Structure and Dynamics in Solid State Sodium Ion Electrolytes based on Organic Ionic Plastic Crystals

By

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A thesis submitted to the Institute of Frontier Materials, Deakin University, in fulfilment of the requirements for the degree of Doctor of Philosophy

Institute of Frontier Materials
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October 2014
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ACKNOWLEDGEMENT

First of all, I would like to thank my principal supervisor Prof. Maria Forsyth for her great guidance, encouragement and continuous support throughout this project. The support and guidance from Dr. Weimin Gao, my associate supervisor is highly appreciated.

My heartfelt thanks also goes to Prof. Peter Hodgson who facilitated the scholarship, encouraged and motivated me into this project and Prof. Simon De Leeuw for his mentoring in molecular dynamics simulation techniques and writing the codes for the analysis.

I will extend many thanks to Dr. Patrick Howlett, Dr. Jim Efthimidias, and Dr. Anthony Somers for the training and assisting on some of the lab equipment used for the characterization and also to Dr. Shveta Pandiancherri and Dr. Judith Jankowski who assisted with the purification of the materials used in the project. Dr. Daniel Gunzelmann and Dr. Pimm Vongsvivut who helped with the solid state NMR and Raman measurements respectively and Dr. Aaron Seeber for his help in the analysis of synchrotron x-ray diffraction data deserve gratitude, without them those advanced techniques for characterization would not have been possible. The discussions and comments with Dr. Fangfang Chen and Dr. Kate Nairn is highly commendable. I would like to extend my heartfelt thanks to all ACES/IFM colleagues who made conducive and friendly research environment for me at IFM/Deakin.

Millions of thanks goes to all my family members who provided me their love, understanding and support in these years of study, particularly the Chimdi brothers and sisters Mr. Abebe, Eng. Gelana, Mr. Kumsa, Dr. Achalu, Mr. Dejene, Mrs. Fayise, Gelane, Nagase and Bule. Last but not least, my parents Mr. Chimdi Yarimo and Mrs. Soboke Gose who raised me with high moral and ethical values that helped me tackle the waves of life with patience and endurance deserve a very special place and are always in my heart.
ABSTRACT

The first part of this thesis emphasizes the experimental characterization study of the binary mixtures of the organic ionic plastic crystals (OIPCs) and sodium salts of the same anion. The OIPCs studied include N-ethyl-N-methylpyrrolidinium bis-(trifluoromethanesulfonyl)amide ([C2mpyr][NTf2]), N-ethyl-N-methyl pyrrolidinium tetrafluoroborate ([C2mpyr][BF4]), and N, N-dimethylpyrrolidinium dicyanamide ([C1mpyr][N(CN)2]). In the second part of the thesis, the molecular dynamics simulation study on N-ethyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) amide ([C2mpyr][NTf2]) and Na[N(CN)2] mixed with N,N,N,N-tetramethyl ammonium dicyanamide ([Me4N][N(CN)2]) will be presented. These materials were investigated with the aim to explore their potential as Na ion solid-state electrolytes based on OIPCs. The phase behavior, structural and dynamic properties of these materials were explored using advanced experimental techniques such as DSC, SEM, EIS, FTIR/Raman, SXRD and solid-state NMR.

The solid state phase behaviour of the organic ionic plastic crystal [C2mpyr][NTf2], upon mixing with the sodium salt, Na[NTf2] have shown a eutectic composition at 15 mol% with a eutectic temperature at 63°C. The conductivity did not increase significantly at or below room temperature, however the material containing 40 mol% Na[NTf2] has an ionic conductivity of 10^-4 S cm^-1 in the solid state at 60°C, which is more than 3 orders of magnitude higher than the pure OIPC. The Synchrotron XRD, solid-state NMR and SEM, FTIR/Raman studies all indicate the presence of two distinct phases across all of the compositions studied. One phase is
identical to that of the pure \([C_2\text{mpyr}][\text{NTf}_2]\) and the other phase is a mixed cation compound, quite distinct from the pure \(\text{Na}[\text{NTf}_2]\) material. The higher eutectic temperature (63 °C) in the sodium based system compared to lithium (30 °C) leads to purely solid state conductivity over the entire composition range up to 63 °C.

Upon mixing sodium tetrafluoroborate (NaBF\(_4\)) salt with the organic ionic plastic crystal (OIPC) N- methyl-N-ethyl-pyrrolidinium tetrafluoroborate, \([C_2\text{mpyr}][\text{BF}_4]\) in the range of composition between 1 and 20 mol% of Na\(^+\) content there was no change in the solid-solid transitions observed. Slight increase in conductivity to the extent of \(\sim 10^{-5}\text{S.cm}^{-1}\) at 65°C had been observed in 4 mol % NaBF\(_4\)/C\(_2\text{mpyr}\) BF\(_4\) whilst slight decrease with the increased level of concentration of Na\(^+\) content. In the SEM micrographs, precipitates in the inter-grain boundaries and on the grain surface have shown the existence of additional phase as confirmed by different Na environment in \(^{23}\text{Na}\) nuclei. Room temperature solid-state NMR data from \(^{19}\text{F}\) nuclei have shown different BF\(_4\) environments and/or the possibility of different phases is consistent with the additional peak observed at \(\sim 550\ \text{cm}^{-1}\) in the FTIR spectra and \(\sim 785\ \text{cm}^{-1}\) in the Raman spectra. The nuclei \(^1\text{H}, \ ^{13}\text{C}\) showed identical environment for the cation \(C_2\text{mpyr}^+\) apart from line narrowing which indicates fast cationic motion.

The binary mixture of the \(\text{Na}[\text{N(CN)}_2]\) salt and \([C_1\text{mpyr}][\text{N(CN)}_2]\) OIPC have shown the existence of eutectic melting transition at ~89 °C, below which all compositions are entirely in the solid phase at 20 mol% Na\(^+\) content. The microstructure for all the mixtures indicated a phase separate morphology where precipitates can be clearly observed. Most likely these precipitates indicate a Na rich second phase as observed in the \(\text{Na}_x[C_2\text{mpyr}]_{1-x} [\text{NTf}_2]\) mixed systems. This
was also confirmed from the vibrational spectroscopy $^1$H, $^{13}$C and $^{23}$Na NMR spectra are obtained and show that the cations are relatively mobile in these mixtures. The lower concentrations of Na[N(CN)$_2$] present complex $^{23}$Na MAS spectra suggesting more than one sodium ion environment is present in these mixtures consistent with complex phase behavior. Unlike other OIPCs, the conductivity of Na$_x$[C$_{1}$mpyr]$_{1-x}$ [N(CN)$_2$] mixtures remain relatively constant and above $10^{-4}$ S.cm$^{-1}$ at ~80°C, even in the solid state. However, given such high conductivities suggest that these materials may be promising to be used for in solid-state electrochemical devices.

Structural and dynamic properties of [C$_2$mpyr][NTf$_2$] OIPC have been studied through MD simulation combined with experimental investigations. Excellent agreement had been observed between simulated lattice parameters and SXRD experimental results at different temperatures with a volume change of 5.4% at the temperature of 363K (phase I) compared to at 153K (phase IV). The RDF have shown that sharp peaks observed in the lower temperature phase IV at 153K are ordered and the broadening of RDF peaks beyond 213K and above show that the cations and anions undergo disorder also correlates with phase changes of differing lattice structure observed from the synchrotron XRD experiment. The addition of 1% and 2% vacancies in the OIPC at 333K (phase I), did not affect all the RDFs investigated. This could be due to the insignificant increase in the size and concentration of defects at this temperature that did not contribute in the crystal restructuring and plasticity of the OIPC. Further study is required to conclude the effect of vacancies on the RDF with increased concentration.

The dihedral distribution function for the anion NTf$_2$, have shown two main peaks
of proper dihedral of 90 (trans) and 180° (cis) conformers between 213K and 333K whilst more peaks observed at 153K correspond to frozen conformers of the ordered structure. The trans conformer decreases as temperature increases, and dramatically at 333K which represents phase I, i.e. the plastic phase, for the C2mpyrNTf2 crystal. The dramatic increase of cis conformers in phase I at 333K is consistent with the Raman observation in [C1mpyr][NTf2]. The addition of 1% and 2% vacancies to this crystal structure led to further reduction of the trans conformer and dominance of cis conformer.

Similarly, the dihedral distribution function of C2mpyr+ at 153K in phase IV showed that the cation exists in an eq-envelope trans conformational state. However, the variations in the dihedral distribution of C2mpyr+ at temperature above 213K arise from the disorder in the plastic crystal from the phase III and beyond. Therefore, the conformational states of ax-envelope and/or twist conformations and/or the combinations triggered by the onset of rotation possibly exist in the other phase above 213K (in phase III). However, further studies need to be done with variable temperature Raman spectroscopy for comprehensive conclusion.

In the rotational autocorrelation studies, it has been observed that the rotational relaxation times decay dramatically as temperature increase and all calculated rotational relaxation times were within the simulation times of 5ns. Both the cation and anion exhibit slow dynamics in phase III and a slight possibility of anisotropic rotation whilst the fast rotation was observed in the anion and cation at temperature as high as 383K. The slower rotational relaxation decay time in the anion at all the temperatures is due to much larger inertia compared to the cation. In general, the
inspection of the rotational autocorrelation function it can be concluded that the rotation vectors cannot decay to zero whilst the cation and anion are in fixed position (i.e. not fully tumbling or diffusing). Hence at 383K, full decay of these vectors explain that the both cation and anion may undergo isotropic rotation after the melt. Furthermore, at 333K when vacancies are incorporated into the lattice, the cation and anion rotational dynamics are significantly enhanced.

Despite the start of the onset of slow anisotropic rotation in the anion and cation from phase III at 213K, there were no evidence of anionic or cationic diffusion in the MD simulations, which may be due to the shorter simulation time. The calculated anion and cation self-diffusion coefficients in this OIPC are three orders of magnitude lower than that of the ILs (~10^{-10} m^2/s) and slightly over the values 10^{-13} – 10^{-15} m^2/s in perfect crystals in phase I at 363K. The addition of vacancies did not significantly alter the self-diffusion of both cation and anion in the OIPC.

Structural and dynamic properties of Na+ doped [Me4N][N(CN)2] OIPC was also carried out using the MD simulation in the temperature range of 200-500K. The RDF investigation of the mixed system (through the central atoms NT and ND1 for the cation and anion as well as Na atom) show sharp, split peaks which exhibit the features of ordered crystalline materials with the first and second co-ordination shells concentrated within the regions 4 to 7 Å and 8 to 12 Å respectively, at temperatures below 300K, with the addition of 5% and 15% Na+ content. With increasing temperature above 300K, these RDF peaks become broadened, shifted and diminished due to thermal disorder (exacerbated upon with the presence of 15% Na+ content). In general, the mixed system of 15% Na+ undergoes higher disorder compared to the 5% Na+ system may be due to the creation of more defects. At
temperatures 400K and above, in phase II of the OIPC and beyond, the RDF exhibit broadened, featureless peaks reflecting amorphous, liquid like behavior observed in all anion/cation species upon addition of both 5% and 15%Na⁺.

The rotational autocorrelation functions undergo fast decays in both anion and cation systems (within less than 100ps) upon addition of both 5% and 15%Na⁺ content at temperatures above 300K in phase III. We observe a slower decay in the C-N bond vector in the [N(CN)₂]⁻, in the 15%Na⁺ doped [Me₄N][N(CN)₂] compared to the 5%Na⁺ doped [Me₄N][N(CN)₂] system. Furthermore, the rotation in the [Me₄N]⁺ cation is enhanced whilst the rotation in the anion is restricted with the addition of more Na⁺ cations in the OIPC with increasing temperatures.

The calculated self-diffusion coefficients from 3ns simulation time of the Me₄N⁺, Na⁺ cations and [N(CN)₂]⁻ anion at 300 K was found to be in the range of ~10⁻¹² m²/s, in 5% and 15% Na⁺ contents is an order of magnitude greater than in crystalline solids. With the increasing temperature to 500K, the self-diffusion coefficients of all ionic species increased by an order magnitude over the 300K values, with 5%Na⁺. However, in the 15% Na⁺ OIPC system, the calculated self diffusion coefficients of the ionic species is slightly lower than for the 5% system, in the temperature range of 350-500K. These ionic species attained full diffusion comparable to that of ILs ~10⁻¹⁰ m²/s at 500K which is attributed to the system reaching a liquid state.
LIST OF FIGURES

Figure 1-1 Schematics of an electrochemical device........................................... - 2 -
Figure 1-2 The structure of the OIPCs and the sodium salt in the mixture........ - 6 -
Figure 1-3 DSC trace of a pure [C₂mpyr][NTf₂] OIPC with rich solid-solid transitions ................................................................. - 7 -
Figure 1-4 Point defects (I) in a 2D lattice reperesenting a) vacancy b) interstitial impurity c) self interstitial d) substitutional impurity and (II) in an ionic crystals representning a) Shottky b) Frenkel defects ..................................... - 12 -
Figure 1-5 Schematic representation of a dislocation that has a) edge and b) screw with arrows indicating the region of imperfection and direction of applied force ........................................................................................................... - 13 -
Figure 1-6 The SEM micrographs of pure [C₂mpyr][NTf₂] OIPC [28]............. - 15 -
Figure 1-7 The asymmetric units of cation–anion pair in [C₂mpyr][NTf₂] for the a) monoclinic phases at 153K( left ) and b) triclinic phase at 213K (right).- 17 -
Figure 2-1 Schematic diagram of force field of bonded terms. a) Bond stretching, b) bond angle bending, and c) dihedral rotation........................................... - 45 -
Figure 2-3 Atomic positions and labels in the NTf₂ anion......................... - 49 -
Figure 2-4 Dihedral angle formed by 4 atoms defined by vectors b₁ and b₂ in the first plane, vectors b₂ and b₃ in the second plane.............................. - 50 -
Figure 2-5 Vectors defining the rotational autocorrelation function in cation and anion of [C₂mpyr][NTf₂] ............................................................................. - 50 -
Figure 3-1 DSC traces of pure [C₂mpyr][NTf₂] and mixtures (1-50 mol%) of Na[NTf₂] with [C₂mpyr][NTf₂] ................................................................. - 58 -
Figure 3-2 Phase diagram for [C₂mpyr][NTf₂] / Na[NTf₂] system shows solid-solid phase transition temperatures T_{III-II}, T_{II-I} and liquidus temperature T_{L} indicating both equilibrium and metastable phase transitions respectively. - 60 -
Figure 3-3 Micrographs showing a comparison of [C₂mpyr][NTf₂] OIPC (a) pure, 200 mm scale bar; (b) mixed with 1% mol Li[NTf₂], 200 mm scale bar; (c) mixed with 2% mol Na[NTf₂], 100 mm scale bar and (d) mixed with 2% mol Na[NTf₂], 20 mm scale bar.......................................................... - 62 -
Figure 3-4 Ionic conductivity of pure and Na⁰ mixed [C₂mpyr][NTf₂] with variable Na[NTf₂] concentration. (The ionic conductivity of pure and 1 mol % Li⁰ mixed [C₂mpyr][NTf₂] is compared in the inset [13]) .......................... - 63 -
Figure 3-5 FTIR spectra of pure and mixed materials Na[NTf₂], [C₂mpyr][NTf₂], Na₀.₀₄[C₂mpyr]₀.₉₆[NTf₂] and Na₀.₁₅[C₂mpyr]₀.₈₅[NTf₂] at different frequencies (a) 450–680 cm⁻¹, (b) 950–1250 cm⁻¹. Additional weak peaks/shoulders are indicated at 534, 576, 598, 651 cm⁻¹ and 1150 cm⁻¹. c) no change in peaks of pure OIPC and mixtures in the spectral region of 2800-3200 cm⁻¹ ............ - 67 -
Figure 3-6  Raman spectra of pure and mixed materials Na[NTf₂], [C₂mpyr][NTf₂], Na₀.₀₄[C₂mpyr]₀.₉₆[NTf₂] and Na₀.₁₅[C₂mpyr]₀.₈₅[NTf₂] at different frequencies (a) 240–380 cm⁻¹, (b) 700–780 cm⁻¹ and (c) 2800–3200 cm⁻¹

