an area fit would contain contributions of the neighboring peaks.
25 When fitting the spectrum as a whole the area was more reliable as the strongest peak
26 (peak 4) would overpower the others in an intensity fit.
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34 The diffusion coefficients for the ¹H, ⁷Li and ¹⁹F nuclei as a function of salt con-
35 centration are shown in figure 2 which represent the PC molecules, lithium cation and
36 fluorinated BF₄ anion, respectively. For most salt concentrations the PC molecules were
37 the fastest diffusing entity followed by the BF₄ anion then the lithium cations. This is
38 counter-intuitive as the lithium ions are the smallest entity and therefore since all ions
39 and molecules are traveling through the same medium, should exhibit the largest dif-
40 fusion coefficient. This was attributed to the fact that solvents such as PC which are
41 polar protic, have been found to solvate the cation more favourably than the anion[33].
42 This is due to the cation having a high charge density which is more attractive than
43 the dispersed charge of the anion. Also the structure of PC contains a carbonyl group
44 (C=O) which protrudes from the ring, containing a small negative charge which will
45 easily bond with the lithium positive charge. This results in the effective radius of the
46 lithium ions being large due to the solvation shell [34]; this diffusion order has been seen
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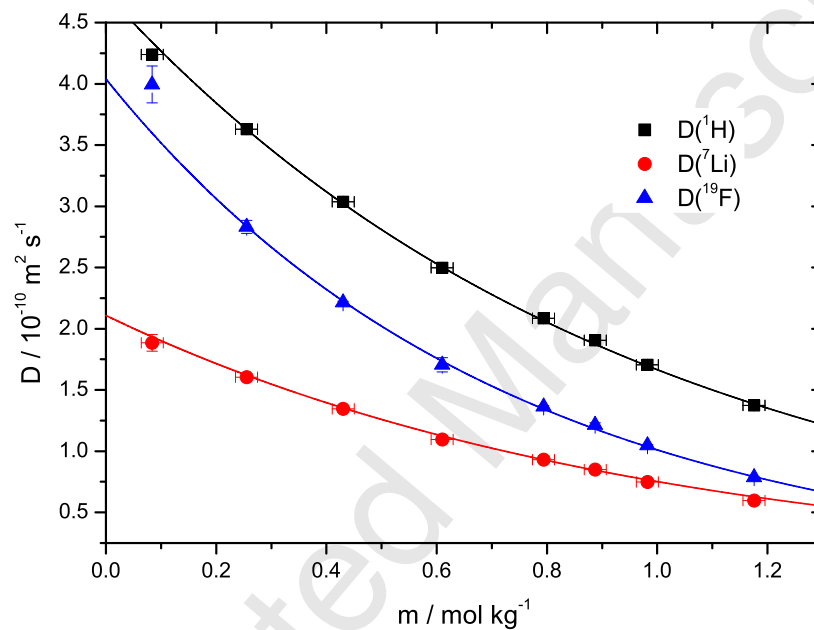


Figure 2: Self diffusion coefficients for PC/LiBF₄ liquid electrolytes with increasing salt concentration. All diffusion measurements carried out at 293 K. ¹H, ⁷Li and ¹⁹F nuclei are displayed which represent the PC molecules, lithium cation and fluorinated anion (BF₄) respectively. The error values for the diffusion were determined from both the fitting of the diffusion decay curve and repeat readings and were of the order $0.05 \times 10^{-10} \text{m}^2 \text{s}^{-1}$. The data has been fitted with equation 6.

Temperature / K	$D_0 / 10^{-10} \text{ m}^2 \text{ s}^{-1}$			$A_D / \text{mol kg}^{-1}$		
	^1H	^7Li	^{19}F	^1H	^7Li	^{19}F
283	—	1.66	3.08	—	0.87	0.70
293	4.99	2.15	3.95	0.98	0.96	0.75
303	6.23	2.81	4.94	1.07	1.02	0.79
313	7.72	3.50	6.00	1.13	1.08	0.83
323	9.16	4.21	7.30	1.19	1.15	0.86
333	11.6	4.99	9.04	1.15	1.23	0.89
343	12.5	5.91	10.5	1.33	1.33	0.93
353	—	8.26	12.2	—	1.23	0.99

Table 1: Salt concentration fitting parameters A_D and D_0 for diffusion constants for PC/LiBF₄ liquid electrolytes using ^1H , ^7Li and ^{19}F nucleus which represents the solvent molecules, cation and anion respectively.

in many different lithium salts in various other solvents [35, 36, 19, 18, 11]. There are a considerable number of publications on the diffusion of the solvent molecules, cation and anion of lithium based salts in various solvents using this method [18, 19, 11, 37, 21]. With increasing salt concentration the diffusion of the lithium cations and BF₄ anions converge; ionic association is the likely cause of such a convergence in the case where the BF₄ anions are associating with lithium-solvent clusters. This convergence has been seen elsewhere in a system containing EC:EMC (ethylene carbonate : ethylene methylene carbonate) (2:8) with LiBF₄ [38].

The salt concentration dependence of the diffusion measurements were fitted to a simple exponential in the form;

$$D(m) = D_0 \exp\left[-\frac{m}{A_D}\right] \quad (6)$$

where D_0 is the diffusion at infinite dilution, m is the molal salt concentration and A_D is an exponential fitting parameter. The A_D factor determines the rate at which the diffusion decreases with increasing salt concentration. A smaller value of A_D corresponds to the diffusion decreasing at a faster rate. If the diffusion decrease was caused purely from the increase in viscosity of the system then it would be expected that the A_D values

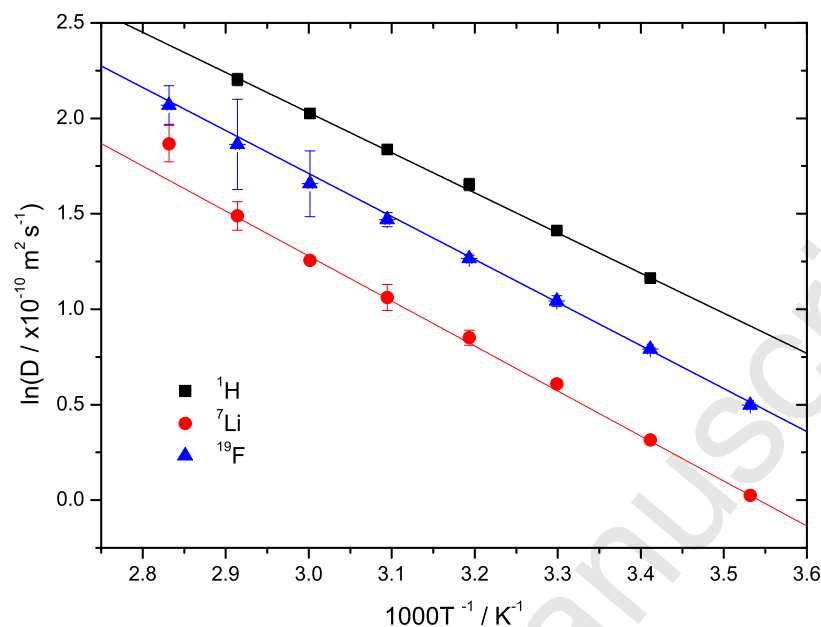


Figure 3: Arrhenius plot for self diffusion coefficients for PC/LiBF₄(0.43 mol kg⁻¹) liquid electrolyte. Here linear fits have been applied suggesting Arrhenius type temperature dependence. ¹H, ⁷Li and ¹⁹F nuclei are displayed which represent the PC molecules, lithium cation and fluorinated anion (BF₄) respectively.

would be the same for all nuclei. The parameters of these fits are displayed in table 1. It was observed that the order of the A_D values were $^1\text{H} > ^7\text{Li} > ^{19}\text{F}$, which meant that the fluorine species had the most significant variation with increasing salt concentration. These values can be compared with similar values determined for the viscosity, which is discussed further in section 3.3. All A_D values were observed to increase with increasing temperature which was attributed to the increase in ions to solution.