Figure 3-7  Indexed synchrotron XRD patterns acquired for (a) [C₂mpyr][NTf₂] and (b) Na₀.₁₅[C₂mpyr]₀.₈₅[NTf₂] at temperatures of 273, 303 and 328K (i.e., phases III, II and I respectively), (c) compares the [C₂mpyr][NTf₂], Na[NTf₂] and Na₀.₁₅[C₂mpyr]₀.₈₅[NTf₂] patterns at 303K and (d) compares the [C₂mpyr][NTf₂] and Na₀.₁₅[C₂mpyr]₀.₈₅[NTf₂] patterns at 273K with * indicating mixed phase

Figure 3-8  ¹H, ¹⁹F, ¹³C, ¹⁵N and ²³Na MAS solid-state NMR spectra (a – e respectively) at ambient temperature (295K) for the binary mixtures from 0 to 100 mol% Na⁺ content

Figure 3-9  ¹H static solid-state NMR spectra for the binary mixtures a) Na₀.₀₄[C₂mpyr]₀.₉₆[NTf₂] and b) Na₀.₁₅[C₂mpyr]₀.₈₅[NTf₂] acquired between 268K (283K) and 349K of Na[NTf₂] salt and 15% mol doped Na₀.₁₅[C₂mpyr]₀.₈₅ NTf₂ show that they belong to one single signal

Figure 3-10  ¹H VT-MAS solid-state NMR spectra for the binary mixtures a) Na₀.₀₄[C₂mpyr]₀.₉₆[NTf₂] and b) Na₀.₁₅[C₂mpyr]₀.₈₅[NTf₂] acquired between 268K (283K) and 349K of Na[NTf₂] salt and 15% mol doped Na₀.₁₅[C₂mpyr]₀.₈₅ NTf₂ show that they belong to one single signal

Figure 3-11  ¹⁹F VT-MAS solid-state NMR spectra for the binary mixtures a) Na₀.₀₄[C₂mpyr]₀.₉₆[NTf₂] and b) Na₀.₁₅[C₂mpyr]₀.₈₅[NTf₂] acquired between 268K and 349K

Figure 3-12  ²³Na VT-MAS solid-state NMR spectra for Na₀.₁₅[C₂mpyr]₀.₈₅[NTf₂] acquired at 295K, 313K and 349K

Figure 4-1  DSC traces of ) pure sample of [C₂mpyr][BF₄] and 0-20mol% Na[BF₄] mixed with [C₂mpyr][BF₄]

Figure 4-2  Micrographs of Na⁺ mixed [C₂mpyr][BF₄] OIPC with a-b) mixed with 4% mol Na[BF₄] c) 2um and d) 1um

Figure 4-3  EDX elemental map analysis of Na₀.₀₂[C₂mpyr]₀.₈[BF₄] 25um showing minor, dispersed Na presence while C and F are clearly the majority

Figure 4-4  Nyquist plot of 4%Na⁺ content in [C₂mpyr][BF₄] OIPC

Figure 4-5  Ionic conductivity of pure and Na⁺ mixed [C₂mpyr][BF₄] with variable Na[BF₄] concentration

Figure 4-6  FTIR spectra of pure [C₂mpyr][BF₄] and mixture with Na[BF₄] salt in the spectral regions of a) 500-600cm⁻¹ b) 800-1200cm⁻¹ c) 1200-1600cm⁻¹ and d) 2800-3100cm⁻¹
Figure 4-7  Raman spectra of pure \([\text{C}_2\text{mpyr}]\text{[BF}_4\text{]}\) and mixture with \(\text{Na[BF}_4\text{]}\) salt in the spectral regions of a) 300-650cm\(^{-1}\) b) 650-850cm\(^{-1}\) c) 900-1600cm\(^{-1}\) and d) 2800-3100cm\(^{-1}\) .......................................................... - 111 -

Figure 4-8  DSC traces of pure \([\text{C}_1\text{mpyr}]\text{[N(CN)}_2\text{]}\) and mixtures (0–50 mol%) of \(\text{Na[N(CN)}_2\text{]}\) with \([\text{C}_1\text{mpyr}]\text{[N(CN)}_2\text{]}\). .......................................................... - 114 -

Figure 4-9  Partial phase diagram for \(\text{Na[N(CN)}_2\text{]}\) mixed with \([\text{C}_1\text{mpyr}]\text{[N(CN)}_2\text{]}\) OIPC ........................................................................................................ - 116 -

Figure 4-10  Micrographs of \([\text{C}_1\text{mpyr}]\text{[N(CN)}_2\text{]}\) OIPCs. a) pure (scale bar 25 \(\mu\text{m}\)); b) pure (scale bar 10 \(\mu\text{m}\)); c) containing 5 mol% \(\text{Na[N(CN)}_2\text{]}\) (scale bar 25 \(\mu\text{m}\)) and d) containing 20 mol% \(\text{Na[N(CN)}_2\text{]}\) (scale bar 25 \(\mu\text{m}\)) .......... - 118 -

Figure 4-11  Nyquist plots of \(\text{Na}_{0.05}[\text{C}_1\text{mpyr}]_{0.95}\text{[N(CN)}_2\text{]}\) from 25–40°C, showing an increase in ionic conductivity.............................................................. - 119 -

Figure 4-12  Ionic conductivity of \(\text{Na}_{x}[\text{C}_1\text{mpyr}]_{1-x}\text{[N(CN)}_2\text{]}\) as a function of \(\text{Na[N(CN)}_2\text{]}\) concentration. ............................................................................... - 120 -

Figure 4-13  FTIR spectra of pure and mixed materials at different frequencies a) 400 – 700cm\(^{-1}\), b) 1200–1600cm\(^{-1}\) and c) 1900–2400cm\(^{-1}\) for \([\text{C}_1\text{mpyr}]\text{[N(CN)}_2\text{]}\) and binary mixtures with \(\text{Na[N(CN)}_2\text{]}\) salt .......................... - 126 -

Figure 4-14  Deconvoluted FTIR spectrum for a) 0% Na (pure OIPC) in 475 – 560cm\(^{-1}\), b) 20% Na (475–560 cm\(^{-1}\)), c) 0% Na (pure OIPC) in 1220–1375 cm\(^{-1}\) and d) 20% Na in 1220–1375 cm\(^{-1}\) spectral regions .................. - 129 -

Figure 4-15  Raman spectra of \([\text{C}_1\text{mpyr}]\text{[N(CN)}_2\text{]}\) and binary mixtures with \(\text{Na[N(CN)}_2\text{]}\) salt. a) 500–780 cm\(^{-1}\), b) 870–1100 cm\(^{-1}\), c) 2100–2300 cm\(^{-1}\) and d) 2800–3200 cm\(^{-1}\) .......................................................... - 133 -

Figure 4-16  \(^1\text{H RT - MAS solid-state NMR spectra of pure Na[N(CN)}_2\text{]}\) (blue) and mixtures \(\text{Na}_{0.05}[\text{C}_1\text{mpyr}]_{0.95}\text{[N(CN)}_2\text{]}\) (red) and \(\text{Na}_{0.2}[\text{C}_1\text{mpyr}]_{0.8}\text{[N(CN)}_2\text{]}\) (green) ....................................................................................... - 135 -

Figure 4-17  \(^13\text{C RT - CP MAS solid-state NMR spectra of pure Na[N(CN)}_2\text{]}\) (blue) and \(\text{Na}_{0.05}[\text{C}_1\text{mpyr}]_{0.95}\text{[N(CN)}_2\text{]}\) (red) and \(\text{Na}_{0.2}[\text{C}_1\text{mpyr}]_{0.8}\text{[N(CN)}_2\text{]}\) (green) mixtures. .......................................................... - 135 -

Figure 4-18  \(^{23}\text{Na RT-static (upper) and MAS (lower) solid-state NMR spectra of pure Na[N(CN)}_2\text{]}\) (blue) and \(\text{Na}_{0.05}[\text{C}_1\text{mpyr}]_{0.95}\text{[N(CN)}_2\text{]}\) (red) and \(\text{Na}_{0.2}[\text{C}_1\text{mpyr}]_{0.8}\text{[N(CN)}_2\text{]}\) (green) mixtures. .............................................................................. - 136 -

Figure 5-1  The ionic species constituting pure \([\text{Me}_4\text{N}]\text{[N(CN)}_2\text{]}\) OIPC ........ - 149 -

Figure 5-2  Volume of the simulated box as a function of temperature, starting from the crystallographic data of monoclinic phase at 153K............................ - 152 -

Figure 5-3  The plots of the radial distribution function (RDF) as a function of interatomic distance \(r\) of the central nitrogens of the cation \(\text{N1}\) and the anion \(\text{N3}\) with their corresponding co-ordination number in a, b – cation-cation ; c, d - cation-anion and e, f - anion-anion interactions obtained at different temperatures from NPT simulation. .................................................. - 154 -

Figure 5-4  Variation of radial distribution function (RDF) as a function of vacancy and their corresponding co-ordination number in a, b – cation-cation ; c, d - cation-anion and e, f - anion-anion interactions. .................. - 158 -
Figure 5-5 The dihedral angle of the anion NTf₂ defined by CSNS-SNSC dihedrals with the orientation of S–C bonds in the two planes a) C₁ (cis) conformation and b) C₂ (trans) conformation adopted from [63].

Figure 5-6 The distribution of dihedral angles CSNS in [NTf₂]⁻ at different phase temperatures from 153 to 333K.

Figure 5-7 Distributions of dihedral angle ±90° and ±180° in [NTf₂]⁻ at 333 K in three models with different percentages of doped vacancies.

Figure 5-8 Distribution of dihedral CNCC in [C₂mpyr]⁺ at different phase temperatures from 153-333K.

Figure 5-9 Schematic representation of [C₂mpyr]⁺ conformers adopted from the crystal structure at 153K ([64, 69].

Figure 5-10 Schematic representation of trans a) eq-envelope trans at 153K b) ax-envelope of [C₂mpyr]⁺ conformers extracted from the trajectory of [C₂mpyr]⁺-[NTf₂]⁻ at 333K.

Figure 5-11 Vectors in cation and anion defined for rotational autocorrelation function calculations. a) vector \(u_{1pp}\) describes an axis perpendicular to the plane C1-N1-C4 in pyrrolidinium ring b) vector \(u_{2pp}\) is selected along the C5-C6 bond c) the vectors \(u_{1mm1}\) and \(u_{2mm}\) are selected along the S1-C15 and S2-C16 bonds, respectively.

Figure 5-12 Rotational autocorrelation functions of vectors \(u_{1pp}(a)\) and \(u_{2pp}(b)\) in the cation of [C₂mpyr][NTf₂] at different temperatures.

Figure 5-13 The average of calculated rotational autocorrelation functions of vectors \(u_{1mm1}\) and \(u_{2mm}\) in the anion at different temperatures.

Figure 5-14 Dynamical evolution of the ionic species inspected in (top-bottom) a) pure OIPC b) inclusion of 1% vacancy and c) inclusion of 2% vacancy in pure OIPC at 333K (phase I).

Figure 5-15 Rotational autocorrelation function \(u_{1pp}(a)\) and \(u_{2pp}(b)\) of the cation and \(u_{1mm} = u_{2mm}\) (c) of the anion in [C₂mpyr][NTf₂].

Figure 5-16 The simulated (black) and fitted (red) rotational autocorrelation fitted to double exponential decay.

Figure 5-17 Mean-squared displacement for the diffusion analysis of the (a) cation and (b) anion in [C₂mpyr][NTf₂] at temperatures (273K and 363K).

Figure 5-18 Variation in centre of mass mean-squared displacement of the a) cation and b) anion in [C₂mpyr][NTf₂], due to vacancy inclusion at 333K.

Figure 5-19 The radial distribution function (RDF) of the anion–cation system at 200K with the addition: a) 5% and b) 15% Na⁺ into the OIPC.

Figure 5-20 Temperature dependent radial distribution function (RDF) of the anion–cation systems a) [Me₄N⁺][Me₄N⁺], b) [Me₄N⁺][N(CN)₂]⁻, c) [N(CN)₂]⁻-[N(CN)₂], d) [Na⁺]-[N(CN)₂]⁺ with the addition 5% Na⁺ (solid) and 15% Na⁺ into the OIPC.

Figure 5-21 Vectors defining the rotation autocorrelation function, C-N bond vector in [Me₄N⁺]⁺ (\(u_{1pp}\)); vector perpendicular to [N(CN)₂]⁻ plane (\(u_{1mm}\)); vector in the [N(CN)₂]⁻ plane (\(u_{2mm}\)) and the C-N bond vector in the [N(CN)₂]⁻ (\(u_{3mm}\)).
Figure 5-22  Rotational autocorrelation function of a) C-N bond vector in [Me₄N]⁺ (u1tpp); b) anion vector perpendicular to [N(CN)₂]⁻ plane (u1tmm); c) anion vector in the [N(CN)₂]⁻ plane (u2tmm) and d) C-N bond vector in the [N(CN)₂]⁻ (u3tmm) in 5% Na doped with [Me₄N][N(CN)₂] OIPC............ - 190 -

Figure 5-23  Rotational autocorrelation function defined by a) C-N bond vector in [Me₄N]⁺ (u1tpp); b) vector perpendicular to [N(CN)₂]⁻ plane (u1tmm); c) vector in the [N(CN)₂]⁻ plane (u2tmm) and d) C-N bond vector in the [N(CN)₂]⁻ (u3tmm) in 15% Na⁺ doped with [Me₄N][N(CN)₂] OIPC........ - 193 -

Figure 5-24  The means square displacement of (a)[Me₄N]⁺, (b) [N(CN)₂]⁻, and (c) Na⁺ ions in 5% Na⁺ doped [Me₄N][N(CN)₂] OIPC. ............................... - 198 -

Figure 5-25  Mean square displacement of (a)[Me₄N]⁺, (b) [N(CN)₂]⁻, and (c) Na⁺ ions in 15% Na⁺ doped [Me₄N][N(CN)₂] OIPC. .................................... - 201 -

LIST OF TABLES

Table 3.1 Enthalpy (in J/g) for the phase transitions calculated from the area under the peaks in DSC traces and the corresponding transition temperatures of doped systems ................................................................. - 59 -

Table 3.2 Assignment of observed Raman and FTIR bands of [C₂mpyr][NTf₂] at room temperature based on different literatures on related anions and cations - 69 -

Table 3.3 Lattice parameters determined for [C₂mpyr][NTf₂] OIPC. ............... - 78 -

Table 4.1 The onset solid-solid transition temperatures (±1°C) of the pure and mixed systems with their corresponding enthalpy change (in J/g within the error margin of ±10%) ............................................................ - 97 -

Table 4.2 Assignment of observed Raman and FTIR bands of [C₂mpyr][BF₄] at room temperature based on literature reports [8, 18-20] for related cations and anions .......................................................... - 106 -

Table 4.3 Peak solid-solid transition temperatures (±1°C) of the pure and mixed systems with their corresponding enthalpy changes (in J/g within an error margin of ±10%) ............................................................ - 115 -

Table 4.4 Assignment of observed Raman and FTIR bands of [C₁mpyr][N(CN)₂] at room temperature based on literature reports [21, 38, 39] for related cations and anions .......................................................... - 123 -

Table 4.5 Summary of the fit parameters in the FTIR region of 475–560 cm⁻¹ - 129 -

Table 4.6 Summary of the fit parameters in the FTIR region of 1220-1375cm⁻¹. - 130 -

Table 5-1 Comparison of the simulation results with X-ray diffraction data at 153K (monoclinic phase) ........................................................................ - 150 -

Table 5-2  Comparison of simulated and experimental occupied volumes per pair of ions at different temperatures .......................................................... - 152 -

Table 5-3  Relaxation time of two vectors u₁tpp and u₂tpp in the cation ............... - 178 -
Table 5-4 Calculated self-diffusion coefficient \( D \) in \( \times 10^{-13} \text{ m}^2/\text{s} \) anion and cation. - 182 -

Table 5-5 Rotational relaxation time calculated from the two step exponential decay in 5% Na mixed with [Me4N][N(CN)2]OIPC. - 194 -

Table 5-6 Self-diffusion of cationic and anionic species in 5% and 15% Na\(^+\) doping in [Me4N][N(CN)2]OIPC \( \times 10^{-11} \text{ m}^2/\text{s} \). - 199 -