The temperature range of the diffusion measurements was 293-353 K; the upper limit here was set due to concerns of temperature gradients in the samples at high temperatures which is a known problem in NMR diffusion measurements. A new type of NMR tube has been devised elsewhere [39] to avoid this problem, however here standard NMR tubes were used. Arrhenius plots for the diffusion are shown in figure 3, which involves plotting the natural log of the diffusion values against the inverse of temperature. If the resulting Arrhenius plots can be fitted well with a linear fit then the system is considered to exhibit

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6 Arrhenius type temperature dependence. Linear fits have been applied to figure 3, it can
7 be readily observed that the linear line fits the data well, suggesting Arrhenius type
8 dependence of the form;

$$D = D_{\infty} \exp\left[\frac{E_D}{RT}\right] \quad (7)$$

10
11 where D_{∞} is a diffusion at infinite temperature and E_D is the energy required for the ac-
12 tivation of diffusion. VTF type temperature dependence has been seen for other systems
13 with LiPF_6 in carbonated solvents ethylene carbonate (EC), dimethyl carbonate (DEC)
14 and propylene carbonate (PC), however this dependence was seen for measurements in a
15 much wider temperature range (233-353 K)[21]. Therefore it was expected that the dif-
16 fusion values would exhibit VTF type temperature dependence at a larger temperature
17 range. The activation energy E_D shown in figure 4 increased with salt concentration.
18 This is intuitively reasonable as at high salt concentrations the solution is more vis-
19 cous and hence requires more energy for the ions to translate, therefore increasing the
20 activation energy.
21
22

23 The activation energy of the lithium ions is greater than that of the fluorine, sug-
24 gesting again that the lithium ions are larger than the fluorine ions, therefore requiring
25 more energy to move through the liquid. However, the activation energies converge at
26 high salt concentrations, supporting the hypothesis that the fluorine and lithium become
27 more associated at high salt concentrations.
28

29 3.2. Conductivity

30 In this section the conductivity results of LiBF_4 in propylene carbonate are discussed.
31 Propylene carbonate is a popular choice of solvent both as a single solvent [40] and as
32 part of a multiple solvent system[41, 14, 15, 42] with various, usually lithium based salts.
33 Conductivity measurements of PC/ LiBF_4 solutions have been measured previously else-
34 where [43, 13], however in this paper the conductivity measurements will be used along
35 with the diffusion measurements to determine the ionic association of the solution. In
36 the previous publication of the conductivity behaviour of PC/ LiBF_4 solutions [43, 13],
37 the conductivity was determined using an LCR meter with an overall accuracy of 0.5%
38 quoted. It should be noted that the conductivity measurements were in good agreement
39 with the measurements taken previously[43, 13]. Ding has previously measured the con-
40 ductivity of a PC/ LiBF_4 (0.2863 mol kg^{-1}) liquid electrolyte at 292.5 K as 2.976 mS cm^{-1}
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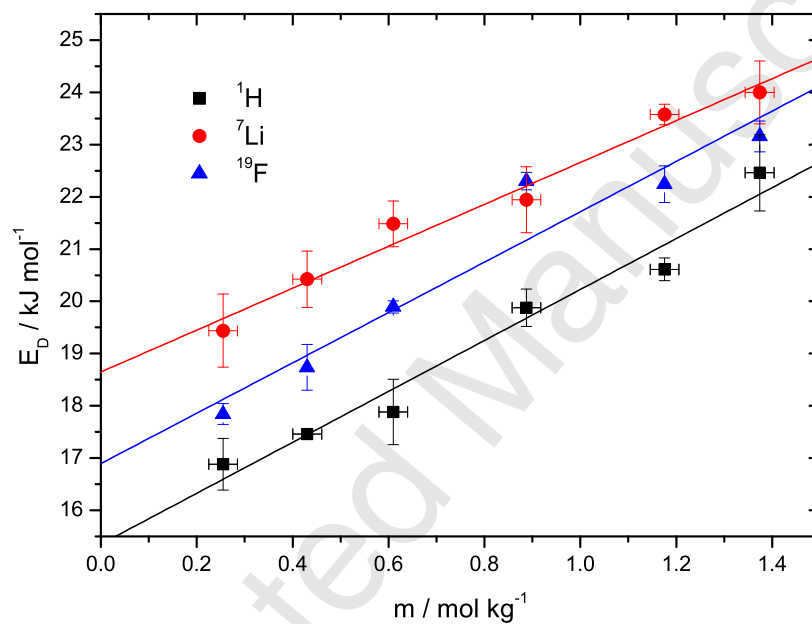


Figure 4: Activation energies for self diffusion coefficients for PC/LiBF₄ liquid electrolytes for ¹H, ⁷Li and ¹⁹F nuclei are displayed which represent the PC molecules, lithium cation and fluorinated anion (BF₄) respectively. The errors included were determined from the fitting of the Arrhenius equation to the data and were found to be the order of 0.1 kJ mol⁻¹. All data was fitted with linear lines.

[43], comparing this value to the closest possible value measured here of PC/LiBF₄ (0.26 mol kg⁻¹) at 293 K gave (2.77±0.03) mS cm⁻¹. In the same publication the conductivity of a PC/LiBF₄ (0.8373 mol kg⁻¹) liquid electrolyte at 292.5 K was 3.134 mS cm⁻¹ [43], again comparing this value to the closest possible value measured here of PC/LiBF₄ (0.89 mol kg⁻¹) at 293 K gave (3.03±0.03) mS cm⁻¹. Therefore both of these examples show that the data measured here are in good agreement with those measured earlier, with the slight discrepancies being attributed to the difference in salt concentration and temperature.

Conductivity measurements were carried out over a temperature range of 253-353 K in 10 K intervals. A frequency range of 1-10⁷ Hz was used in these measurements. A Cole-Cole plot was used to determine the point at which the imaginary impedance was zero. The high frequency semi-circles normally characteristic of a Cole-Cole plot were absent in this research due to the conductive nature of the electrolytes studied. However the high frequency end of the semi-circle along with the linear diffusive layer response was present. The bulk resistance of the sample that was used in equation 2 was determined as the real impedance when the imaginary impedance was zero on the Cole-Cole plot.

The temperature dependence of the conductivity was determined in the same manner as the diffusion, Arrhenius plots for PC/LiBF₄ (0.08, 0.89 and 1.18 mol kg⁻¹) liquid electrolytes are shown in figure 5. Both linear (dashed) and non-linear (solid) fits were applied and it has been determined that the non-linear Vogel-Tamman-Fulcher (VTF) type dependence is the optimum fit for the conductivity data in the form;

$$\sigma(T) = \sigma_0 \exp\left[\frac{-E'_\sigma}{R(T - T_0)}\right] \quad (8)$$

where the pre-exponential factor σ_0 is thought to be related to the number of charge carriers [44], E'_σ is a temperature dependent energy term which is dependent on the free energy barrier opposing mobility and T_0 is the ideal glass transition temperature. The values of these parameters have been determined for varying salt concentration of LiBF₄. The ionic conductivities of liquid electrolytes are commonly seen to exhibit VTF type temperature dependence [19, 45].

It was found that the value of T_0 was independent of salt concentration, so was set to the average value of 155 K. This was in agreement with work previously reported that showed that T_0 is independent of salt concentration in systems containing poly(ethylene

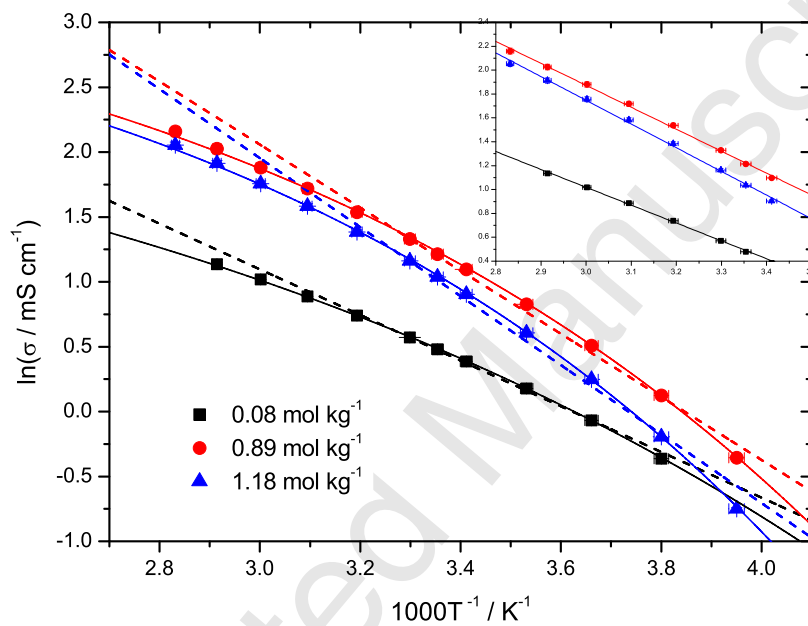


Figure 5: Arrhenius plot for conductivity data of PC/LiBF₄ (0.08, 0.89 and 1.18 mol kg⁻¹) liquid electrolytes. Both linear (dashed) and non-linear (solid) fits have been used here, where the linear fit represents Arrhenius type behaviour and non-linear fit (equation 8) represents a VTF type temperature dependence. The errors included here were seen to be around 2% due to very reproducible data between repeat readings. Inset shows the reduced temperature range Arrhenius type behaviour of the liquid electrolytes.

glycol) with LiCF_3SO_3 , LiClO_4 , NaClO_4 , LiBF_4 and NaBF_4 [44]. Figure 6 shows that the activation energy of the conduction mechanism increases with increasing salt concentration; attributed to the ions requiring more energy as the liquid becomes more viscous. The value of σ_0 was seen to increase with salt concentration and this is attributed to the increase in the number of ions in solution.

It would be reasonable to assume that if the diffusion measurements exhibited Arrhenius type temperature dependence that the conductivity would exhibit similar temperature dependence. The conductivity measurements covered a temperature range of 253-353 K, where as the diffusion measurements were limited to 293-353 K. Non-Arrhenius type temperature dependence is usually seen at temperatures near to the glass transition temperature of the sample. Therefore the diffusion temperature dependence was assumed to be Arrhenius at the temperature range measured, however would likely be non-Arrhenius at lower temperatures. In order to compare the activation energies of the diffusion and conductivity, the temperature range of the conductivity was analysed with a reduced temperature range of 293-353 K. The inset of figure 5 shows Arrhenius plots for the reduced temperature range for PC/ LiBF_4 (0.08, 0.89 and 1.18 mol kg^{-1}) liquid electrolytes. It should be noted that for the temperature range 293-353 K the conductivity data Arrhenius type temperature dependence and therefore the diffusion data was assumed to be Arrhenius due to the limited temperature range. Arrhenius type temperature dependence when in the temperature range 298-343 K has been witnessed elsewhere for a different liquid electrolyte [46]. Similar to the diffusion Arrhenius fitting the conductivity data was fitted to an Arrhenius equation of the form;

$$\sigma(T) = \sigma_{\infty} \exp\left[\frac{E_{\sigma}}{RT}\right] \quad (9)$$

where σ_{∞} is the conductivity at infinite temperature and E_{σ} is the activation energy of the ionic conduction. The activation energies of the VTF fits and the reduced temperature Arrhenius fits are shown in figure 6 which shows that the activation energy increases with salt concentration for both fitting procedures. The activation energies were seen to exhibit a linear relationship with salt concentration much like the activation energies of the diffusion constants. The activation energies of the Arrhenius fits were all seen to be larger than the corresponding VTF activation energies. This result was reasonably intuitive from simply observing the equations as the VTF equation is scaled by the ideal

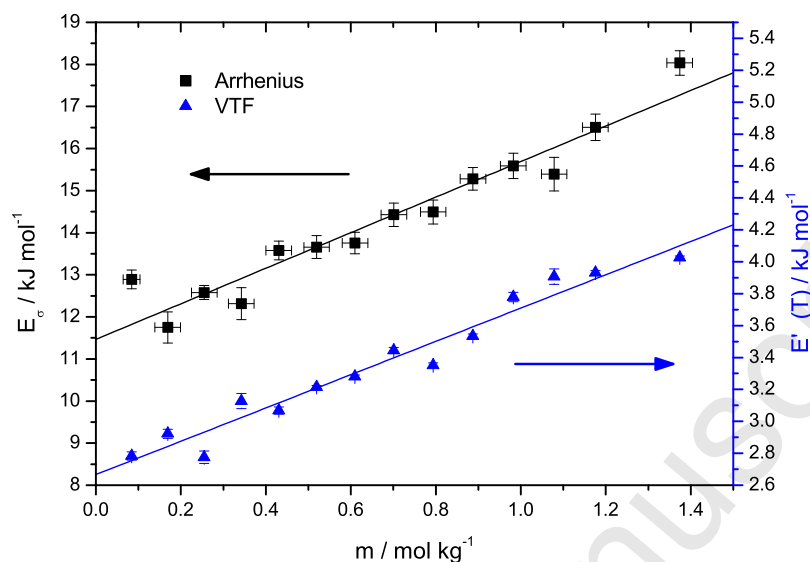


Figure 6: VTF energy term (E'_σ) and Arrhenius activation energy (E_σ) for reduced temperature range (293-353 K) for conductivity measurements of PC/LiBF₄ liquid electrolytes. For the VTF energy term T_0 was held constant for at 155K for all fits.

glass transition temperature.

Figure 7 shows the conductivity of liquid electrolytes as a function of salt concentration for PC/LiBF₄ at 253 K, 293 K, 313 K and 333 K. Analysis of figure 7 clearly shows that the conductivity increases with increasing salt concentration at low salt concentrations, then above a critical salt concentration the ionic conductivity begins to decrease. The peak was attributed to a competition between number of ions added to solution, viscosity and ionic association of the solution. Increasing the salt concentration introduces more charge carriers into the solution, however, viscosity of the solution also increases hindering the motion of the ions. The ionic association is defined as the measure of how many of the salt ions added to the solution are free for conduction. The balance between these factors is manifested as a broad peak in conductivity with salt concentration; seen commonly in other systems[13]. Aihara et al [47] have measured the conductivity of PC/LiBF₄ liquid electrolytes at 1.0M of salt at room temperature (293 K). They found the conductivity to be around 3.0 mS cm⁻¹ which was in very good agreement with the value obtained here of (3.00±0.06) mS cm⁻¹. The black linear line shown in figure 7 was

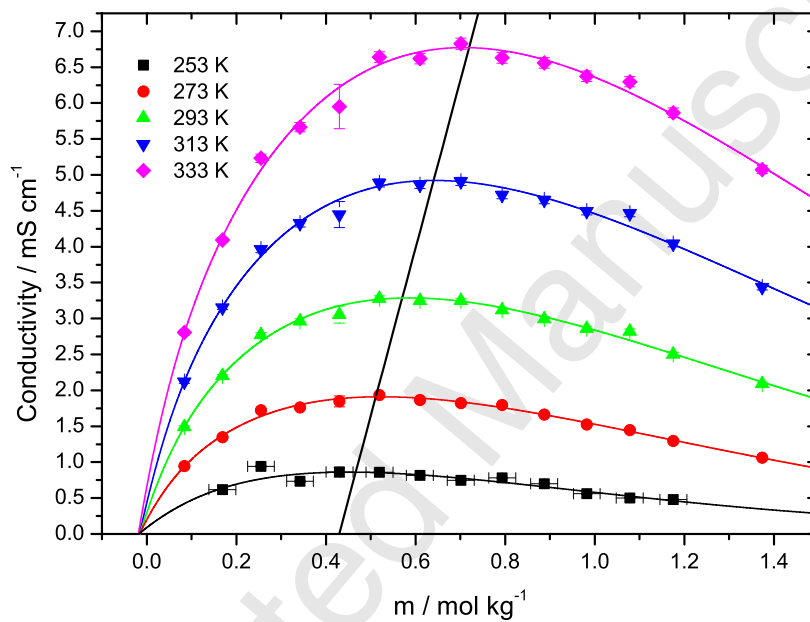


Figure 7: Conductivity for PC/LiBF₄ liquid electrolytes against salt concentration. Measurements shown taken at 253 K, 293 K, 313 K and 333 K for all salt concentrations. Casteel-Amis (equation 10) fits have been employed to the data (solid lines). The linear black line has been included to highlight the shift in the position of the maximum with temperature. Error in salt concentration taken as 0.02 mol kg⁻¹ which was determined as the most reliable the samples could be produced.

the fitted through the position of the maximum for each temperature. It can be readily noted that the linear line had a positive gradient suggesting that the position of the peak shifted with increasing temperature, this has been discussed further in the discussion section.