ABBREVIATIONS

OIPC Organic Ionic Plastic Crystal
[C\textsubscript{2}mpyr][NTf\textsubscript{2}] N-ethyl–N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide
[C\textsubscript{2}mpyr][BF\textsubscript{4}] N-ethyl–N-methylpyrrolidinium tetrafluoroborate
[C\textsubscript{1}mpyr][N(CN)\textsubscript{2}] N-ethyl–N-methylpyrrolidinium dicyanamide
Na [NTf\textsubscript{2}] Sodium bis (trifluoromethanesulfonyl) imide
Na [BF\textsubscript{4}] Sodium tetrafluoroborate
Na [N(CN)\textsubscript{2}] Sodium dicyanamide
DSC Differential Scanning Calorimeter
EIS Electrochemical Impedance Spectroscopy
EDX Energy-dispersive X-ray spectroscopy
SEM Scanning Electron Microscopy
FTIR Fourier Transform Infrared Spectroscopy
NMR Nuclear Magnetic Resonance Spectroscopy
CP Cross Polarization
MAS Magic Angle Spinning
MQ-MAS Multiple Quantum Magic Angle Spinning
XRD X-Ray Powder Diffraction
QM Quantum Mechanical
MC Monte Carlo
MD Molecular Dynamics
VMD Visual Molecular Dynamics
NAMD Nanoscale Molecular Dynamics
AMBER Assisted Model Building with Energy Refinement
CHARMM Chemistry at HARvard Macromolecular Mechanics
GROMACS Groningen MAchine for Chemical Simulation
OPLS Optimized Potentials for Liquid Simulations
**TABLE OF CONTENTS**

**ACKNOWLEDGEMENT** ........................................................................................................ i

**ABSTRACT** ........................................................................................................................... i

**LIST OF FIGURES** .............................................................................................................. vii

**LIST OF TABLES** ................................................................................................................ xi

**ABBREVATIONS** ............................................................................................................... xii

**TABLE OF CONTENTS** .................................................................................................... xiii

**CHAPTER 1.** Introduction and Literature Review .......................................................... - 1 -

1.1. Introduction ........................................................................................................ - 1 -

1.2. Organic Ionic Plastic Crystals (OIPC) ............................................................... - 6 -

1.2.1. Overview ........................................................................................................ - 6 -

1.2.2. Phase Behaviour .............................................................................................. - 8 -

1.2.3 Mechanical, Structural and Transport Properties .................................... - 10 -

1.2.4. The [C2mpyr][NTf2] System.................................................................... - 16 -

1.2.5. The [C2mpyr][BF4] system............................................................................ - 20 -

1.2.6. The [C1mpyr][N(CN)2] system................................................................ - 23 -

1.3. Scope of the thesis ............................................................................................ - 25 -

1.3.1. Research Objectives and Questions......................................................... - 25 -

1.3.2. Research Questions......................................................................................... - 26 -

1.3.3. Research Aims ................................................................................................ - 26 -

1.4. References .......................................................................................................... - 27 -

**CHAPTER 2.** Research Methodology ........................................................................... - 33 -

2.1. Materials Preparation .......................................................................................... - 33 -

2.1.1. Preparation of [C2mpyr][NTf2] and mixtures with Na[NTf2] ....................... - 33 -

2.1.2. Preparation of [C2mpyr][BF4] and mixtures with Na[BF4] ..................... - 34 -

2.1.3. Preparation of [C1mpyr][N(CN)2] and mixtures with Na[N(CN)2] ........... - 34 -

2.2. Experimental Characterization Techniques ...................................................... - 35 -

2.2.1. Differential Scanning Calorimetry (DSC) .............................................. - 35 -
4.1. Brief Overview................................................................................................................. - 95 -

4.2. Thermal, Structural and Transport Properties of Mixtures of NaBF₄ Salt with N-ethyl-N-methylpyrrolidinium tetrafluoroborate [C₂mpyr][BF₄] Solid State OIPC ................................................................. - 95 -

4.2.1. Phase Behaviour for [C₂mpyr][BF₄] with Na[BF₄] ........................................ - 95 -

4.2.2. Morphology and topography ........................................................................ - 97 -

4.2.3. Ionic conductivity ................................................................................................ - 100 -

4.2.4. IR/Raman spectroscopy ...................................................................................... - 105 -

4.2. Thermal, Structural and Transport Properties of Mixtures of Sodium Dicyanamide Salt with N,N-Dimethylpyrrolidinium Dicyanamide Solid State OIPC .......................................................... - 113 -

4.3.1. Phase behaviour of C₁mpyr][N(CN)₂] and its binaries with Na[N(CN)₂] - 113 -

4.3.2. Morphology ......................................................................................................... - 117 -

4.3.3. Ionic conductivity .................................................................................................. - 119 -

4.3.4. IR/Raman spectroscopy ....................................................................................... - 122 -

4.3.5. Solid state NMR ..................................................................................................... - 134 -

4.3. Conclusions.................................................................................................................... - 137 -

4.4.1. Na[BF₄]/[C₂mpyr][BF₄] binary mixtures.............................................................. - 137 -

4.4.2. Na[N(CN)₂]/ [C₁mpyr][N(CN)₂] binary mixtures .............................................. - 138 -

4.4. References..................................................................................................................... - 139 -

CHAPTER 5. Molecular dynamics simulation of OIPCs......................................................... - 142 -

5.1. Overview..................................................................................................................... - 142 -

5.2. Simulation Procedures ............................................................................................... - 146 -

5.2.1. [C₂mpyr][NTf₂] OIPC ......................................................................................... - 146 -

5.2.2. [Me₄N][N(CN)₂] OIPC Doped with Na[N(CN)₂] Salt ........................................ - 148 -

5.3. Structural Properties of [C₂mpyr][NTf₂] OIPC...................................................... - 150 -

5.3.1. Unit Cell Parameters ............................................................................................. - 150 -

5.3.2. Volume Changes .................................................................................................. - 151 -

5.3.3. Radial Distribution Function (RDF) and the Co-ordination Number... - 153 -

5.4. Dynamical properties of [C₂mpyr][NTf₂] OIPC ................................................... - 159 -

5.4.1. Brief overview ...................................................................................................... - 159 -

xv
5.4.2. Dihedral Distribution in [NTf₂]⁻ Anion and [C₂mpyr]⁺ Cation - 159 -

5.4.3. Rotational Autocorrelation Functions - 168 -

5.4.4. Self–Diffusion D of the individual ionic species - 179 -

5.5. Structural Properties of [Me₄N][N(CN)₂] OIPC Doped with Na[N(CN)₂] Salt – The Radial Distribution Functions (RDF) - 183 -

5.6. Dynamical Properties of [Me₄N][N(CN)₂] OIPC Doped with Na[N(CN)₂] salt – Rotational Autocorrelation Functions - 188 -

5.7. Dynamical Properties of [Me₄N][N(CN)₂] OIPC Doped with Na[N(CN)₂] Salt – Self-diffusion - 196 -

5.8. Conclusions - 202 -

5.9. References - 204 -

CHAPTER 6. Conclusions and Recommendations - 209 -

6.1. The Na [NTf₂] / [C₂mpyr][NTf₂] Binary Mixture - 209 -

6.2. NaX / [Cₓmpyr][X], X=[BF₄], [N(CN)₂] Binary Mixtures - 210 -

6.3. MD simulations in [Cₓmpyr][NTf₂] OIPC - 212 -

6.4. MD simulations in Na⁺ Doped [Me₄N][N(CN)₂] OIPC - 215 -

6.5. Recommendations and Future Work - 218 -

APPENDICES - 219 -
CHAPTER 1. Introduction and Literature Review

1.1. Introduction

Global population explosion, energy thirsty industrial expansion and the sprawling of urban areas all over the world require huge energy resources in the ranges of several Terawatts in the decades ahead. According to International Energy Agency [1] world energy outlook report 2011, in the years between 2010 and 2035, the non-OECD countries alone account for 90% of population growth, 70% of the increase in economic output and 90% of energy demand growth. It is expected that the number of transport vehicles will be doubled from the current trends to 1.7 billion by the year 2035 leading to demands for proportional increase in the fossil fuel unless alternative electric vehicle technologies penetrate the market. Furthermore, the current state of lifestyle is heavily reliant on technology with large consumptions from power grids.

Extensive studies in the area of energy research suggest that it is high time to brainstorm and look for the way forward to seek more tangible alternatives. Can global energy demands be met with the conventional energy sources, mainly fossil fuels? Is there any geopolitical concern with the fossil fuels producing countries – such as turmoil in parts of the Middle East and North Africa (MENA) countries? How about the environmental concerns over greenhouse gas emissions? Can nuclear-based power stations be viable alternative power sources after the experience of the explosion in Fukushima Daiichi nuclear power plant, in 2011?
Evidence suggests that fossil energy sources are diminishing in volume of share to be replaced by renewable energy sources, mainly by hydropower and wind. In the coming two decades, the consumption of fossil fuels as primary energy is projected to 75% by 2035 [1]. Thus, alternatives to fossil fuels need to be investigated further. In the past few decades, environmentally benign energy sources which cope with the life style and prospective demands are being considered. Energy research laboratories and companies have intensified their search for novel materials suitable for energy storage and sources.

**Figure 1-1 Schematics of an electrochemical device**

Fuel cells, batteries photovoltaics, and super-capacitors are among different types of electrochemical devices under due consideration. In an electrochemical device two electrodes (anode and cathode) are separated by an electrolyte as shown in Figure 1.1. Electrolytes contain mobile cations (positive ions) and anions (negative ions) so as to enable the transport of ions to sustain current flow in the circuit. They can be generally grouped into different categories as liquid or polymeric, crystalline or
amorphous solid state ion conductors and molten salts [2]. The function of an electrochemical device is in part governed by the rate at which the ions are transported to the electrodes. The higher the ion transport across the electrolyte, the higher is the conductivity, a key requirement for high performance devices.

Ionic plastic crystals (IPCs) attracted wide interest as innovative materials in electrochemical devices for sustainable energy and applications in power source due to their inherent material characteristics. Their thermal and mechanical stability, enhanced conductivity [3] and diffusivity resulting from the constituent ions exhibiting orientational and/or rotational disorder [4] in an ordered crystal, makes them potential candidates for future innovative electrolytic materials.

These novel materials have wider applications in batteries, fuel cells, photo-electrochemical cells and also super capacitors because they are highly conductive in both solid and liquid states. They can be solid electrolytes at room or higher temperature and could exist as inorganic materials such as lithium sulphate (Li₂SO₄) [5] and sodium phosphate (Na₃PO₄) [6-8], organic materials and combination of both, with one or more solid-solid phase transitions. Plastic crystal materials are typically ordered crystalline materials at lower temperatures. At higher temperatures, they exhibit one or more solid–solid phase transitions associated with the onset of different rotational / orientational motions and an increase in entropy; ie they display more disorder. Organic Ionic Plastic Crystals typically display plastic behavior at moderate temperatures (below 100°C) compared to their Inorganic counterparts [4].
In comparison with other materials, ionic plastic crystals have significant advantages over glasses, ceramics, liquid and polymer electrolytic materials. Glasses and ceramics are brittle although they may have high concentration of mobile ions and a low activation energy for conductivity and are often termed fast ion conductors. On the other hand, liquid electrolytes may be corrosive and volatile and require a support material in order to be used in devices. In polymer electrolytes, ion mobility is limited by low salt solubilities and segmental motion of the polymer. However, plastic crystal phases provide better thermo-mechanical stability while the crystalline material creeps readily under relatively low forces and can deform without fracture under stress [4]. Thus, OIPCs have desirable transport and mechanical properties for use in devices.

In the last few decades, a number of ionic plastic crystals with multiple phase transitions and rotator phases, including the families of quaternary ammonium, imidazolium, pyridinium, choline and pyrrolidinium- cations etc. with the combination of dicyanamide, dihydrogenphosphate, hexafluorophosphate, iodide, bromide, tetrafluoroborate, triflate, bis(trifluoromethanesulfonyl) imide-anions etc. [3, 9-31] were investigated mainly for electrolytes in batteries[32, 33] and fuel cells [27] at ambient temperatures. The study on solid state electrolytes is an important area of research in order to improve the thermal, mechanical, structural, electrical stability in batteries and fuel cells. In these studies, the doped or mixed systems showed enhanced conductivity over the pure materials as one of the requirements for the improvement of electrochemical performance.
Our current research will shed light on potential solid state electrolyte materials doped with sodium (Na) salts to have better understanding of the effect of this cation on structure and transport properties compared with the Li+ ions which have previously been incorporated into these OIPC systems. The ionic radius of Na ions is 1.15 angstroms while Li has an ionic radius of 0.72 angstroms [34]. If doping with the Na cation results in enhanced conductivity then applications particularly in energy storage would be immense. Na+ doped solid-state electrolyte for ambient temperature applications would be favored due to their thermal and mechanical stability, low cost and environmentally friendliness. In conclusion, this research project deals with the thermal, structural, morphology and transport properties of OIPC/sodium salts mixtures using various experimental techniques and molecular dynamics (MD) modeling and simulation.

In understanding and optimizing these novel solid state materials for their best use the interrelationship between the structure, morphology and their transport mechanisms at various levels - at molecular/atomic, microscopic and hierarchical levels need to be studied. Molecular dynamics and different experimental techniques are used for wider range of characterization and investigation of different properties. The structure of the OIPCs and the salts to be investigated in this research project were shown in Figure 1.2.
1.2. Organic Ionic Plastic Crystals (OIPC)

1.2.1. Overview

Plastic crystals are defined as materials which consist of a three dimensional (3D) crystalline lattice with orientational and/or rotational disorder with respect to molecular or ionic species without affecting the long range order. Timmermanns [36] identified a class of organic plastic crystals as rotator phases, rich in solid-solid transitions below their melting temperature with final entropy of fusion below 20J K⁻¹mol⁻¹. This criterion was applicable for a range of organic molecular species such as succinitrile, cyclohexane and pentaglycerine [4]. Generally speaking, these class of materials have been studied extensively and are known to display a large
enthalpy or entropy change [36] below the melt associated with more degrees of freedom they possess compared to a fully ordered crystalline phases. higher the disorder and the more the plasticity such a material has [4]. However, some of the ionic plastic crystals were found to be exceptions to Timmermanns criterion probably due to the contribution of higher entropy associated with some internal degrees of freedom that could be triggered only at the melting point [35], for example if disorder in the anion sub-lattice was triggered only at the melting temperature whereas the cation sub-lattice undergoes disorder at a lower temperature solid-solid phase transition (or vice versa).

Without exception, organic ionic plastic crystals are rich in solid-solid transitions below their melting temperature. DSC is one of the most versatile instruments for the measurement of heat flow – endothermic/exothermic - as a function of temperature and thereby measure phase transitions. As it is well known, most of these plastic crystals have one or more solid-solid phase transitions before the melting temperature. Figure 1.3 shows a typical DSC trace of an archetypal entropy of melting. This property makes these materials viable candidates for ionic

![DSC trace of a pure [C$_2$mpyr][NTf$_2$] OIPC with rich solid-solid transitions](image)

Figure 1-3 DSC trace of a pure [C$_2$mpyr][NTf$_2$] OIPC with rich solid-solid transitions
conduction at ambient temperature and beyond either as a pure material or mixed with other salts. The addition of low levels of dopant ions such as Li$^+$ [17, 21, 22, 37, 38] were observed to enhance ionic conductivity significantly. On the other hand, a group of inorganic ionic plastic crystals exhibiting “paddle wheel motion” with anions such as (SO$_4$)$_2^-$ [5], (PO$_4$)$_3^-$[7], (H$_2$PO$_4$)$_1^-$ [27] had been of great interest for conducting Li$^+$, Na$^+$ ions in batteries, however they undergo transition to the plastic phase at very high temperatures (>300°C)[6, 7]. In the current research, we are dealing with pyrrolidinium cation species [C$_2$mipyr, C$_1$mipy] in combination with anions [NTf$_2$, [BF4] and [N(CN)$_2$] within the scope of experimental characterisation and molecular dynamics simulation. The experimental investigation deals with pure materials and mixtures of the salts with the OIPC, keeping the anion the same.