The Casteel-Amis equation[48] was used to fit the data in Figure 7 and has the form,

$$\sigma(m) = \sigma_{Max} \frac{m}{m_{Max}}^a \exp \left\{ b(m - m_{Max})^2 - \frac{a}{m_{Max}} (m - m_{Max}) \right\} \quad (10)$$

where m is the salt concentration in molality, σ_{Max} is the maximum conductivity at any given temperature, m_{Max} is the salt concentration at which the conductivity is at a maximum and a and b are fitting parameters. The Casteel-Amis equation is a semi-empirical equation which is commonly used for determining the salt concentration dependence of liquid electrolytes[49, 50, 51]. A Casteel-Amis plot is shown in figure 8 where the conductivity and salt concentration have been normalised by using the value of σ_{Max} and m_{Max} for each temperature respectively. Casteel-Amis plots have been prepared to show that the conduction mechanism in the liquid electrolyte is unchanged with both increasing temperature and salt concentration. All of the curves overlap suggesting that the ions are conducting in the same manner regardless of temperature and concentration.

3.3. Viscosity

Viscosity measurements have been taken for PC/LiBF₄ liquid electrolytes at salt concentrations in the range of 0.08-1.37 mol kg⁻¹ at temperatures between 298-333 K. The viscosity in figure 9 was seen to increase with salt concentration. This trend was expected as the more salt introduced to the system the more it will impede the flow of the ions. The rise in temperature gives more energy towards activation and therefore allows higher mobility of the ions. The salt concentration dependence is classically characterised by the Jones and Dole equation[52];

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc \quad (11)$$

where η is the bulk viscosity of the system, η_0 is the viscosity of the pure solvent in this case PC, c is the concentration of the salt in the solution and A and B are fitting parameters. A is related to the mobility and interactions of the ions in solution and B

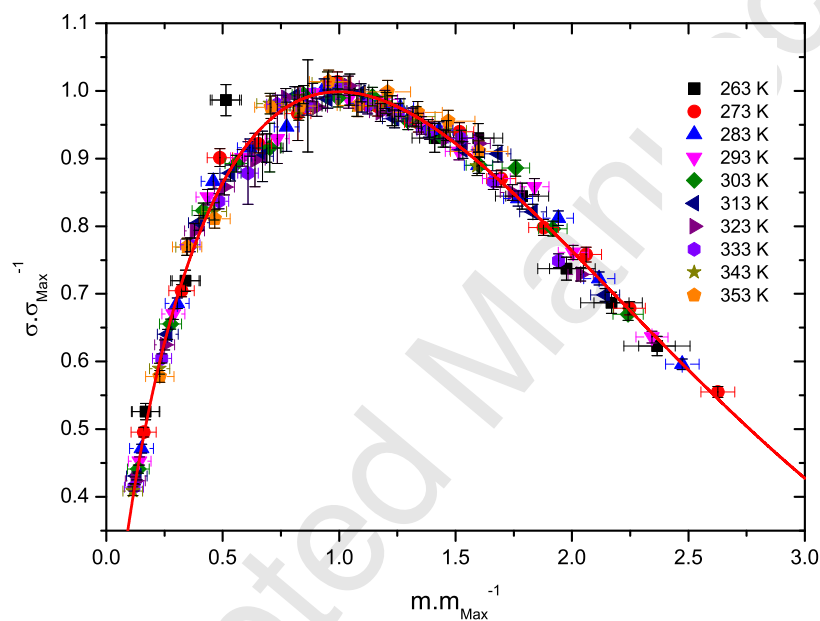


Figure 8: Casteel-Amis plot for PC/LiBF₄ liquid electrolytes, normalised for relevant maximum values. Temperature taken from 253 K to 353 K for all salt concentrations. Casteel-Amis (equation 10) was fitted to all data (solid line).

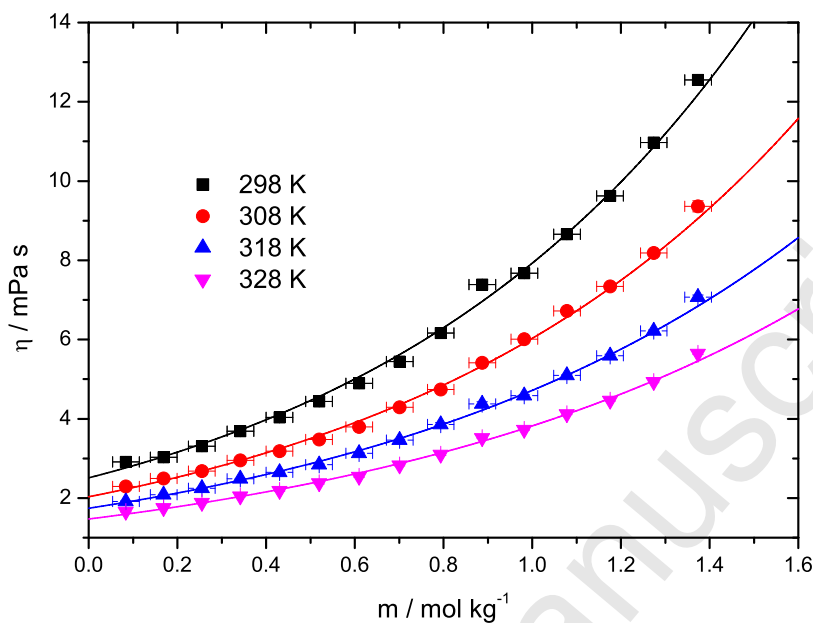


Figure 9: Viscosity against salt concentration for liquid electrolytes containing PC/LiBF₄ at various temperatures. The data has been fitted with a simple exponential of the form of equation 13.

is related to the interactions between the ions and solvent molecules[53]. Equation 11 is only valid for salt concentrations $c < 0.1\text{M}$ [54] and therefore cannot be used here.

For electrolytes at higher salt concentrations it has been shown that adding extra terms at higher orders of magnitude were introduced to allow fitting of these concentrations. Jones and Talley [55], Kaminsky [56] among others introduced a quadratic term to equation 11 in the form;

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc + Dc^2 \quad (12)$$

where the Dc^2 term includes all solute-solvent and solute-solute interactions that were previously unaccounted for in equations 11. The concentration range for this equation is $c < 0.2\text{M}$; which again is too limited for this system. There are also many other empirical fits to salt concentration dependence of the viscosity data of liquid electrolytes including equations by Vand, Afzal, Othmer, Kestin, Klugman, Feldenkamp and Einstein a summary of which is in references [57] and [58]. In this research it was found that the

Temperature / K	A_η / mol kg ⁻¹	η_0 / mPa s	
		Extrapolated	Measured
298	0.86	2.49	2.51
303	0.88	2.26	2.28
308	0.91	2.02	2.08
313	0.96	1.88	1.91
318	1.00	1.74	1.75
323	1.02	1.59	1.62
328	1.05	1.47	1.50
333	1.09	1.38	1.40

Table 2: Viscosity salt concentration fitting parameters A_η and viscosity of pure PC (η_0) for PC/LiBF₄ liquid electrolytes. Both extrapolated η_0 values and those measured by Barthel *et al* are included [31].

best fit was a simple exponential of the form;

$$\eta(m) = \eta_0 \exp\left[\frac{m}{A_\eta}\right] \quad (13)$$

where η_0 is the viscosity of the pure solvent, m is the molal salt concentration and A_η is a fitting constant. This equation was the same form as the diffusion salt concentration equation (equation 6); the salt concentration fitting parameters are displayed in table 2. The extrapolated pure solvent viscosity was comparable to the measured viscosity measured elsewhere [31] suggesting that fit was valid. By comparing A_η with the earlier discussed A_D for the diffusion measurements it revealed that for the hydrogen and lithium measurements $A_\eta < A_D$ which means that the diffusion was decreasing at a slower rate than described by the viscosity. This result therefore suggests that the ionic radii of the hydrogen and lithium nuclei decreases with salt concentration. The inverse was observed for the fluorine measurements as $A_\eta > A_D$ which suggests that the diffusion is decreasing at a faster rate than described by the viscosity, suggesting an increase in ionic radii with salt concentration. The A_η parameter was observed to increase with temperature which was attributed to a decrease in the viscosity of the system.

Arrhenius plots of viscosity have been produced in figure 10 and linear fits suggest

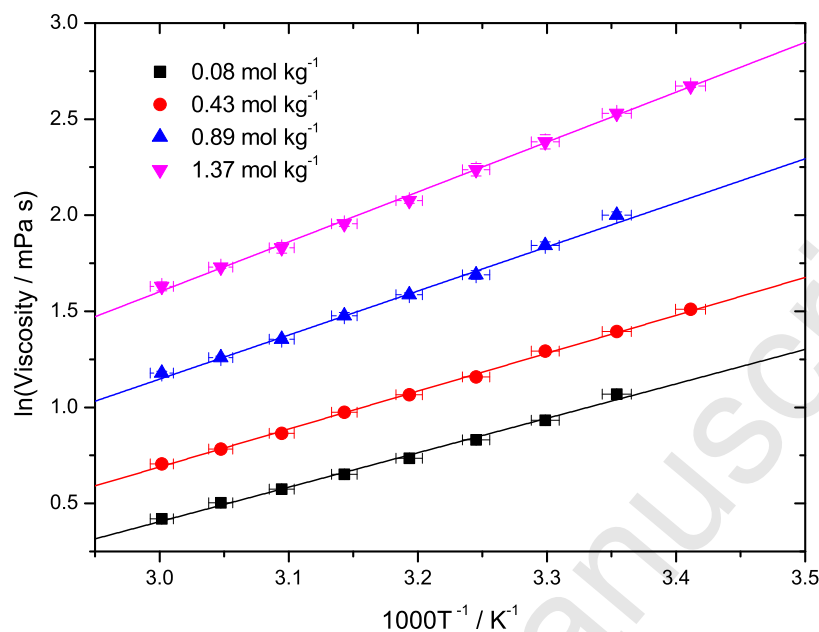


Figure 10: Arrhenius plot for PC/LiBF₄ liquid electrolyte viscosity. Linear fits have been used here, suggesting that the temperature behaviour is Arrhenius.

Arrhenius type behaviour, expressed via:

$$\eta(T) = \eta_{\infty} \exp\left[\frac{E_{\eta}}{RT}\right] \quad (14)$$

where η_{∞} is the viscosity at infinite temperatures and E_{η} is the activation energy of the motion of the ions. The viscosity and diffusion have both been shown to display Arrhenius type behaviour, whereas the conductivity exhibits VTF type dependence. The difference in the temperature dependence type was attributed to the larger temperature range of the conductivity measurements, as VTF temperature dependence is usually observed close to the glass transition temperature of the sample. Therefore the diffusion and viscosity measurements were too high to observe the VTF dependence. These trends have been seen elsewhere with different liquid electrolyte systems [59].

4. Discussion

Table 3 shows the activation energies for the diffusion, conductivity and viscosity processes. As with the other processes the activation energy of viscosity increased with

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6 increasing salt concentration, which suggests that the energy required for the ions to
7 translate and thus the activation energy increases with salt concentration. In order to
8 compare the different activation energies, the conductivity activation energy was taken
9 as the reduced fit Arrhenius values. The diffusion activation energies at low salt con-
10 centration (0.26 mol kg^{-1}) were $(16.9 \pm 0.5) \text{ kJ mol}^{-1}$, $(19.4 \pm 0.7) \text{ kJ mol}^{-1}$, $(17.8 \pm 0.2) \text{ kJ}$
11 mol^{-1} for the ^1H , ^7Li and ^{19}F nuclei, respectively which suggested that the size order
12 of each nuclei was $^1\text{H} < ^{19}\text{F} < ^7\text{Li}$ as a larger activation energy suggests a larger radius.
13 It would be expected that the activation energies of the diffusion and viscosity would
14 be comparable as both mechanisms are purely translational, however the diffusion are
15 microscopic measurements and the viscosity measurements are macroscopic. The activa-
16 tion energy of the viscosity for the PC/LiBF₄ (0.26 mol kg^{-1}) sample was $(15.1 \pm 0.1) \text{ kJ}$
17 mol^{-1} which was comparable to the diffusion activation energies. The reduced temper-
18 ature range conductivity activation energy was $(12.6 \pm 0.2) \text{ kJ mol}^{-1}$ which is lower than
19 the other activation energies. The conductivity was not a purely translational mechan-
20 ism and therefore it was assumed that the degree of ionic association would affect the
21 activation energy.
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31 The activation energies at high salt concentration (1.37 mol kg^{-1}) were (22.5 ± 0.7)
32 kJ mol^{-1} , $(24.0 \pm 0.6) \text{ kJ mol}^{-1}$, $(23.2 \pm 0.3) \text{ kJ mol}^{-1}$ for the ^1H , ^7Li and ^{19}F diffusion,
33 respectively which again suggested a size order of $^1\text{H} < ^{19}\text{F} < ^7\text{Li}$; this trend was un-
34 affected by salt concentration. It should be noted that the activation energies of the
35 fluorine and lithium nuclei have converged at higher salt concentration suggesting that
36 the fluorine radius has increased. At higher salt concentrations the fluorine was likely
37 associating with the lithium ions, therefore observing a convergence of the activation
38 energies. The activation energy of the viscosity for the PC/LiBF₄ (1.37 mol kg^{-1}) sample
39 was $(21.6 \pm 0.2) \text{ kJ mol}^{-1}$ which again was comparable to the diffusion activation energies.
40 The reduced temperature range conductivity activation energy was $(18.0 \pm 0.3) \text{ kJ mol}^{-1}$
41 which was observed to be lower than the other activation energies. It should be noted
42 that the ratio of conductivity and viscosity activation energies was practically unchanged
43 with salt concentration which suggests that the increase in the activation energy of the
44 conductivity was primarily due to the viscosity. It was also observed that the activa-
45 tion energies of the diffusion and viscosity converged at high salt concentration. The
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Salt Conc. / mol kg ⁻¹	Activation Energy / kJ mol ⁻¹				
	Diffusion			Conductivity	Viscosity
	¹ H	⁷ Li	¹⁹ F		
0.08	—	—	—	12.9	14.9
0.26	16.9	19.4	17.8	12.6	15.1
0.43	17.5	20.4	18.7	13.6	16.4
0.61	17.9	21.5	19.9	13.8	17.5
0.89	19.9	21.9	22.3	15.3	19.1
1.18	20.6	23.6	22.2	16.5	20.5
1.37	22.5	24.0	23.2	18.0	21.6

Table 3: Activation energies for diffusion constants using ¹H, ⁷Li and ¹⁹F nuclei which represents the PC molecule, cation and fluorinated anion (BF₄) respectively as well as activation energies of viscosity and reduced temperature range conductivity for PC/LiBF₄ liquid electrolytes. All activation energies determined from Arrhenius fitting of the data. The error on the activation energies were all found to be of the order 0.1 kJ mol⁻¹.

conductivity activation energies were within 20% of the viscosity energies, where as the diffusion activation energies of were within 10%, 20% and 15% for the ¹H, ⁷Li and ¹⁹F of the viscosity energies respectively.