1.2.2. Phase Behaviour

Thermal measurements can be used to infer phase behaviour in materials. For example, information regarding the rotational or orientational disorder mechanisms of OIPCs can be inferred from thermal behaviour i.e. whether a phase transition occurs gradually over a temperature range or abruptly, caused at a first order phase transition. In both cases the phase transition can result from rotational disorder of one or more principal axes or the position of the molecules, although in former case it may be a co-operative process. Thus, the onset of rotation heralds the existence of defects and vacancies in the material, which in turn is believed to define the origin of diffusion and conductivity.
First order phase transitions are characterised by discontinuous changes in enthalpy ($\Delta H$), entropy ($\Delta S$), and volume ($\Delta V$), for which the quantities $H$, $S$ and $V$ are determined from the first derivative of Gibbs energy with respect to temperature and pressure [39]. In some cases in materials, the quantities defining transition are second order changes of Gibbs energy with respect to temperature and pressure- as in the quantities like heat capacity, isothermal compressibility and volume expansivity. Such transitions are called second order phase transitions. Second order phase transitions attribute to variations in unit cell dimensions gradually without breaking bonds as distortions occur [39]. The phase transition processes may be easier to distinguish in pure plastic crystals than in the combination of additives or mixture with other materials. In the case of ionic plastic crystals mixed with additives, fillers or dopants, distinct crystalline phase may exist accompanied by changes in the physicochemical properties. However, such changes in phase behaviour of additives/mixtures can be traced through thermal measurements. Phase diagrams are important tools to determine the composition of phases as a function of temperature or pressure.

Thermal properties of organic salt based on cations such as pyrrolidinium, quaternary ammonium, imidazolium, pyridinium, choline with a combination of anions such as dicyanamide, dihydrogenphosphate, hexafluorophosphate, iodide, bromide, tetrafluoroborate, triflate, bis(trifluoromethanesulfonyl) imide, thiocyanate, phosphonium [10-14, 17, 19, 21-23, 26, 28, 38-43] were widely investigated using different techniques in past work. The effect of adding fillers ($\text{Al}_2\text{O}_3$, $\text{TiO}_2$, $\text{SiO}_2$) within these OIPCs has also been examined [26, 28-30, 40, 44]. Thus, most of the previous work identified the occurrence of solid-solid phase
transitions and the enthalpy and entropy changes associated with each of the
transitions of the abovementioned systems.

Despite significant work in the experimental characterisation of some of the OIPC
materials for nearly two decades, the theoretical understanding using molecular
dynamics (MD) simulation have received lesser attention. Adebahr et.al and Hooper
et.al [9, 45] separately investigated tetraammonium dicyanamide OIPC using MD.
They predicted the structure and transport properties in their respective work. The
correlation between the conductivity and the volume change as a function of
temperature was observed. The material has shown substantial volume increase over
the phase transitions except for phase I, which had only a slight change in volume
compared to the melt. They concluded that the isotropic rotation is predominant in
phase I until translational motion takes over finally in the melt as predicted
experimentally [46, 47]. The liquid phase of these organic salts known as ionic
liquids have received more attention with respect to the MD. For example, the
thermodynamic, structural and transport properties of different varieties of ionic
liquids with cations pyrrolidinium, quaternary ammonium, imidazolium,
pyridinium; with a combination of dicyanamide, hexafluorophosphate, iodide,
bromide, tetrafluoroborate, triflate, bis(trifluoromethanesulfonyl)imide, thiocyanate
anions [45, 48-54] were investigated.

1.2.3 Mechanical, Structural and Transport Properties

Crystalline solids exhibit a periodic repetition in the positions of atoms or molecules
within the parameters described by the unit cell. However, such arrangements can
be interrupted by defects, imperfections or impurities in the crystalline solid. Lattice
imperfections or deformations such as point defects (vacancy, interstitials, impurities), line defects (dislocations), plane defects (grain boundaries) are common in solid crystals. In point defects, the constituent atom/molecule/ion is either is missing (vacancy) or misplaced from its regular position (interstitial) or replaced by other species in the crystal structure (impurity). Figure 1.4 (I) shown below depicts the point defects in conventional crystals that are generally classified as vacancies, self-interstitial, and substitutional or interstitial impurity. Vacancies are vacant spaces unoccupied by the species of the crystal. They commonly occur at high temperatures when atom/molecule/ions change their positions frequently and randomly thereby forming empty lattice sites. A self-interstitial atom is an extra atom that occupies the interstitial void in the crystal structure. Both self-interstitial and interstitial impurity atoms occur only in low concentrations to be lodged in the interstitial site while they distort and stress the already tightly packed lattice structure. A substitutional impurity represents a species of different type replacing the species in the bulk lattice. Interstitial impurity atoms are much smaller than the atoms in the bulk matrix and the substitutional impurity atoms are of size close to the bulk atom. It is easier for smaller size interstitial impurity atoms to fit into an empty space between the bulk species of the lattice. In most cases diffusion (mass transport by atomic motion) can only occur because of vacancies.
Plastic crystal phases exist in between solid and liquid phases, with a crystalline lattice that undergoes rotational/orientational molecular disorder. They categorically either creep under the influence of gravity or easily deform under stress without fracture. The existence of point defects in ionic plastic crystals is dictated by the neutrality of charge of the ion pairs forming a crystal. They are categorised as Frenkel or Schottky defect [55]. The schematic representation of Frenkel and Schottky defects are shown in Figure 1.4 (II). In ionic crystals, an ion displaced from a regular position to an interstitial site leaves behind a vacancy and the created vacancy-interstitial site is termed as Frenkel defect. In some cases, cations are displaced because their size is smaller than the anions. In close packed systems, it is often difficult to create interstitial at low temperature due to the additional energy that is needed to displace ions from the regular lattice. However, thermal vacancy concentration would be higher to transport cations at high temperatures, in the vicinity of melting temperature. In Shottky defect, pair vacant sites are created by missing ion-pairs from their regular lattice sites. Alkali halides [56] are the best
example for the Schottky defect, in which the vacant sites facilitate atomic diffusion.

The other possible type of defect in ionic plastic crystals is related to line imperfections – dislocations- which is caused by misalignment in the crystal. Dislocations are resulted from plastic deformation, processes during solidification or crystal growth and thermal stresses that result from rapid cooling. These imperfections are thermodynamically unstable as compared to point defects. Due to these imperfections, regular arrangement of atoms/ions can be disrupted along the line at the end of the plane and are generally classified as edge and screw dislocations or the combination of both. Figure 1.5 shows schematic depictions of dislocation in crystals [55]. In screw dislocation, imperfections run in a spiral form down its axis resulting from planes displaced relative to each other caused by shear stress. In contrary to the edge dislocation, there are no preferred slip planes in screw dislocation.

![Figure 1-5 Schematic representation of a dislocation that has a) edge and b) screw with arrows indicating the region of imperfection and direction of applied force](image)

- 13 -
Interfacial defect, mainly grain boundaries, are the most relevant to OIPCs. In an interfacial defect mechanism, two or more crystalline structure or orientations are placed on either sides of the boundary. These distortions are thermodynamically unstable, as in line defects, and are formed from clusters of line defects in a plane with a thickness exceeding an atomic diameter. However, grain boundaries are also important in that they present paths for the mobility of species (diffusion) and also affect the mechanical properties.

So far, the types of imperfections in crystalline solids have been discussed. In the next few paragraphs, details on some examples of defects relevant to OIPCs will be presented. Lattice defects and impurities have been suggested to contribute to mechanical stability [55] in plastic crystals. The mobility or mass transport of species in these materials is facilitated by the imperfections in the crystal and besides that they play a vital role in mechanical, morphological, topological and structural properties. Studies suggest that lattice defects and imperfections: vacancies, dislocations and grain boundaries are not only responsible for the mechanical properties, but they are heavily involved in diffusion mechanisms and ionic conductivity. Self-diffusion is mainly attributed to vacancies and interstitials, while pipe diffusion is facilitated through dislocations and grain boundaries [55].

Several studies involving Scanning Electron Microscopy (SEM), Positron Annihilation Lifetime Spectroscopy (PALS) have been carried out [10-14, 17, 18, 21, 35, 57], in order to understand the interrelationship between morphology, topology and microstructure of organic ionic plastic crystal materials and their
transport properties. Ishida et al. studied the behaviour of self-diffusion in a large number of ammonium salts [20, 58]. They described that the diffusion mechanism was triggered by Schottky vacancy and/or vacancy-pair mechanisms. Studies on pure samples of \([\text{C}_2\text{mpyr}]\text{[NTf}_2\text{]}\) and mixtures with \(\text{Li}[\text{NTf}_2]\) [17, 21, 22]; \([\text{C}_x\text{mpyr}]\text{[BF}_4\text{]}\) (x=1-3) and mixtures with \(\text{Li}[\text{BF}_4]\) salts [11-14, 26, 28-30, 43] and \([\text{C}_1\text{mpyr}]\text{[N(CN)}_2\text{]}\) and mixtures with \(\text{Li} [\text{N(CN)}_2]\) salts [35] are the most relevant to this project.

**Figure 1-6 The SEM micrographs of pure \([\text{C}_2\text{mpyr}]\text{[NTf}_2\text{]}\) OIPC [28]**

SEM micrographs of pure \([\text{C}_2\text{mpyr}]\text{[NTf}_2\text{]}\) and \([\text{C}_x\text{mpyr}]\text{[BF}_4\text{]}\) (x=1-3) plastic crystal phases show spherical morphology unlike that of perfect crystals and the motion of dislocations and grain boundaries were observed as shown in the Figure 1.6. Perfect crystals have sharp edges, flat surfaces and regular shapes. Spherical morphology, motion of dislocations and grain boundaries in this plastic crystal is
attributed to plastic deformation. It has been suggested that the crystallographic slip plane occurs by the motion of dislocations under mechanical or thermal stress [4, 11-14, 26, 28-30, 43, 55]. Besides that, evidence shows that the occurrence of slip and the mobility of dislocations are interrelated and dependent on intermolecular bonding interactions. The lattice vacancies in \([\text{C}_2\text{mpyr}]\text{[NTf}_2\text{]}\) and \([\text{C}_x\text{mpyr}]\text{[BF}_4\text{]}\) (\(x=1-3\), where 1, 2 and 3 represent methyl, ethyl, propyl respectively) plastic crystal phases were investigated by using the PALS technique. The number, size and ionic motion were determined for the better understanding of conduction mechanism. These studies concluded that the hopping of ions between vacancies can occur relatively independently, in a correlated way as cation-anion pairs, or as ions diffusing through extended defects as the likely routes for conduction mechanisms.

### 1.2.4. The \([\text{C}_2\text{mpyr}]\text{[NTf}_2\text{]}\) System

In the next few paragraphs, we will explore previous studies related to pure \([\text{C}_2\text{mpyr}]\text{[NTf}_2\text{]}\) and doping with \(\text{Li}^+\) salts. The pyrrolidinium salts were investigated either for their plastic behavior or as ionic liquids in the last two decades. MacFarlane and Forsyth groups [6-10, 13, 15, 17-19, 22, 24, 33, 36, 39-42] [10-14, 17, 19, 21-23, 26, 28, 33, 38, 43, 59-61] have extensively reported and studied different pyrrolidinium cations with different anions. \([\text{C}_2\text{mpyr}]\text{[NTf}_2\text{]}\) had been of interest for its rich solid-solid phase transitions. Henderson et al.[62] studied the crystal structure of \([\text{C}_2\text{mpyr}]\text{[NTf}_2\text{]}\) using x-ray diffraction techniques in two different phases at -120°C and -60°C – ordered (Phase IV) and disordered (Phase III). They found that all ions are ordered in phase IV and all the ions are disordered in Phase III while retaining the crystal packing similar to the ordered phase IV.
Figure 1.7 shows the two pairs of asymmetric units in phases IV and III indicating that the NTf₂⁻ anions adopt to C₂ conformation [63] while both C₂mpyr⁺ cations adopt an envelope (C₃) conformation. These will be discussed in more detail in the context of the experiments later.

![Figure 1-7](image)

*Figure 1-7  The asymmetric units of cation–anion pair in [C₂mpyr][NTf₂] for the a) monoclinic phases at 153K (left) and b) triclinic phase at 213K (right).*

In the disordered phase III, the two cations overlay each other along the central nitrogen (blue) with the centre passing through middle of two carbons on the pyrrole ring. The anions are related through a unique inversion. This cation-anion combination is featured for its excellent electrochemical and thermal stability. The plastic crystal behavior is possibly related to weaker anion-cation interactions mainly because the charge on the anion is delocalized among the sulfur, nitrogen and oxygen atoms in part with CF₃ groups also being electron-withdrawing. The anion exists in a trans (favoured) and cis conformations with CF₃ group on the opposite and same sides of S–N–S plane respectively [64, 65]. However, in many metal NTf₂ salts, cisoid is favoured over transoid conformation and is not well understood [64, 65]. This ability to exist in different conformers also possibly contributes to the plasticity in these materials.
Numerous previous studies have shown that the pure sample of [C\text{2mpyr}][\text{NTf}_2] undergoes several solid-solid transitions [9, 22, 28, 62]. Thus, the transition from ordered phase IV to disordered phase III was observed at -85°C followed by phase III to phase II transition occurring at 17°C. The solid-solid transition before the melting point of [C\text{2mpyr}][\text{NTf}_2] at 91°C, occurred at 45°C is the transition from disordered phase II to disordered phase I. The melting curve of the material is characterized by narrow, sharp peak in this material.

Previous studies conducted on the solid-solid transition phases in the pure and doped materials concluded that conformational flexibility, pronounced ionic mobility as a result of dynamic rotational disorder in the cation C\text{2mpyr} and/or anion NTf\text{2} contribute to low lattice energies and inefficient packing [64-67]. Furthermore, these studies established the correlation between the low lattice energies, ionic radius and the thermal behavior. It was concluded that the lower the lattice energies the lower the melting points.

SEM measurements of [C\text{2mpyr}][\text{NTf}_2] have established the presence of varied grain sizes, grain boundaries and regular slip planes as shown in Figure 1.6. Besides that PALS measurements previously established the Schottky-type defects [20, 58, 68-70] were likely responsible for cation–anion dynamics in a co-operative motion in some ammonium salts and pyrrolidinium hexafluorophosphate, with the same analogy applicable to [C\text{2mpyr}][\text{NTf}_2]. The crystal structure and vacancies undergo changes with temperature as shown via the DSC, X-ray diffraction and PALS measurements. The possible types of motion– rotational and translation motion of the cation-anion as a whole or their constituent functional groups CF\text{3}, CH\text{3} is also temperature dependent. For example, the CH\text{3}, CF\text{3} group rotation and isotropic
tumbling increases as temperature increases. NMR measurements on 
[C2mpyr][NTf2] [15] showed significant increase of cation mobility with the 
temperature and hence contribute to the conductivity in this material.

Lithium bis(trifluoromethanesulfonyl)amide (Li[NTf2]) salt had previously been 
doped into C2mpyr[NTf2] to create a potential solid state electrolyte for Li batteries. 
The doping of smaller quantities of Li[NTf2] to the OIPC [C2mpyr][NTf2] system 
resulted in an increase of three orders of magnitude in ionic conductivity [21, 22] in 
phase I and II. With 33% of doping with Li[NTf2] salt, the material exhibited a 
conductivity as high as 10^{-4} \text{ S cm}^{-1} in phase I, at ambient temperature, before the 
euteric temperature of \sim 34^\circ\text{C}. It was proposed that vacancies are created while 
distorting the crystal lattice with the addition of small amounts of dopant. The 
creation of higher vacancy concentration occurs as temperature increases, with more 
ions diffuse and an increase in conductivity results. One reason for the higher 
conductivity may also be due to the fact that, at a higher concentration the formation 
of a liquid phase occurs in a binary mixture, and hence a greater concentration of 
mobile ions result. This may also result in even higher conductivity through the 
liquid phase.

The OIPCs were considered as ideal electrolytes for lithium batteries for their 
inherent properties: non-flammability, non-volatility, plasticity, thermal and 
electrochemical stability[43]. For example, pyrazolium NTf2 [71], pyrrolidinium 
NTf2 [22, 23, 61], [BF4] [42] and other OIPCs [72, 73] were investigated for lithium 
devices. The ionic liquids of pyrrolidinium NTf2 [74] had also been investigated and 
shown stable electrochemistry [33].
Despite two decades of study on OIPC in general and $[C_2\text{mpyr}][\text{NTf}_2]$ in particular, our understanding of transport mechanisms and the realization of these materials as a potential candidate in solid state electrolytes is still in its infancy [43]. In the journey to full understanding and design of novel solid state electrolytes, our current research utilizes the power of advanced experimental techniques and MD simulations. To our knowledge, there has been no molecular dynamics study carried out in relation to the OIPC $[C_2\text{mpyr}][\text{NTf}_2]$ phases and the mixture with any other salts. Thus, our current research will shed light mainly on the interrelationship between the structural and transport properties by investigating the effect of dopants of different sizes and charges.

1.2.5. The $[C_2\text{mpyr}][\text{BF}_4]$ system

The family of N-methyl,N-alkylpyrrolidinium tetrafluoroborate OIPCs have been extensively studied [11-14, 26, 28, 42, 75, 76] at the fundamental level and as electrolytes for potential applications in electrochemical devices. The following paragraphs describe these previous studies with respect to phase behavior and transport properties of pure N-methyl,N-alkylpyrrolidinium tetrafluoroborate OIPCs and their mixtures with Li[BF$_4$].

The thermal behaviour of pure $[C_x\text{mpyr}][\text{BF}_4]$ (with $x=1-3$) has previously been reported and it was shown that multiple solid state phases exist for these materials. In particular the $[C_1\text{mpyr}][\text{BF}_4]$ and $[C_2\text{mpyr}][\text{BF}_4]$ OIPCs are rich in solid-solid phase transitions. These OIPCs have shown a significantly lower entropy of fusion,
much smaller than the entropy of 20 J K\(^{-1}\) mol\(^{-1}\) set as Timmerman’s criteria for plastic crystals, and much lower than the entropy of fusion for the [C\(_2\)mpyr][NTf\(_2\)] discussed above.

In case of the [C\(_2\)mpyr][BF\(_4\)] OIPC [42], the phase transition from Phase VI to phase V occurs at \(-68^\circ\)C followed by the next transition peak from phase V to IV at \(-55^\circ\)C. A smaller and sharp transition was observed upon reaching a temperature of \(-41^\circ\)C that was assigned to the transition peak from phase IV to phase III. Furthermore, the next solid-solid transitions from phase III to II at \(-29^\circ\)C is much sharper and is followed by the final solid–solid transition (from phase II to I) which occurs at 68°C and the final melting of this OIPC to occur at 280°C. The same study has found that the [C\(_2\)mpyr][BF\(_4\)] OIPC exhibits plastic crystal phase behavior, with the entropy of fusion of 5.0 J K\(^{-1}\) mol\(^{-1}\), which is one of the smallest entropy of fusion for the pyrrolidinium based OIPCs. This OIPC is also of particular interest due to its wider solid state thermal window in the plastic crystal phase, extending from \(-70^\circ\)C to 280°C in phase I.

The microstructures and plastic behaviour of the N-methyl,N-alkylpyrrolidinium tetrafluoroborate, [C\(_x\)mpyr][BF\(_4\)] with x=1-3 and their Li\(^+\) mixed systems was also extensively studied [13, 14, 75]. The studies have shown that the microstructure in these OIPCs exhibit extensive lattice defects such as grain boundaries, slip planes and dislocation pits, which are the attributes of plastic crystalline phases associated with the strong rotational/orientational disorder in these materials. Furthermore, it was suggested [13] that the dislocations created from the coalescence of vacancies and crystallographic slip in single and polycrystalline specimens are also responsible for the plastic flow.
The transport properties of pure [C\textsubscript{x}mpyr][BF\textsubscript{4}] with x=1-3 [11-14, 77] and Li\textsuperscript{+} mixed systems [28, 75, 76] as well as the binary and ternary mixture with the polymers such as aPEO and PVP [11, 14] were also previously studied. In the study of pure [C\textsubscript{1}mpyr][BF\textsubscript{4}], it had been shown that the conductivity of the OIPC increases until it reaches the solid-solid transition from the phase II to I transition. Following this transition, a conductivity plateau occurs, in phase I of this OIPC, which coincides with lower apparent cation mobility as evidenced by the \textsuperscript{1}H NMR data and Raman spectroscopy [77]. This was also consistent with the structural changes observed from the XRD [77]. Upon addition of a Li[BF\textsubscript{4}] salt [75] the conductivity of this OIPC was enhanced, particularly with the addition of 8\%wt or more of Li[BF\textsubscript{4}] into the OIPC in phase II. This was followed by a decrease in an order of magnitude, in phase I which was suggested to be consistent with the findings in the pure OIPC; there appears to be a lattice restructuring and reduced ionic mobility upon reaching phase I. Variations in conduction behaviour had also been reported in different phases of the binary/ternary mixtures of [C\textsubscript{2}mpyr][BF\textsubscript{4}] / Li[BF\textsubscript{4}] / PVdF nanofibres [76] and [C\textsubscript{3}mpyr][BF\textsubscript{4}] [11, 14] mixed with Li[BF\textsubscript{4}] /aPEO and PVP polymer. It was suggested that the enhanced conductivity in phase II in [C\textsubscript{2}mpyr][BF\textsubscript{4}] / Li[BF\textsubscript{4}] / PVdF nanofibres is due to the favoring of a metastable disordered phase, whilst the decrease in conductivity in phase I is attributed to the disruption of the Li transport mechanism caused by the interactions on the surface of the fibres. Efthimidias et al [11, 14] reported that the conductivity increases in phase II upon mixing the PVP into the [C\textsubscript{3}mpyr][BF\textsubscript{4}] /Li[BF\textsubscript{4}] binary mixture whereas, in stark contrast, the addition of aPEO into the same binary system decreases the conductivity. The effect of some solubility of the Li[BF\textsubscript{4}] salt into the polymer component was suggested to have a great role in the conduction
mechanism. It was concluded that the block to ion transport in the grain boundaries when a blocking polymer such as PVP is present, leads to the decrease in conductivity, particularly in phase II. On the other hand, intra-granular ionic transport were responsible for the increase the conductivity in phase I. In the aPEO polymer containing matrix of [C₃mpyr][BF₄] / Li[BF₄] the aPEO itself may facilitate ion transport.

In general, thermal, microstructural and transport properties of the mixtures of Li[BF₄] salt with [Cₓmpyr][BF₄] with x=1-3 OIPC were presented. So far, to our knowledge, no significant work has been published in relation to the Na[BF₄] mixed with these OIPCs. Therefore, in the current project, the phase behavior, structural and dynamic properties of binary mixtures of Na[BF₄] / [C₂mpyr][BF₄] will be elucidated at different Na⁺ concentration.

1.2.6. The [C₁mpyr][N(CN)₂] system

The N-methyl,N-alkylpyrroldinium dicyanamide [Cₓmpyr][N(CN)₂] system, except for x=1 (methyl), exist as ionic liquids (ILs). The [N(CN)₂]⁻ anion containing ionic liquids were extensively studied [78, 79] for applications in the area of electrodeposition for their strong complexing ability towards the transition metal ions. The lower viscosity in [N(CN)₂] anion based ILs compared with their [BF₄] and [NTf₂] counterparts make them ideal for electrochemical applications due to their higher conductivity. The only pyrrolidinium based OIPC with dicyanamide anion is dimethylpyrrolidinium dicyanamide [C₁mpyr][N(CN)₂].

Several studies in the pyrrolidinium based OIPCs [11-14, 35, 61] have demonstrated the occurrence of several solid-solid transitions, which is usually associated with
increasing rotational motion and/or disorder. \([\text{C}_{1}\text{mpyr}]\text{[N(CN)\textsubscript{2}}]\) OIPC also undergoes solid-solid phase transitions. It had been reported [35] that lowest temperature solid-solid transition occurs at \(\sim -2^\circ\text{C}\) and culminating with the final melting peak at \(\sim 120^\circ\text{C}\). The pure \([\text{C}_{1}\text{mpyr}]\text{[N(CN)\textsubscript{2}}]\) OIPC have shown the highest conductivity at temperatures below \(\sim 80^\circ\text{C}\) compared to \(\text{NTf}_2\), \([\text{BF}_4]\) and \(\text{PF}_6\) counterparts. Moreover, the OIPC display high degree of plasticity before the final melt. Thus, the high conductivity of \(\sim 10^{-4} \text{ S cm}^{-1}\) at \(\sim 80^\circ\text{C}\) in a solid state can be linked to the presence of extended defects or vacancies [35].

The addition of Li salt [35, 61, 75, 76] into \([\text{C}_{1}\text{mpyr}]\text{[N(CN)\textsubscript{2}}]\) OIPC has shown a change in thermal behaviour and ionic conductivity. With the increasing Li\(^+\) content in the binary mixture, an additional melting transition peak (eutectic melting) appeared at \(\sim 30^\circ\text{C}\). The effect on the conductivity was also observed to be tremendous. The ionic conductivity dramatically increased with the addition of small amount of Li\(^+\) content (as low as 2\(^\%\) mol Li[\text{N(CN)\textsubscript{2}}]), but this is likely to be due to presence of a liquid phase perhaps along the grain boundary.

The binary mixture of lithium salts with different OIPCs has been extensively reported and the demonstration of these mixed systems in lithium metal devices has been demonstrated. However, the effect of mixing \([\text{C}_{1}\text{mpyr}]\text{[N(CN)\textsubscript{2}}]\) OIPC with the Na[\text{N(CN)\textsubscript{2}}] has not been reported. This present research will investigate on the mixtures of an OIPC with a sodium salt, in order to gain a better understanding of the effect of the Na\(^+\) cation on thermal, morphological and transport properties of the binary mixtures.
1.3. **Scope of the thesis**

1.3.1. **Research Objectives and Questions**

There is considerable interest in the field of solid-state electrolytes based on organic ionic plastic crystal (OIPC) salts, specifically at ambient temperature for electrochemical cells and devices. Ionic conduction of these materials in both solid and liquid states makes them favourable candidates for electrolyte in batteries and fuels cells. The mobility of ions in a largely immobile (ordered) crystal lattice makes them qualify for solid-state ion conduction mechanisms. In this research, mechanisms of ion transport, phase behaviour and morphology will be investigated based on the Na\(^+\) doped into pyrrolidinium salts – [C\(_2\)mpyr][NTf\(_2\)], [C\(_2\)mpyr][BF\(_4\)] and [C\(_1\)mpyr][N(CN)\(_2\)].

Various experimental techniques to be discussed in the next chapter will be employed to investigate phase behaviour of the mixed systems with the addition of sodium salts, up to the molar concentration of 70%, in order to compare with a pure sample. This allows better understanding of phase behaviour in relation to ionic conductivity and diffusion mechanisms. The structure and transport properties will be investigated using complimentary techniques such as DSC, SEM, FTIR/Raman, solid-state NMR spectroscopy and synchrotron XRD. Emphasis will be given to examine the role of anion/cation and the effect of chemical structure on conductivity and diffusion with the help of experimental characterization techniques and molecular dynamics simulation.
Based on already available structural data from the experiments, correlation between the structural, thermal properties (phase behaviour, enthalpy and entropy changes) and dynamic properties (diffusion coefficient, conductivity) will be calculated based on molecular dynamics simulation in some of these materials. The obtained values will be used to validate the experimental results and further clarify transport mechanisms. In general, this research is intended to investigate thermal, structural, morphological and transport properties of \([\text{C}_2\text{mpyr}][\text{NTf}_2], [\text{C}_2\text{mpyr}][\text{BF}_4]\) and \([\text{C}_1\text{mpyr}][\text{N(CN)}_2]\) doped with small inorganic cations using various experimental techniques and molecular dynamics modelling and simulations. In summary the following are the aims of the research project.

1.3.2. Research Questions

- What is the influence of adding the Na cation on the phase behaviour, structure, transport and conduction processes in a number of OIPCs including \([\text{C}_2\text{mpyr}][\text{NTf}_2], [\text{C}_2\text{mpyr}][\text{BF}_4]\) and \([\text{C}_1\text{mpyr}][\text{N(CN)}_2]\) ?
- Can the experimental and MD understanding from this work benefit the design of OIPC novel materials to be used for sustainable energy?

1.3.3. Research Aims

1. To understand the thermal, structural and transport properties of the pure plastic crystals \([\text{C}_2\text{mpyr}][\text{NTf}_2], [\text{C}_2\text{mpyr}][\text{BF}_4]\) and \([\text{C}_1\text{mpyr}][\text{N(CN)}_2]\) and the doping with \(\text{Na}^+\) salts using experimental techniques such as Differential Scanning Calorimetry (DSC), Electrochemical Impedance Spectroscopy (EIS), Scanning Electron Microscope (SEM), Atomic Force Microscope
(AFM), X-ray powder diffraction (XRD) and Nuclear Magnetic Resonance (NMR).

2. To investigate the structural and transport properties and the conduction mechanism of the pure crystals and doped systems using molecular dynamics simulation.

1.4. References


12. Efthimiadis, J., et al., Solid state ion transport and phase behaviour in composites of N,N-methyl propylypyrrolidinium tetrafluoroborate and


CHAPTER 2. Research Methodology

2.1. Materials Preparation

2.1.1. Preparation of \([\text{C}_2\text{mpyr}][\text{NTf}_2]\) and mixtures with \(\text{Na}[\text{NTf}_2]\)

Highly purified ionic plastic crystal \(N\text{-ethyl-}N\text{-methylpyrrolidinium}\) bis (trifluoromethyl-sulfonil) amide \(([\text{C}_2\text{mpyr}][\text{NTf}_2])\) of purity of 99\% was purchased from Solvionics (ASIS scientific Pty. Ltd.), sodium bis (trifluoromethylsulfonil) amide \((\text{Na}[\text{NTf}_2])\) salts of purity 96\% were purchased from Sigma Aldrich Inc. In the preparation of purified sample, 12g of commercially available \([\text{C}_2\text{mpyr}][\text{NTf}_2]\) was dissolved in 150 mL dry acetonitrile and 100 mg activated carbon was added to the solution and stirred over night at room temperature. The black solid was removed via filtration using filter paper and syringe paper. The solvent was removed under reduced pressure. The white solid was dried at high vacuum for 48h giving 11.5g, 96\%. Similarly, 1g of commercially available \([\text{Na}][\text{NTf}_2]\) was dissolved in 10 mL dry acetonitrile placed in the fridge. The white precipitate was removed via filtration using filter paper and syringe paper. The solvent was removed under reduced pressure. The white solid was dried at high vacuum for 48h giving 950g, 95\%.

Due to the hygroscopic nature of the samples, all ionic salts were stored and loaded for the experiment under a high purity argon environment in a glove box. Doping of the samples was carried out under the same environment. Pure sample of \([\text{C}_2\text{mpyr}][\text{NTf}_2]\), the dopants \(\text{Na}[\text{NTf}_2]\) were weighed on molar basis to get mixed. Thereafter, the samples were allowed to completely dissolve for 4 hours at 90°C using stirring centrifuge running at 300rpm. The samples were cooled for 6 hours
and transferred to a vacuum drier. The samples were dried at 110 °C under vacuum for 15 h, and stored in a glove box under Argon environment. Dopant samples of 1, 2, 4, 6, 8, 10, 15, 30, 35, 40 and 50 mole % of Na[NTf₂] were prepared and used in this experiment.

2.1.2. Preparation of [C₂mpyr][BF₄] and mixtures with Na[BF₄]

The N-ethyl-N-methylpyrrolidinium tetrafluoroborate ([C₂mpyr][BF₄]) OIPC was purchased from io-li-tec (98%) and purified by recrystallization using dry acetonitrile (Merck) and ethyl acetate (Chem-Supply) at room temperature. The Na[BF₄] salt was purchased from Solvionic SA (98% purity) and used as received. Pure samples of [C₂mpyr][BF₄] and Na[BF₄] were weighed on molar basis to get mixed in dry acetonitrile under nitrogen atmosphere for over 5 hours. After the solvent was removed in a rotatory evaporator and the samples were dried overnight on a vacuum line at 60°C. Due to their hygroscopic nature, all the samples were stored and loaded for the experiment under a high purity argon environment in a glove box. For the purpose of experimental characterisation, mixed samples of different concentrations of Naₓ[C₂mpyr]₁₋ₓ[BF₄] were prepared and used.