4.1. Ionic Association

Using the diffusion coefficients of the anion and cation along with the Nernst-Einstein equation (equation 15) a predicted value of conductivity can be determined,

$$\sigma(T) = \frac{nq^2}{k_B T} [D(^{19}\text{F}) + D(^7\text{Li})] \quad (15)$$

where n is the number of ions per unit volume of charge q added to the electrolyte. $D(^{19}\text{F})$ and $D(^7\text{Li})$ correspond to the diffusion coefficients of the BF₄ anion and lithium cation, respectively; obtained from pulsed-field gradient NMR experiments. Using this equation requires the assumption that there is no association between anion and cation. Therefore the difference between the measured conductivity and that determined from equation 15 is the degree of ionic association can be calculated using:

$$\alpha = \left(1 - \frac{\sigma_{\text{Measured}}}{\sigma_{\text{Predicted}}} \right) \quad (16)$$

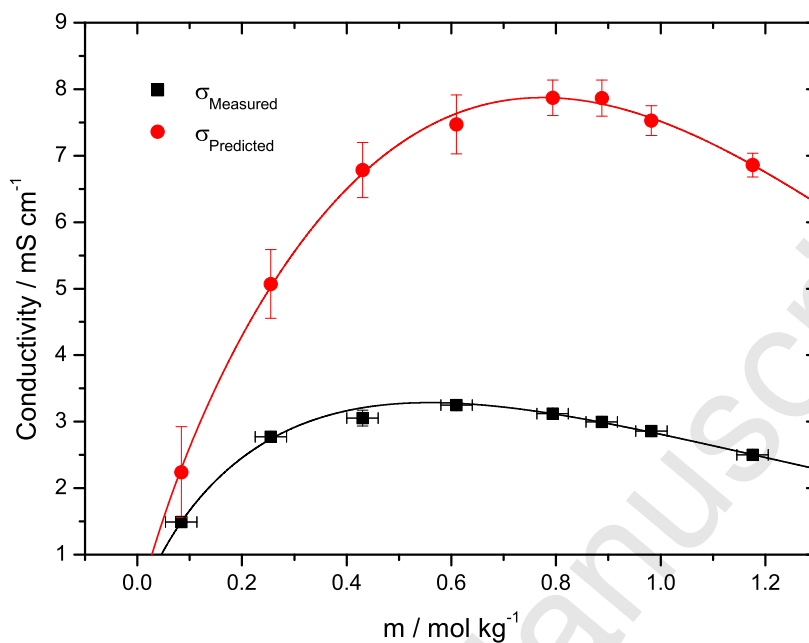


Figure 11: Conductivity for both directly measured (square) and predicted (circle) from the Nernst-Einstein equation with salt concentration for PC/LiBF₄ at 293 K. Both sets of data were fitted with the Casteel-Amis equation (equation 10).

where α is the degree of ionic association and σ_{Measured} and $\sigma_{\text{Predicted}}$ refer to the directly measured conductivity and conductivity predicted from equation 15, respectively. Therefore the degree of ionic association is the number of ions which are neutral entities within the liquid electrolyte which do not contribute to the conductivity. The Nernst-Einstein equation is a commonly used tool to determine the level of ionic association (sometimes expressed as the ionic dissociation) for liquid electrolytes[45, 60, 61].

Figure 11 shows the predicted conductivity was significantly higher than the corresponding measured conductivity. It also shows that the predicted conductivity exhibits a peak, but at a significantly higher salt concentration than the measured conductivity. Since the viscosity is the same for each case, this difference has been attributed to ionic association and will be discussed later in section 4.2. Using equation 16 and the ratio of measured and predicted conductivity the ionic association was calculated.

Figure 12 shows the degree of ionic association for these liquid electrolytes as a function of salt concentration. It can be seen that there is an increase of ionic association with

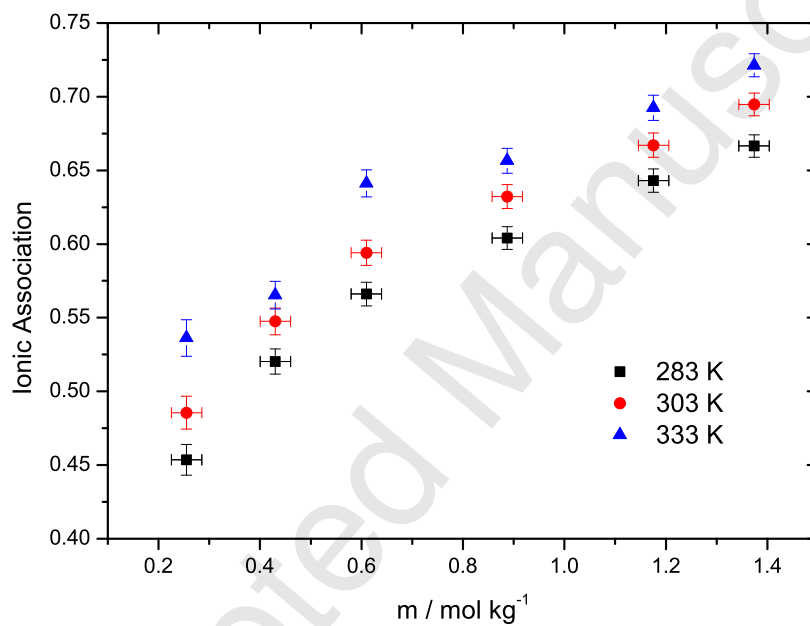


Figure 12: Degree of ionic association against salt concentration for PC/LiBF₄ at 293 K. Error values were determined from error propagation from the values of diffusion of both the cation and anion as well as the the measured conductivity.

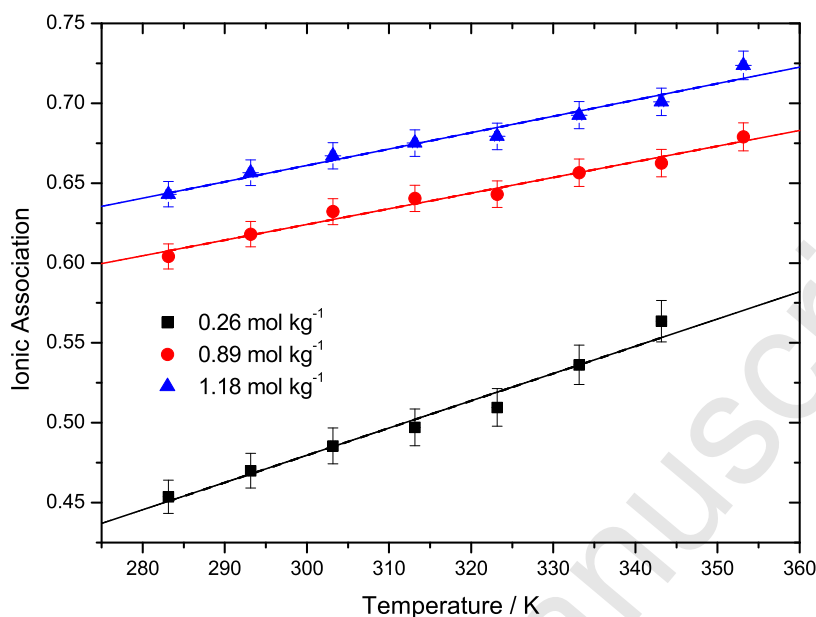


Figure 13: Degree of ionic association against temperature for PC/LiBF₄ liquid electrolytes. Error values were determined from error propagation from the values of diffusion of both the cation and anion as well as the the measured conductivity. Linear fits have been applied to the data.

salt concentration, a similar result has been shown for six different lithium based salts with gamma-butyrolactone (GBL) as the solvent [11]. Also highlighted by the Aihara *et al* research (ref [11]) was that the order of association for the six different salts were LiSO₃CF₃ > LiBF₄ > LiBETI ≈ LiBOB ≈ LiTFSI ≈ LiPF₆. This suggests that the salt used here (LiBF₄) had one of the largest ionic associations of the six salts analysed in their research. The trend with increasing salt concentration was attributed to an increased density of ions, resulting in a decreased inter-ion distance.