2.1.3. Preparation of [C₁mpyr][N(CN)₂] and mixtures with Na[N(CN)₂]

N,N-dimethylpyrrolidinium dicyanamide OIPC, [C₁mpyr][N(CN)₂], 99% purity, and Na[N(CN)₂] salt, 98% purity, were purchased from Solvionic. The purchased [C₁mpyr][N(CN)₂] was purified further as follows: 10 g of [C₁mpyr][N(CN)₂] was dissolved in 150 mL dry acetonitrile, and 100 mg activated carbon was added to the solution and stirred overnight at room temperature. The black solid was removed
via filtration using filter paper and syringe filter. The solvent was removed under reduced pressure, and the white solid was then dried under high vacuum for 48h; the final yield was 9.4 g. Similarly, 2 g of purchased Na[N(CN)₂] was dissolved in 500 mL dry methanol and heated to 30°C. The white precipitate was removed via hot filtration and then the solvent was removed under reduced pressure. The final white solid was dried under high vacuum for 48 h; the final yield was 1.8 g. Pure, dry [C₅mpyr][N(CN)₂] and Na[N(CN)₂] were weighed and then mixed at 60°C. Because of their hygroscopic nature, all samples were stored and loaded for experiments under a high purity argon environment in a glove box. Samples with different molar concentrations of Na[N(CN)₂], denoted as Naₓ[C₅mpyr]₁₋ₓ[N(CN)₂], were prepared and examined.

### 2.2. Experimental Characterization Techniques

In this section the experimental characterization techniques relevant to this research work are presented. The techniques outlined below were used for the investigation of thermal, structural and transport properties of organic ionic plastic crystals (OIPCs).

#### 2.2.1. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) has been one of the most versatile methods to study thermal properties. A Mettler Toledo differential scanning calorimeter (DSC) - DSC822° [1] with an operational temperature range of measurement from –150 °C to 700 °C equipped with FR5 ceramic sensors of 56 AuAuPd thermocouples was used to investigate the physical and chemical
properties of a material as a function of temperature or time. The equipment comprised of a heating furnace that holds two crucibles made from Aluminum pans, the heating and cooling units. One of the crucibles was sealed empty and used as a reference. In the other crucible, vacuum dried powder samples of less than 10 mg were put into the crucibles in the Argon environment glove box and sealed without piercing, to avoid air into the samples. Precision of the measurements was controlled by the heating and cooling units in the equipment and an external computer control with STAR® V6.10 software [2] for the analysis of the results. In our experiment thermal properties of the samples (both pure and doped or mixed systems) were recorded over a temperature range of $-150$ to $150^\circ\text{C}$ with a scanning rate of $10^\circ\text{Cmin}^{-1}$. The DSC calorimeter was calibrated against the peaks corresponding to cyclohexane transition temperatures and compared the DSC measurements of the OIPCs with the previous results. Calculated mean temperatures (enthalpies) and their standard error for different phases from repeated experiments were reported. The measurements allowed us to trace changes in thermal energy flow and determine thermodynamic properties including phase and other structural transitions over the abovementioned range of temperature. From the same measurement it was possible to obtain heat capacities and solid-solid phase transitions and the melting point of the materials.

2.2.2. Electrochemical Impedance Spectroscopy (EIS)

EIS measurements are used to identify which materials exhibit enhanced ionic conductivity for possible choice in electrochemical devices. The impedance spectra for the pure and doped samples were obtained using a potentiostat (SP-200,
BioLogic Science Instruments) [3] with nine bandwidths, excellent electronic stability and on-board operating system equipped with ECLab software [4]. In-built analog filters allowed the removal of unwanted noise and with a frequency range up to 7 MHZ.

The samples were pressed into pellets using a KBr hydraulic press with 7 tons of load applied for 5 minutes. Pellets in the range of thickness of 0.5-0.8 mm and a diameter of about 13mm were prepared and then sandwiched between two circular steel blocking electrodes. Samples were handled and hermetical sealed under Argon environment in a glove box. The spectral data were collected over a frequency range of 50 mHz to 7 MHz in a temperature range from -30 to 80 °C at 5 and 10 °C intervals under single sine wave acquisition mode at 200mV signal voltage amplitude and auto current mode.

Temperature was controlled using a Eurotherm model 3504 (Invensys Eurotherm Operations Management) temperature controller [5]. Dry ice pellets in a custom made container were used as cryogenics to cool down to the initial temperature. An equilibration time of 45 min was used to trigger and stabilize the temperature at -30 °C before the beginning of the measurement. An interval of 30 min was allotted between measurement temperatures in both conditions of 5 and 10 °C steps (7 min and 51 seconds per scan step). Test experiments were carried out to check for stability and reproducibility in the Nyquist plots for the samples. Nyquist plots of impedance spectral data were used to determine the sample resistance from the intercept or the first touch-down of the real axis.
2.2.3. **Scanning Electron Microscopy (SEM)**

Scanning Electron Microscopy (SEM) was used to study topography and morphology of the [C$_2$mpyr][NTf$_2$], [C$_2$mpyr][BF$_4$] and [C$_1$mpyr][N(CN)$_2$] and mixtures with Na salts at ambient temperature, at microstructural and nanoscale. High resolution JCM -5000 Neoscope (Jeol Ltd.)[6] and Supra 55 [7] with high and low vacuum modes and three alternative accelerating voltages of 5, 10 and 15kV were instrumental in the collection of SEM micrographs at significantly small working distances (2mm) and magnifications as high as X20000. The scanning accelerating voltage of 5kV at high vacuum was suitable for the investigation of [C$_2$mpyr][NTf$_2$], [C$_2$mpyr] [BF$_4$] and mixtures with Na salts. In the case of [C$_1$mpyr][N(CN)$_2$] and mixtures with Na salts, the charging effect was controlled by limiting the applied accelerating voltage to the maximum of 1kV at ambient temperature. Powder samples were prepared in a glove box and put on carbon tape. For the SEM micrographs, the samples were not coated. The powder samples were sprinkled on the sticky carbon tape by gently pressing with a spatula. The loose particles were removed by turning the sample holder upside down. Due to the higher hygroscopic nature of these samples, the materials were transferred into the vacuum chamber without exposure to air.

2.2.4. **Raman / FTIR Spectroscopy**

Raman measurement was conducted using a Renishaw InVia Raman Micro spectrometer (Renishaw plc, Gloucestershire, UK), equipped with a 633-nm HeNe laser (RL633 HeNe, Renishaw plc, Gloucestershire, UK)[8] and a thermo-electrical cooled CCD detector. The original laser power measured at the sample of ca 12
mW was reduced to 1-6 mW to prevent heating and photochemical damage to the samples. Acquisition parameters used for spectral data collection included 10s exposure time and 4-cm\(^{-1}\) spectral resolution. Spectral analysis was performed using WiRE 3.4 (Renishaw) software[9].

ATR-FTIR spectral data was acquired on an Alpha FTIR spectrometer (Bruker Optik GmbH, Ettlingen, Germany)[10] equipped with a deuterated triglycine sulfate (DTGS) detector. To perform ATR-FTIR measurements, the default transmission compartment was replaced by a single-reflection diamond ATR sampling module (Platinum ATR QuickSnap™) with 45° angle of incidence and a 2×2 mm\(^2\) active sensing surface. A background spectrum was individually acquired on a clean surface of the ATR diamond crystal prior to each sample measurement, which was subsequently conducted by pressing a few milligrams of the samples against the sensing surface of the ATR crystal using a metal clamp. The pressure applied by an ergonomic metal clamp was estimated to be less than 20 MPa. The ATR-FTIR acquisition parameters used in OPUS 7.0 software suite [11] throughout the study included 4 cm\(^{-1}\) spectral resolution, 64 co-added scans, Blackman-Harris 3-Term apodization, Power-Spectrum phase correction, and zero-filling factor of 2.

### 2.2.5. Synchrotron X-ray Diffraction (SXRD)

X-ray and neutron diffraction techniques had been used to study structural properties of a select few of these materials [12]. Synchrotron X-ray Powder Diffraction (SXRD) on pure sample \([\text{C}_2\text{mpyr}][\text{NTf}_2]\) and 15% mol doped with Na[NTf\(_2\)] was conducted at the Australian Synchrotron, Powder Diffraction
Beamline 10 [13]. The beamline uses an array of 16 MYTHEN 1D microstrip silicon detectors with each module spanning about 5 degrees in 20 to enable collection of data covering over 83°. The single-photon counting mode and high dynamic range of the beamline provide an excellent signal-to-noise at the photon energy of 12.4keV and current of ~200mA. The powder samples were sealed in 0.3 mm glass capillaries within an argon atmosphere glove box. Prior to data collection, the wavelength was set at 1.00025Å using a Si 111 double crystal monochromator and calibrations were made with NIST reference material LaB₆. Cyberstar hot-air blower was used to control temperature within thermal stability of the order 0.1-0.2K for all data collection temperatures. Data were recorded for 5 min at each of the two detector settings after the control sensor had reached the set point temperature and equilibrated for 3 min.

2.2.6. Solid State Nuclear Magnetic Resonance Spectroscopy

Pure OIPC samples together with Na salt mixtures were investigated using multinuclear solid state NMR techniques on Bruker Ultrashield WB 500 MHz [14] instrument equipped with Avance III spectrometer and BCU II temperature controller at the IFM NMR facility, Deakin University.

The powder samples were prepared and sealed in 2.5 and 4 mm solid-state probe under argon atmosphere in the glove box. The measurements were carried out at constant temperature of 295K to investigate the variation of the environment for different composition and variable temperature effects on the phases were studied using ¹H, ¹⁹F, ¹³C, ²³Na and ¹⁵N nuclei. The MAS measurements with ¹H, ¹⁹F nuclei
were performed in a 2.5 mm probe at Larmor frequencies of 500 and 470.5 MHz with the spinning speed of 27.5 kHz. In the proton measurement, solid echo sequence of 140 kHz, relaxation delay 2-10s was used. On the other hand, $^{19}$F measurements were performed in the solid echo sequence of 140 kHz with the relaxation delay of 8-10s.

In the CP-MAS measurements with the $^{13}$C and $^{15}$N nuclei the 4.0 mm rotor was set to a spinning speed of 12.5 kHz and Larmor frequency of 75.5 MHz respectively. CP contact times of 3–4 ms and 8–10ms and recycle delay times of 2–3 s and 4–5 s were used respectively. Protonated carbon atoms in the samples were differentiated due to the variation of CP contact time and proton decoupling was achieved in the CP-MAS experiments. Two different techniques were used in the measurement with $^{23}$Na. On this nuclei, MAS measurements were performed at a Larmor frequency of 79.4 MHz, spinning rate of 12.5 kHz in a 2.5 mm rotor probe. Solid echo sequence of 114 kHz, relaxation delay 0.3-0.6 s was used in addition to MQ-MAS technique[15].

### 2.3. Computational Methods

#### 2.3.1. Overview on Computer Simulation Methods

Computer simulations have been widely introduced into different fields of study (both biological and physical science areas) to demonstrate the relation between the microscopic and macroscopic behavior of materials. The method defines the interaction between particles in matter under study through either quantum mechanical model or force field (potential function) or combination of both
descriptions. In the quantum mechanical model (QM), solutions to Schrödinger equation are sought while in molecular mechanics (MM) the analytical solutions are based on the notions of classical mechanics, mainly solving Newton’s second law of motion. In the scope of this research, we do not deal with Schrödinger equation which is the basis for QM methods. Quantum-mechanical (QM) method best suit processes that involve few hundreds of atoms and requiring the analysis of chemical reactions and electronic transition processes such as charge transfer or excitation. On the other hand, the processes in matter are complicated with large number of configurations that require large numbers of atoms (mostly over 10,000 atoms) to simulate such behaviour.

In molecular mechanics, it is possible to derive information from a single trajectory of the molecule. However, in simulation methods thousands to millions of trajectories are required to produce meaningful results due to the configurational and conformational changes (changes in the geometry) associated with these molecules. Therefore, realistic and explicit simulation that probes the energy landscape is essential. Under such circumstances, Molecular Dynamics (MD) and Monte Carlo (MC) become a natural choice depending on the nature of motion (statics, dynamics) to be studied. Both MD and MC are based on principles of classical mechanics, thermodynamics and statistical mechanics. MC as a stochastic approach explores the energy landscape by randomly probing the geometry or the configuration space of the molecular system. The deterministic approach, MD simulates the actual time evolution of the molecular system and its trajectory. They both are used to calculate structural and thermodynamic properties of molecular
systems from thermal fluctuations and energies obtained from simulation. Both MC and MD can predict static properties of the molecular systems.

Contrary to other simulation methods such as QM and MC, MD simulation alone can provide dynamic properties of molecular systems. In molecular dynamics simulation, the evolution of the molecular system can be studied from time intervals of the order of femtoseconds (fm) to several nanoseconds (ns). Given the initial coordinates and velocities at t=0, it is possible to determine the trajectory at later time t. Thus, in larger system of molecules the computational complexity calls for long periods of time (in the order of nanoseconds (ns)) or expensive computational time on supercomputers, clusters or GPUs of several processors to obtain reasonable results.

In dealing with simulations, an empirical potential energy function or force field is required. A force field based on molecular mechanics (MM) provides motionless, idealized geometry of a molecule (cluster of molecules) with a corresponding minimum for a potential energy. However, molecules undergo different types of motions such as thermal motions such as rotational, translational motion etc. which dictates them to change their geometry through time and hence the dynamic properties are studied based on time averages. There are a number of popular and well-developed force fields to cope with MD simulation. These include AMBER [16, 17], CHARMM [18-20], DREIDING[21], GROMACS [22, 23], OPLS-AA [24, 25] and DL POLY [26, 27]etc.. Some of these force fields are formulated to deal with biomolecules. For example, CHARMM force field is typically suitable for proteins, carbohydrates and lipids while AMBER in most cases is for nucleic acids. In our current research, CHARMM force field is modified to deal with ionic plastic crystals that share either the same species of cation or anion with ionic liquids.
In our current project, we utilize the advantages of MD simulation to understand the interrelationship between the structure, morphology and the transport mechanisms of materials at various levels - at molecular/atomic, microscopic levels in pure and doped ionic plastic crystal materials. MD simulation can in principle be utilized in predicting the physical and chemical properties for future design purposes.

2.3.2. Ensembles

In dealing with MD simulation, there are different types of ensembles with different characteristics that need to be considered depending on the type of properties to be calculated. The most widely used ensembles include micro-canonical ensemble (NVE), canonical ensemble (NVT), isobaric-isothermal ensemble (NPT). NVE ensemble corresponds to an isolated system in which the number of particles (N), volume (V) and internal energy (E) are all constant. In canonical ensemble, the number of particles (N), volume (V) and temperature (T) are fixed while in isobaric-isothermal ensemble (NPT), the number of particles (N), pressure (P) and temperature (T) are kept constant. Grand canonical Ensemble (µVT) is characterized by constant chemical potential (µ), constant volume (V) and constant temperature (T). If the quantities T, P could be kept constant, how are they controlled? The control of these quantities in an ensemble is done through the coupling of a heat bath (thermostat) and pressure bath (barostat)[28-32].

2.3.3. Molecular Model Construction

The construction of the models which replicate a real crystal system can be obtained from experimental data from x-ray, neutron diffraction and NMR spectroscopy. Under circumstances where there is no experimental data available, construction of
hypothesized macromolecules (polymer chains, super-cells) from the fragments, or parts which constitute them, is doubtful for several reasons. One of the reasons is having the right geometry, bonding, bending and torsion and other interactions cannot be validated. The most important part which is lacking is the force field which depends on the type of interactions.

2.3.4. Force Field

The potential energy function or the force field $V$ depends only on the positions of the interacting atoms or molecule. For the molecules, the potential energy function or the force field is given in terms of the internal co-ordinates of bond lengths, bond angles, dihedral angles, and the co-ordinates between the atoms or molecules. In general, the force field (equation 2.1) is the sum of bonded $V_b$ and non-bonded $V_{nb}$ interactions in simplistic form. The bonded interaction is the sum of the contributions due to bond lengths ($V_l$), bond angles ($V_\theta$), dihedral angles ($V_\phi$) etc. while non-bonded $V_{nb}$ interactions are from the long range Coulombic ($V_{qq}$) and short range Van der Waals ($V_{vdw}$) interactions.

$$V = V_b + V_{nb} = V_l + V_\theta + V_\phi + V_{qq} + V_{vdw} + V_{other} \quad \text{Equation 2.1}$$

Figure 2-1 Schematic diagram of force field of bonded terms. a) Bond stretching, b) bond angle bending, and c) dihedral rotation
The interaction potentials corresponding to bond length (stretching) and bond angle (bending) are in most cases the harmonic approximation in terms of bond stretch $b$ and bond angle $\theta$ (see schematic in Figure 2.1) as shown in equation 2.1 which defines the most commonly used force field. The Van der Waals interactions are modeled by using Lennard-Jones potential. The schematic plot in Figure 2.2 summarizes the dependence of different interaction types on interatomic distance.

The force field, under acronym CHARMM- the Chemistry at HARvard Macromolecular Mechanics (v.27), energy function is used in our work. In CHARMM, the bonded interaction contribution consists of stretching, bending,
torsion, Urey-Bradley, impropers while non-bonded interaction contribution is composed of van-der-Waals, and electrostatics [18-20].

2.3.5. Setting up MD Simulations

The calculations in the molecular dynamics could be set once all the files are ready and an appropriate force field is set. Typical software that can undertake the calculations desired here are the NAnoscale Molecular Dynamics (NAMD) and DLPOLY [34-36] or interactive VMD[37, 38] packages. There are several other software packages used for the same purpose. NAMD and DLPOLY can be run either on stand-alone or parallel computers. For any calculation to be carried out using NAMD and DLPOLY requires a configuration file with information which specifies what type of calculation needs to be undertaken. Thus, the types of output or amounts of output, at what time step the trajectories are taken, what type of ensemble need to be used, how big the cell size and the type of symmetry, how the bonded and non-bonded interactions are handled are all specified in the configuration file to run the calculation. Different types of the calculations (minimization, equilibration and production) are run under the different conditions to yield different outcomes. In the end, the results of these calculations can be analysed appropriately and presented in the form of graphs, tables and also in the form of animation of the trajectories.

2.4. Analysis of Structural and Dynamical Properties

2.4.1. Calculation of the Radial Distribution Function (RDF)
The radial distribution function (RDF) or the pair distribution function (PDF) describes how the atoms/ions in a material system are packed around each other as we go radially outwards. The radial distribution function is a useful tool in understanding the structure of a system in both ordered and disordered systems. In a crystalline solid phase, RDF is characterized by an infinite number of sharp peaks. The heights and breadth of these peaks provide ample information on the lattice structure. Experimentally, RDF can be deduced from x-ray or neutron diffraction studies.

The RDF is expressed in terms \([39, 40]\) of average density of atoms/ions in the system \(\rho\), average volume \(4\pi r^2 dr\) and the average number of atoms/ions \(n(r)\) in each shell as follows (eq. 2.2) or equation 2.3 where i and j are indices for i\(^{th}\) and j\(^{th}\) atom and \(\delta(r - |r_{ij}|)\) a Dirac delta function.

\[
\rho \ 4\pi r^2 \ g(r) \ dr = \langle n(r) \rangle \tag{Equation 2.2}
\]

\[
g(r) = \frac{\nu}{2\pi r^2 N^2} (\sum_{i<j} \delta(r - |r_{ij}|)) \tag{Equation 2.3}
\]

The radial distribution functions \(g(r)dr\) of the \([C_{2mpyr}] [NTf_2] OIPC\) in Figure 5.3 were calculated between the central nitrogens of the cation N1 and the anion N3. The co-ordination number \(N\) of the system from the spherical shell radius \(r_0\) where \(g(r) = 0\) to the minima of the next shell at radius \(r\) is directly related to the radial distribution function \(g(r)\) as shown in the equation 2.4.

\[
N = 4\pi \int_{r_0}^{r} \rho r^2 g(r) \ dr \tag{Equation 2.4}
\]
2.4.2. Calculation of Dihedral Distribution

From the bond vectors connecting the atom positions of C15→S1→N3→S2 (see Figure 2.3), the vectors $\mathbf{b}_1$ (C15-S1) and $\mathbf{b}_2$ (S1-N1) define a plane, as do the vectors $\mathbf{b}_2$ (S1-N1) and $\mathbf{b}_3$ (N3-S2) were constructed as shown in Figure 2.4. The other set of dihedrals were also constructed from the orientations of S1←N3←S2←C16. If $\mathbf{n}_A$ and $\mathbf{n}_B$ are the normals to the planes $A$ and $B$, formed by the vectors $\mathbf{b}_1$ and $\mathbf{b}_2$, and $\mathbf{b}_2$ and $\mathbf{b}_3$ respectively, then the dihedral angle is defined as

$$\cos \phi_{AB} = \mathbf{n}_A \cdot \mathbf{n}_B$$  \hspace{1cm} \text{Equation 2.5}

The normal to the planes A and B are obtained as the normalized outer product of the vectors defining the plane, i.e.
2.4.3. Calculation of the Rotational Autocorrelation Functions

The vector $\mathbf{u}_{1pp}$, $\mathbf{u}_{2pp}$ and $\mathbf{u}_{mm}$ vectors were given in Figure 2.5 and are defined by the direction of bond vector defined by a normal perpendicular to the pyrrroldinium ring, the normalized ethyl C-C bond vector in the C$_2$mpyr$^+$ cation.

The dihedral angle formed by 4 atoms defined by vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ in the first plane, vectors $\mathbf{b}_2$ and $\mathbf{b}_3$ the second plane.

Equation 2.6

\[ n_A = \frac{\mathbf{b}_1 \times \mathbf{b}_2}{|\mathbf{b}_1 \times \mathbf{b}_2|}; \quad n_B = \frac{\mathbf{b}_2 \times \mathbf{b}_3}{|\mathbf{b}_2 \times \mathbf{b}_3|} \]

Figure 2-4 Dihedral angle formed by 4 atoms defined by vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ in the first plane, vectors $\mathbf{b}_2$ and $\mathbf{b}_3$ the second plane.

Figure 2-5 Vectors defining the rotational autocorrelation function in cation and anion of [C$_2$mpyr][NTf$_2$]
and the S-C bond vectors in the NTf₂⁻ anion respectively. In calculating the rotational autocorrelation function, the orientation \( u_i \) of a molecule/atom \( i \) was normalised from the vector joining two points \( r_1 \) and \( r_2 \) as in equation 2.7. The points \( r_1 \) and \( r_2 \) may not necessarily coincide with atoms in the molecule in calculating the defining the orientation. The decay of the rotational autocorrelation function for molecules/atoms \( i \) and \( j \) is expressed by the average of the cosine of the angle \( \cos \theta \) at time \( t \) averaged for the whole system as given by equation 2.8.

\[
\begin{align*}
u_i &= \frac{r_2 - r_1}{|r_2 - r_1|} \\
\cos \theta_{ij} &= u_i \cdot u_j
\end{align*}
\]

**Equation 2.7**

**Equation 2.8**

### 2.4.3. Calculation of Self-Diffusion

Atoms/ions constitute the molecular systems in a constant move at any given temperature, pressure and are subject to change in displacement from their average positions. The trajectory they follow are quite complex and in a random manner to follow in space due to effects of "collisions" of atoms/ions with each other. Thus, fluctuation from the average positions is imminent at any instant of time \( t \). In a one-dimensional system, the displacement of the atom will either move forward or backward step are equally probable to occur. It is still possible to conclude that the average displacement an atom/ion can be close to zero if we choose to add the displacements together. To obtain better picture the motion of the atom/ion, the non-zero, positive quantity of the square of the displacement from average position at different time \( t \) is favoured. By extrapolating the one–dimensional projection onto a 3D molecular system, the Mean Square Displacement (MSD) of the \( i^{th} \) atom/ion at
time \( t \) is defined by equation 2.9. Under any condition when there is a drift of the centre of mass, it is important to subtract the centre of mass co-ordinates to obtain the right result for MSD.

\[
MSD(t) = \langle \Delta r(t)^2 \rangle = \langle |r_i(t) - r_i(0)|^2 \rangle \tag{Equation 2.9}
\]

From the MSD, important information on the diffusion of atoms/ionic species in a molecular system can be extracted. The slope of mean square displacement (MSD) with time \( t \) yields the diffusion coefficient \( D \) as in equation 2.10. At \( t=0 \), the MSD is zero and resembles a parabola \( t^2 \) at very short times \( t \). In solid materials, atomic/ionic species do not have sufficient kinetic energy to reach a diffusive behaviour, thus the MSD saturates close to a value defined by fluctuations around lattice site. In liquids, the atomic/ionic species in material be able diffuse so that the MSD increases linearly with time.

The self-diffusion coefficient \( D_i \) for species \( i \) can be calculated using the Einstein relation from velocity autocorrelation function or the mean square displacement (MSD) from the slope of MSD versus time \( t \) (equation 2.10).

\[
D = \lim_{t \to \infty} \frac{\langle \Delta r(t)^2 \rangle}{6t} = \frac{MSD}{6t} \tag{Equation 2.10}
\]

Such analysis will be used to define the structure and dynamics in the \([C_2\text{mpyr}][\text{NTf}_2]\) OIPC with and without inclusion of vacancy as well as in the \([\text{Me}_4\text{N}][\text{N(CN)}_2]\) doped with \( \text{Na}[\text{N(CN)}_2] \).
2.5. References


CHAPTER 3. Characterization of an Archetypal OIPC N-ethyl-N-methylpyrrolidinium bis(trifluoromethane-sulfonyl)imide in a Mixture of NaNTf₂ Salt

3.1. Brief Overview

In this chapter, comprehensive experimental studies on [C2mpyr][NTf₂] / Na[NTf₂] mixtures were presented. More specifically, the phase behaviour, temperature dependent structure, morphology, conduction mechanisms and ionic motion of the mixed system were analysed using different advanced techniques such as DSC, SXRD, SEM, NMR and FTIR/Raman. The results and discussions from the measurements using these techniques are presented in the following sub-sections of the chapter.

3.2. Results and Discussion

3.2.1. Thermal Analysis and Phase Behaviour

Samples sealed in Aluminium pans in Argon environment glove box were loaded in the Mettler DSC. Initially, the samples were cooled from ambient temperature to −150 °C at a rate of 10°C/min. They were equilibrated at -150 °C for 25 min and then heated to 150°C. At 150°C, the samples were kept under isothermal condition for another 25 min and allowed to cool at 10°C/min to the ambient temperature.

Pure sample [C2mpyr] [NTf₂] (394.35g/mol) and the binaries with Na[NTf₂] (303.11g/mol) were investigated at different molar concentrations. In the range of temperature there were no glass transitions observed and all the samples were solid at ambient temperatures. The melting temperatures of the pure samples of [C2mpyr] [NTf₂] and Na[NTf₂] were 91°C[1, 2] and 257°C respectively.

As numerous previous studies have shown, the pure sample of [C2mpyr] [NTf₂] undergoes several solid-solid transitions [1, 3-6]. Consistent and reproducible measurements as shown in Figure 3.1, are in agreement with the previous
measurements on the OIPC. Thus, the transition from ordered phase IV to disordered phase III was observed at \(-85 \pm 1^\circ C\) followed by phase III to phase II transition occurring at \(17 \pm 1^\circ C\). The solid-solid transition before the melting point of \([C2mpyr] \,[NTf_2]\) at \(91 \pm 1^\circ C\), occurred at \(45 \pm 1^\circ C\) solid-solid transition from disordered phase II to disordered phase I. The melting curve of the material is characterised by a narrow, sharp peak. Furthermore, the solid-solid transitions from phases IV-III, III-II and II-I of the doped system are consistent and no peak shift from the transitions of the pure OIPC were observed. The differences with the pure OIPC occurred in the phase I, where the transition temperature of \(42 \pm 1^\circ C\) from phase II-I. At lower concentrations of Na[NTf\(_2\)] doping as shown in Figure 3.1, an extra peak is formed at \(63 \pm 2^\circ C\) and melting peak shifts toward lower temperature. The eutectic peak of the Na doped binary system occurs at around \(63 \pm 2^\circ C\) with the concentration of 15% mole of Na[NTf\(_2\)]. The DSC trace of higher concentration of Na[NTf\(_2\)] in the mixed binary system as in Figure 3.1 (35% and 50%Na\(^+\)) shows the flipping of the melt and appearance of additional the melt peak which was absent at eutectic conditions.

From our thermal measurements, the \([C2mpyr][NTf_2]\) OIPC exhibits an entropy of melt transition of about 26.7 J mol\(^{-1}\) K\(^{-1}\) (and a corresponding enthalpy of 24.7 Jg\(^{-1}\)) which is higher than the Timmermann’s criteria suggested for molecular plastic crystals of 20 J mol\(^{-1}\) K\(^{-1}\). The lower entropy/enthalpy of fusion correlates with the plastic deformation inherent to OIPCs and their mixtures. In other words, by the time an OIPC material melts, it has already gained considerable entropy through order-disorder solid-solid phase transitions thus the final entropy change upon melting is smaller. This disorder which may be orientational or rotational disorder, leads to high conductivities in the plastic crystal phases at relatively low
temperatures. Moreover, the onset of rotational motion requires the molecules to move apart to reduce the steric hindrance and to gain enough volume for rotation, thus expansion of the crystal lattice and the creation of more vacancies results [7]. Therefore, a solid-solid phase transition normally accompanies the volume expansion. In the doped or mixed systems, there were two melt transitions observed in phase I. The enthalpy change for the solid-solid transitions contributes more than 20% below the eutectic composition while above 15mol% Na[NTf₂] the solid-solid phase transitions are less than 10% of the enthalpy of melt transition. This indicates that beyond the eutectic composition, the amount of the original OIPC phase is significantly less and points in the direction of an alternative compound. For example the composition Na₀.25[C₂mpyr]₀.75[NTf₂] is possible at 25mol% Na[NTf₂]. Henderson et al suggested that, with addition of Li[NTf₂] to related pyrrolidinium based OIPCs, multiple new compounds were possible at a ratio of 1:2, 1:1 and 2:1 lithium salt to OIPC [8].

![Figure 3-1 DSC traces of pure [C₂mpyr][NTf₂] and mixtures (1-50 mol%) of Na[NTf₂] with [C₂mpyr][NTf₂].](image)

- 58 -
Table 3.1 Enthalpy (in J/g) for the phase transitions calculated from the area under the peaks in DSC traces and the corresponding transition temperatures of doped systems

<table>
<thead>
<tr>
<th>NaNT₂</th>
<th>Phase IV-III</th>
<th>Phase III-II</th>
<th>Phase II-I</th>
<th>Eutectic</th>
<th>melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>% mol</td>
<td>T/°C</td>
<td>ΔH/Jg⁻¹</td>
<td>T/°C</td>
<td>ΔH/Jg⁻¹</td>
<td>T/°C</td>
</tr>
<tr>
<td>0</td>
<td>-84</td>
<td>4.6</td>
<td>18</td>
<td>1.9</td>
<td>42</td>
</tr>
<tr>
<td>1</td>
<td>-84</td>
<td>5.6</td>
<td>17</td>
<td>1.9</td>
<td>42</td>
</tr>
<tr>
<td>6</td>
<td>-85</td>
<td>4.0</td>
<td>18</td>
<td>2.2</td>
<td>42</td>
</tr>
<tr>
<td>15</td>
<td>-84</td>
<td>4.1</td>
<td>18</td>
<td>1.5</td>
<td>42</td>
</tr>
<tr>
<td>35</td>
<td>-87</td>
<td>0.3</td>
<td>18</td>
<td>0.8</td>
<td>46</td>
</tr>
<tr>
<td>40</td>
<td>-87</td>
<td>0.3</td>
<td>18</td>
<td>0.6</td>
<td>46</td>
</tr>
<tr>
<td>45</td>
<td>-86</td>
<td>0.3</td>
<td>19</td>
<td>0.7</td>
<td>46</td>
</tr>
<tr>
<td>50</td>
<td>-86</td>
<td>0.3</td>
<td>18</td>
<td>0.8</td>
<td>42</td>
</tr>
</tbody>
</table>

Phase diagrams play a vital role in the understanding of physical and chemical properties of such mixtures, mainly in the extraction of information on compounds, solid solutions, phase transitions and melting temperatures. As shown in Figure 3.2, the partial binary phase diagram shows that the melting point was depressed by the addition of Na[NTf₂] and the eutectic transition occurs at 63±2°C at a concentration of 15% mole of Na[NTf₂]. The diagram contains several possible areas that contain either one or two phases. The liquidus curve (defined by point xyz) gives the highest temperature at which no more solid phase exists and above it the mixtures are completely molten. Liquids that cross the liquidus curve between points x and y on cooling enter the two phases region α+L, for which α is a primary phase, predominantly of [C₂mpyr][NTf₂]. The solid-solid phase transitions versus the
composition shows that the regions of transition below 42±1°C (phase II-I) are the region of solid solution analogous to [C₂mpyr][NTf₂] phases regardless of the percentage of doping of Na[NTf₂].