The temperature dependence of the ionic association is shown in figure 13, which reveals an increase in the ionic association with temperature. This has been seen in other systems and was attributed to the lowering of free energy of ion pair formation at higher temperatures [25]. This result is somewhat counter intuitive since as the temperature is raised the ions would have more thermal energy and therefore one might expect this to promote ionic dissociation. It has been stated by Olender *et al* [25, 62] that for a chemical reaction such as this, in the form $MA \rightleftharpoons M^+ + A^-$, an equilibrium constant

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6 can be defined as:

$$7 \quad K = \exp\left[-\frac{\Delta G^0}{RT}\right] \quad (17)$$

8
9 where K is the equilibrium constant, G^0 is the difference between the standard Gibbs
10 free energy of the reactants and the products and T is the absolute temperature. The
11 difference in free energy can be simply expressed as:
12
13

$$14 \quad \Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (18)$$

15
16 where ΔH^0 is the change in enthalpy and ΔS^0 is the change in entropy. The enthalpy can
17 be broken down into two different components, the positive energy term for promoting
18 dissociation of the salt ions and a term dependent on the pressure and volume change
19 due to the reaction. It was stated by Olender *et al* [62] that the volumetric term of the
20 enthalpy can outweigh the positive energy term and also be negative due to electrostric-
21 tion. This would allow the ionic association to increase with increasing temperature as
22 observed in this study. It has also been found in research elsewhere that the dielectric
23 constant of a liquid electrolyte can decrease with increasing temperature, which would
24 also increase the ionic association at higher temperatures [63].
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31 32 4.2. Conductivity Peak Shift

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34 It was shown earlier that a peak in the conductivity was observed with salt concen-
35 tration. This was attributed to an initial increase in the number of free ions however
36 an inevitable increase in viscosity eventually dominates the system and the conductivity
37 starts to decrease. It was also stated earlier that there was a shift in the position of
38 the peak with increasing temperature. Figure 14 shows the position of the maximum
39 (m_{Max}) as a function of temperature for the predicted and measured conductivity of the
40 liquid electrolytes. The temperature dependence of the m_{Max} parameter has been shown
41 in other liquid systems based on propylene carbonate [64].
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47 It was observed that the predicted conductivity exhibited a much higher peak posi-
48 tion (m_{Max}) than the measured conductivity. It was stated earlier that since the only
49 difference between the measured and predicted conductivities is the degree of ionic asso-
50 ciation, as the predicted conductivity assumed no ionic association. An increase in the
51 ionic association would result in a lowering of the conductivity and therefore a reduction
52 of the position of the maximum (m_{Max}).
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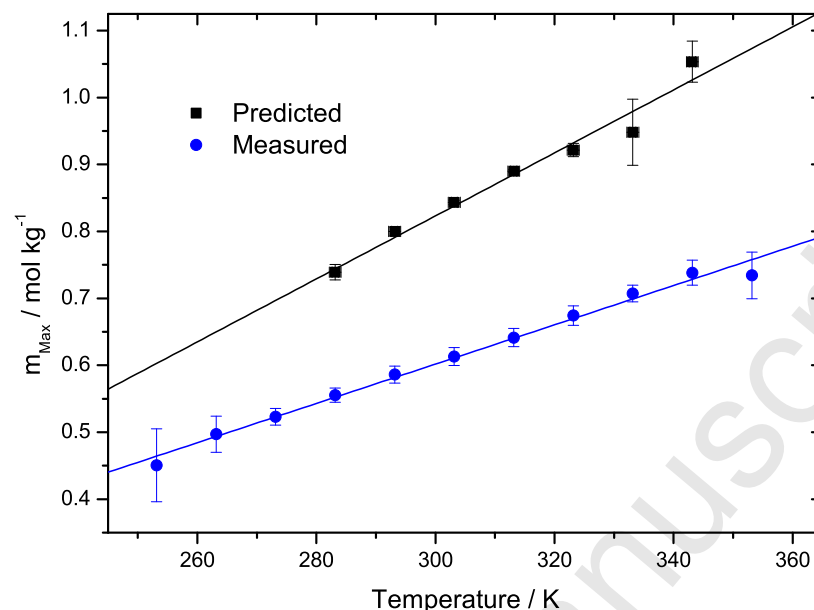


Figure 14: Salt concentration at maximum conductivity (m_{Max}) against temperature for PC/LiBF₄ liquid electrolytes for both measured and calculated conductivity. The data here has been fitted with linear lines.

4.3. Effective Ion Radius

The Stokes-Einstein equation (equation 19) can be used to calculate a value of the effective radius of the ions. The assumptions of using this equation are that the micro-diffusion relates to the macro-viscosity and also that all of the ion structures are spherical,

$$r = \frac{k_B T}{6c_{SE}\pi D\eta} \quad (19)$$

where r is the effective radius of an ion, k_B is Boltzmann's constant, T is temperature, D is the self diffusion coefficient of the relevant ion, η is the bulk viscosity and $6c_{SE}$ is a factor that is usually between 4 and 6 for a perfect slip boundary and stick boundary, respectively [65]. If c_{SE} takes the value of 1, then equation 19 becomes the classical Stokes-Einstein equation which assumes that the translating object is perfectly spherical; therefore a deviance of c_{SE} away from can indicate a non spherical structure. The c_{SE} parameter for the hydrogen diffusion measurements has been determined empirically by taking a ratio of the known Van der Waals radii and the pure solvent measurements. It has been shown elsewhere that the Van der Waals radius of the PC

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6 molecule is 0.276 nm [66]. The average value of the ionic radii measured here for pure PC
7 was (0.153 ± 0.004) nm which is significantly lower due to a deviance from the hard sphere
8 model. By taking a ratio of the measured radius and the radius determined elsewhere
9 yields a correction factor of (0.55 ± 0.01) , which agrees with a value of c_{SE} empirically
10 determined elsewhere for PC [35]. The previously determined value of the radius of PC
11 was done so by using molecular mechanics calculations (MM2) [66]. The authors have
12 determined the size of the molecule in three dimensions x , y and z , which they labeled
13 a , b and c , respectively [66]. They go on to say that if there is a difference between the
14 three parameters then the molecule cannot be considered spherical and the best way to
15 determine the deviance is to use c/a . They found that $a = 0.781$ and $c = 0.430$, which
16 yields a value of the ratio of $c/a = 0.55$ for PC [66]; therefore the value obtained elsewhere
17 perfectly coincides with the value measured directly here.
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25 The correction factor for the BF_4 anion has been analysed elsewhere [66], it was
26 shown in that the factor was $c/a = 0.89$ and $c/a = 0.92$ from crystallographic data and
27 MM2 calculations, respectively. By taking an average of these values it yields $c_{SE} = 0.9$.
28 To determine the c_{SE} factor for the lithium cations was more difficult than for the PC
29 molecules; however it has been determined elsewhere and will be used here as 0.95 [66].
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33 The Stokes-Einstein equation is used frequently to calculate the radius using NMR
34 diffusion constants and viscosity measurements [67, 68, 22]. It should be noted that
35 for the ionic radii to be accurately obtained in this way the diffusive species has to
36 be much larger than the liquid particles driving the Brownian motion, therefore the values
37 reported here are to show the trends with salt concentration rather than a definitive
38 value of the ionic radius. Using the diffusion and bulk viscosity values the effective radii
39 of the fluorinated BF_4 anion, lithium cation and PC molecules can now be determined.
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43 Table 4 shows the effective radius calculations for the PC molecules, cation and BF_4
44 anion with increasing salt concentration at 303 K and 323 K. It can be seen from table 4
45 that the size of the lithium cation is the largest entity, this is due to the cation associating
46 with several solvent molecules [33]. It has been observed elsewhere that on average four
47 PC molecules will associate with a single lithium cation [34]. Since the radius of a single
48 lithium ion is around 0.076 nm [69], it is clear that the lithium ions are solvated by the
49 solvent molecules. It can readily be observed from table 4 that the lithium ions decrease in
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Salt Conc. / mol kg ⁻¹	Ionic Radius / 10 ⁻¹⁰ m					
	303 K			323 K		
	PC	Li	BF ₄	PC	Li	BF ₄
0.00	2.86	—	—	2.88	—	—
0.26	2.68	3.59	2.26	2.82	3.64	2.30
0.43	2.70	3.49	2.38	2.88	3.63	2.55
0.61	2.65	3.46	2.52	2.86	3.57	2.65
0.89	2.29	3.12	2.44	2.48	3.27	2.66
1.18	2.34	3.10	2.63	2.54	3.23	2.83
1.37	2.14	3.01	2.61	2.37	3.16	2.80

Table 4: Ionic radius calculations for PC molecules, lithium cation and BF₄ anion at salt concentrations between 0-1.37 mol kg⁻¹ (corresponding to a molarity of 0-1.5M) at 303 K and 323 K.

radius with increasing salt concentration. For the 303 K calculations the lithium radii range from 0.359-0.301 nm from low to high salt concentration. This result was attributed to an increase in ionic association with increasing salt concentrations, as described above. This would therefore mean that as the ionic association increased the lithium cations would partially lose their PC solvation shell in order to associate to the fluorinated BF₄ anions. Since the radius calculations are strictly averages of all molecules and clusters contained within the liquid electrolyte, the average effective radius of a lithium cation would decrease since the lithium-fluorine LiBF₄ structure is smaller than the solvated lithium one. It has been shown elsewhere that the radius for a lithium ion solvated by four PC molecules is around 0.370 nm [18], this is comparable to the measurements here at low salt concentrations. Therefore it is assumed that at low salt concentrations the ionic association is low and therefore the lithium ions are predominantly solvated by multiple solvent molecules.

The effective radii of the BF₄ anion is also displayed in table 4. It can be observed that unlike the lithium ions the effective radii of the BF₄ anions increases with salt concentration. This was attributed to the increase in ionic association, as the anion and cation start to associate the size will increase. This also offers an explanation to the convergence of the lithium and fluorine diffusion coefficients shown in figure 2. For the

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6 303 K calculations the BF_4 ions were observed to exhibit effective radii in the range 0.226-
7 0.261 nm, from low to high salt concentration. The low salt concentration calculation of
8 0.226 nm is comparable to the known BF_4 anion radius of 0.229 nm [66]. This therefore
9 has a strong indication that the BF_4 anion does not have a solvation shell like the lithium
10 cation. The increase in size with salt concentration is attributed to the increased ionic
11 association at higher salt concentrations.
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15 The effective radii of the PC molecules (from ^1H NMR measurements) has also been
16 displayed in table 4. Similar to the effective radii of the lithium ions, the PC molecules
17 radii decrease with salt concentration. This agrees with the hypothesis that as the cation
18 and anion associate, the lithium-PC structures are being partially separated in favour
19 of ionic association, therefore resulting in a reduction in the average effective radius of
20 the PC molecules. The lithium, PC and BF_4 radii are relatively unaffected by a change
21 in temperature, which has also been seen in previous work in a system of tetraethylene
22 glycol dimethyl ether (TG) with LiCF_3SO_3 [25].
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28 Using this method to calculate the ionic radius can be problematic as it uses micro-
29 diffusion with macro-viscosity. From equation 19 it can be seen that by plotting $\ln(\text{diffusion})$
30 against $\ln(\text{viscosity})$ that the gradient should be close to unity if the equation is valid.
31 It was observed that all values of the gradient for all three nuclei were reasonably close
32 to unity, which suggests that it is valid to use the micro-diffusion with the bulk viscos-
33 ity of the liquid electrolytes. The average gradients over the range of concentrations
34 were (1.05 ± 0.02) , (1.12 ± 0.03) and (1.03 ± 0.02) for the ^1H , ^7Li and ^{19}F measurements,
35 respectively. Therefore since all of these values are close to one it can summarised that
36 using the Stokes-Einstein equation can be assumed to give a good to estimation of the
37 effective radii.
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45 5. Conclusions

46 Pulsed-field gradient diffusion measurements were taken using ^1H , ^7Li and ^{19}F nuclei
47 for PC/ LiBF_4 liquid electrolytes as a precursor to understanding the conduction mech-
48 anism in polymer gel electrolytes. Conductivity and viscosity measurements have also
49 been taken in order to understand the dynamics of the constituents of the solution.
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54 The lithium ion diffusion was found to be slower than the hydrogen and fluorine
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6 due to the lithium ion solvating PC molecules resulting in a large effective radius of the
7 lithium species. The diffusion and viscosity measurements both exhibit Arrhenius type
8 behaviour whereas the conductivity displayed VTF temperature dependence. This has
9 been attributed to the extended temperature range of the conductivity measurements
10 which was 253-353 K, where as the viscosity and diffusion were measured using a range
11 of 293-353 K. Therefore the extension to lower temperatures has revealed the VTF type
12 temperature dependence as we are approaching the glass transition temperature.
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17 All liquid electrolytes were seen to exhibit a peak in conductivity with increasing
18 salt concentration. This was attributed to a competition between number of free ions
19 and viscosity. However, with the increase of temperature the peak exhibits a shift to
20 higher salt concentrations. This has been attributed to the lowering of viscosity at
21 high temperatures allowing more salt to be dissolved before viscous effects become the
22 dominating factor; the ionic association is also believed to affect the position of the
23 maximum.
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28 The Nernst-Einstein equation was used to predict conductivity from NMR diffusion
29 coefficient measurements. It was found that the predicted conductivity was significantly
30 larger than the measured values due to the assumption that the anion and cation travel
31 through the medium as dissociated ions. From the difference between the predicted and
32 measured conductivity the degree of ionic association was calculated for the PC/LiBF₄
33 liquid electrolytes. The ionic association was seen to increase with temperature which
34 has been attributed to the lowering of free energy of ion pair formation at higher tem-
35 peratures. The ionic association also increases with salt concentration and this has
36 been attributed to the increase in ion density in the electrolyte causing more interaction
37 between the anion and cation.
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44 The Stokes-Einstein equation was used to predict the ionic radii of the PC molecules,
45 lithium cation and BF₄ anion. It should be noted that in order to use the Stokes-Einstein
46 equation to calculate the effective radii the radius of the relevant diffusing species has to
47 be significantly larger than the liquid particles driving the Brownian motion. The ionic
48 radii reported here were used to compare the different constituents as well as observing
49 trends with salt concentration. The size order of the constituents were PC molecules,
50 fluorinated BF₄ anion and lithium cations from smallest to largest. The lithium is known
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6 to be well solvated, with a large solvation shell. The BF_4 anions and lithium cation were
7 observed to converge at high salt concentration and this was attributed to increased
8 association between the fluorine and lithium. There was no evidence that the BF_4 anions
9 were solvated as the calculated radii were similar to that measured elsewhere for a single
10 BF_4 ion. The effective radii of the PC molecules were also seen to decrease with salt
11 concentration, this is consistent with the hypothesis that the lithium ions are dissociating
12 from the PC molecules in favour of the fluorinated BF_4 anions.
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