![Phase diagram](image)

**Figure 3-2** Phase diagram for [C₂mpyr][NTf₂] / Na[NTf₂] system shows solid-solid phase transition temperatures TIV-III, TIM-II, TII-I and liquidus temperature TL, indicating both equilibrium and metastable phase transitions respectively.

The other significant observation in the phase diagram is the invariance of the [C₂mpyr] [NTf₂] solid-solid phase transitions as a function of composition across the [C₂mpyr][NTf₂] rich region particularly in the region of solid state mixtures designated by phases II to IV. This suggests that the solid mixtures are the Na⁺ cation doped analogues of the pure [C₂mpyr][NTf₂] phase, exhibit the same dynamic rotational disorder as in the pure plastic crystal material. Similarly, in the liquid state, at high temperatures or above the liquidus curve and the eutectic
transition, liquid solutions of a single phase occur. At intermediate temperatures, regions of partial melting occur as shown in the diagram labelled as phase I. These regions contain a mixture of a crystalline phase and a liquid of different composition to the crystalline phase. The composition of the two phases can be obtained by using Lever’s rule. The partial binary phase diagram presented in Figure 3.2 more clearly shows the phase behaviour of the Na[NTf₂]/[C₂mpyr][NTf₂] system. It can be observed that the melting point is decreased and the eutectic transition occurs at 63 ± 2 °C at 15 mol% Na[NTf₂] content. The solid-solid phase transitions are still evident at all studied Na⁺ contents and indicate that one of the solid phases is very similar to the pure [C₂mpyr][NTf₂]. Table 3.1 presents the enthalpy of transitions for each system. The enthalpy of the melting transition associated with the pure OIPC phase decreases with increasing Na⁺ concentration with a concomitant increase in the enthalpy of the eutectic transition until 15mol%, beyond this concentration, the eutectic transition decreases in enthalpy whilst a new melting transition (liquidus) associated with the β phase appears. This phase diagram is very similar in appearance to the [C₃mpyr][NTf₂]/Li[NTf₂] binaries [9]. The eutectic composition of about 15 mol% was observed from [C₃mpyr] and [C₄mpyr], however Tₑ was approximately 30 °C when Li[NTf₂] was mixed into the [C₂mpyr][NTf₂] OIPC [9]. The implications of the phase changes described here will be further discussed in conjunction with the results from synchrotron XRD and solid state NMR spectroscopy in the following sections.
3.2.2. Morphology and Topography

Microstructural properties (morphology and lattice imperfections) inherent to the \([\text{C}_2\text{mpyr}] \,[\text{NTf}_2]\) OIPC material and mixtures with \(\text{Na}[\text{NTf}_2]\) were probed using SEM, without sample damage and charging effect.

![Micrographs showing a comparison of \([\text{C}_2\text{mpyr}]\,[\text{NTf}_2]\) OIPC](image)

The microstructure in the pure \([\text{C}_2\text{mpyr}]\,[\text{NTf}_2]\) and other OIPCs published elsewhere [10-12] have shown extended defects (eg. slip planes) that account for the plastic deformation in such systems. In this work we present both SEM images Figure 3.3 (a-d) which indicate the morphology of the Li and Na containing \([\text{C}_2\text{mpyr}]\,[\text{NTf}_2]\) systems at ambient temperature. In Figure 3.3, slip planes which
3.2.3. Conductivity

In our current work, ionic conductivity measurement of the pure sample \([\text{C}_{2}\text{mpyr}][\text{NTf}_2]\) and mixtures with \(\text{Na}[\text{NTf}_2]\) were undertaken. The conductivity of \([\text{C}_{2}\text{mpyr}][\text{NTf}_2]\) and mixed systems are shown in Figure 3.4. The plots show the dependence of ionic conductivity on temperature and concentration of \(\text{Na}[\text{NTf}_2]\) salt as compared to the pure OIPC \([\text{C}_{2}\text{mpyr}][\text{NTf}_2]\).

![Figure 3-4 Ionic conductivity of pure and Na⁺ mixed \([\text{C}_{2}\text{mpyr}][\text{NTf}_2]\) with variable Na\([\text{NTf}_2]\) concentration. (The ionic conductivity of pure and 1 mol % Li⁺ mixed \([\text{C}_{2}\text{mpyr}][\text{NTf}_2]\) is compared in the inset [13])](image)
It was observed that the conductivity of the mixed systems is lower than the pure OIPC below the onset temperatures of phase II –I solid-solid transition for all compositions. However, there is a significant increase in conductivity compared to the pure sample for all mixtures in the Phase I region. The conductivity showed an increase of an order of magnitude at 15% and 40% mol Na [NTf₂] to $5 \times 10^{-7}$S/cm compared to the pure plastic crystal and 4% mol Na [NTf₂] at 50°C (in the region corresponding to mixture β+L phases). It further increased by three orders of magnitude to over $\sim 10^{-4}$S/cm at 40mol% Na[NTf₂], over 15 times with 15% and 10 times with 4mol% Na[NTf₂] compared with the pure [C2mpyr] [NTf₂] at 60°C. The conductivity in these temperature regions are still below the eutectic and thus nominally in their solid state and thus showed remarkable increase which could be promising for the solid state electrolytic materials at near ambient temperature.

As shown in the phase diagram above, the phases below the temperature 60°C are all solid, with a possibility of being solid state mixtures of different phases. In the analogy with Li doped [C2mpyr][NTf₂], it can be proposed that the onset of Na+ ion motion occurs when the OIPC matrix undergoes phase transitions to a more disordered phase (Phase III and above) with the most plastic phase, Phase I showing the greatest enhancement in conductivity of about 3 orders of magnitude over the pure sample. Interestingly, the phase behaviour hints of a second, possibly sodium rich, phase that may itself have higher conductivity.

In contrast to the behaviour upon addition of Li[NTf₂], shown as inset in Figure 3.4, it can be seen that the conductivity of the mixed systems is lower than the pure OIPC below the onset temperatures of the phase II–I solid-solid transition for all
Beyond the Phase II–I transition there is a significant increase in conductivity compared to the pure sample, approximately one order of magnitude for the 15 and 40 mol% Na[NTf₂] samples at 50 °C. The conductivity further increased by three orders of magnitude to over ~3 x 10⁻⁴ S/cm in the case of 40 mol% Na[NTf₂] at 60 °C, just below the eutectic melt. According to the phase diagram this composition should still be completely solid at this temperature. This is in contrast with the Li[NTf₂] mixtures where the eutectic temperature occurred at 30 °C, and therefore, above this temperature there would likely be a Li⁺ rich, liquid phase present in the material. This could account in part for the high conductivities observed in those systems even at lower temperatures and compositions [1, 2, 5, 14]. Furthermore, whereas the lithium additions appeared to lead to coarser grain boundaries, the Na[NTf₂] addition instead leads to a dispersed second phase that does not appear to contribute the conduction processes at lower temperatures (i.e, phases IV-II, below 45 °C), as can be inferred from the similarity of the measured conductivity values at these temperatures.

### 3.2.4. FTIR/Raman Spectroscopy

Room temperature FTIR/Raman spectra of the pure OIPC [C₂mpyr][NTf₂], Na[NTf₂] salt and the their mixtures Na₀.₀₄[C₂mpyr]₀.₉₆[NTf₂] , Na₀.₁₅[C₂mpyr]₀.₈₅[NTf₂] are presented in Figures 3.5 and 3.6. The spectra of these samples are rich in bands with noticeable differences between the mixtures and the pure samples of the OIPC and Na[NTf₂] salt. The assignment of the [NTf₂]⁻ anion and [C₂mpyr]⁺ cation vibrational modes was carried out based on previous extensive investigations performed by several research groups. Most relevant to this
work are investigations on ionic liquids and electrolytes \([\text{C}_3\text{mpyr}]\text{[NTf}_2\text{]}\) [5], \([\text{C}_1\text{mpyr}]\text{[NTf}_2\text{]}\) [15], \([\text{C}_x\text{mpyr}]\text{[NTf}_2\text{]}\) [16] and \([\text{hmim}]\text{[NTf}_2\text{]}\) [17].
Figure 3-5  FTIR spectra of pure and mixed materials Na[NTf₂], [C₂mpyr][NTf₂], Na₀.₀₄[C₂mpyr]₀.₉₆[NTf₂] and Na₀.₁₅[C₂mpyr]₀.₈₅[NTf₂] at different frequencies (a) 450–680 cm⁻¹, (b) 950–1250 cm⁻¹. Additional weak peaks/shoulders are indicated at 534, 576, 598, 651 cm⁻¹ and 1150 cm⁻¹. c) no change in peaks of pure OIPC and mixtures in the spectral region of 2800-3200 cm⁻¹.

Furthermore, the effect of sodium cation additions was investigated from the FTIR and Raman spectra. More intense peaks correspond to higher concentrations of sodium in the mixture. The spectra also show the occurrence of new bands with the increase of sodium ion concentration. The [NTf₂]⁻ anion in the NaNTf₂ and the pure OIPC were discriminated from the shift of spectra to lower frequency in the latter case.
As shown in Figure 3.5 (a-c), room temperature FTIR spectra were acquired for

\[ \text{[C}_2\text{mpyr}][\text{NTf}_2], \text{Na[NTf}_2], \text{Na}_{0.04}[\text{C}_2\text{mpyr}]_{0.96}[\text{NTf}_2] \]  

and \( \text{Na}_{0.15}[\text{C}_2\text{mpyr}]_{0.85}[\text{NTf}_2] \) exhibit noticeable differences between the mixed and pure samples. The observed peaks of the \([\text{NTf}_2^-]\) anion and \([\text{C}_2\text{mpyr}]^+\) cation are assigned and summarised in Table 3.2 based on previous investigations \([5, 15-21]\). The vibrational modes dominated by \([\text{NTf}_2^-]\) anion are observed in Raman/IR spectra \((278-798 \text{ cm}^{-1} / 400 - 790 \text{ cm}^{-1})\) respectively. The pyrrolidinium ring modes are observed from 880-1000 cm\(^{-1}\). The vibrational modes above 880 cm\(^{-1}\) are mostly due to the functional groups in the cation \([\text{C}_2\text{mpyr}]^+\). There is no difference in the IR/Raman spectra of the pure and doped materials in the region 2800 – 3100 cm\(^{-1}\) which are attributed to the overtones of methyl and/or alkyl group symmetrical stretching vibrations of the pyrrolidinium cation.

New bands are evident in the FTIR/ATR spectra (Figure 3.5 (a-c)) at 540, 600, 650 and 1150 cm\(^{-1}\) (indicated by dashed lines) which increase in intensity with sodium concentration. The presence of these bands indicates the following changes in the mixed system. The band at 1150 cm\(^{-1}\) in this work corresponds to the twisting of the pyrrolidinium rings \([21]\), possibly due to the different chemical environment created by the addition of \(\text{Na}^+\) observed in the \(^{13}\text{C}\) NMR spectra (Figure 3.7c) and thus supports a change in ring conformation in the Na rich phase. The characteristic FTIR band for the trans conformer occurs at ~607cm\(^{-1}\), while the presence of vibration bands at 600 and 653cm\(^{-1}\) indicate the presence of the cis conformer \([17]\). Thus it appears that the addition of sodium ions into this OIPC favours the presence of the cis conformer.
Table 3.2 Assignment of observed Raman and FTIR bands of [C2mpyr][NTf₂] at room temperature based on different literatures on related anions and cations

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Raman $\nu$/cm$^{-1}$</th>
<th>FTIR $\nu$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$CF$_3$</td>
<td>278(ms)</td>
<td></td>
</tr>
<tr>
<td>$\rho$CF$_3$, $\nu$CS</td>
<td>297(m)</td>
<td></td>
</tr>
<tr>
<td>$\rho$SO$_2$, $\rho$CF$_3$, $\nu$CS</td>
<td>314(w)</td>
<td></td>
</tr>
<tr>
<td>$\tau$SO$_2$</td>
<td>341(w)</td>
<td></td>
</tr>
<tr>
<td>$\omega$SO$_2$</td>
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<td>397(vw)</td>
</tr>
<tr>
<td>$\omega$SO$_2$</td>
<td></td>
<td>408(w)</td>
</tr>
<tr>
<td>$\delta$CF$_3$</td>
<td></td>
<td>512(s)</td>
</tr>
<tr>
<td>$\nu$N-C, $\delta$, SO$_2$</td>
<td>537(vw)</td>
<td>552(w)</td>
</tr>
<tr>
<td>$\nu$N-C, $\delta$, SO$_2$, $\delta$,CF$_3$, $\delta$,R, $\delta^\beta$, R</td>
<td>570(w)</td>
<td>568(s)</td>
</tr>
<tr>
<td>$\delta$,CF$_3$, $\delta^\beta$,SO$_2$, $\delta$,N-SO$_2$</td>
<td>590(w)</td>
<td></td>
</tr>
<tr>
<td>$\delta$, SO$_2$, $\delta^\beta$, R, $\delta$, SNS , $\delta^\alpha$,SO$_2$</td>
<td></td>
<td>611(vs)</td>
</tr>
<tr>
<td>$\delta$,CF$_3$, $\delta$, N-SO$_2$</td>
<td>631(vw)</td>
<td>715(vw)</td>
</tr>
<tr>
<td>$\delta$,CF$_3$</td>
<td>741(vs)</td>
<td>739(m)</td>
</tr>
<tr>
<td>$\nu$, SNS</td>
<td>798(vw)</td>
<td>790(m)</td>
</tr>
<tr>
<td>$\nu$CS</td>
<td>824(vw)</td>
<td></td>
</tr>
<tr>
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<td>879(vw)</td>
</tr>
<tr>
<td>Ring mode</td>
<td>902(m)</td>
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<td>999(w)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1035(vw)</td>
</tr>
<tr>
<td>$\nu$,R, $\nu$CC, $\tau$N-CH$_3$, $\delta$,SNS, $\nu$,$\delta$SNS</td>
<td>1054(w)</td>
<td>1052(s)</td>
</tr>
<tr>
<td>$\nu$SO$_2$</td>
<td>1141(m)</td>
<td>1137(s)</td>
</tr>
<tr>
<td>$\nu$,R, $\nu$N-CH$_3$, $\nu$,CF$_3$,</td>
<td></td>
<td>1177(vs)</td>
</tr>
<tr>
<td>$\nu$,CF$_3$, $\tau$ CH$_2$</td>
<td>1243(ms)</td>
<td></td>
</tr>
<tr>
<td>$\delta^\alpha$,SO$_2$, $\delta$CH$_3$, $\nu$ ( R)</td>
<td>1336(w)</td>
<td>1333(m)</td>
</tr>
<tr>
<td>$\delta^\beta$,SO$_2$, $\nu$ ( R), $\delta^\alpha$,SO$_2$</td>
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<td>1347(m)</td>
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<td></td>
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<td>1405(vw)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1434(vw)</td>
</tr>
<tr>
<td>$\delta$CH$_3$, $\nu^\beta$, R</td>
<td>1455(m)</td>
<td></td>
</tr>
<tr>
<td>$\delta$CH$_3$, $\delta$CH$_3$,</td>
<td></td>
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</tr>
<tr>
<td>$\nu$CH$_3$, $\nu$CH$_3$</td>
<td></td>
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</tr>
<tr>
<td>$\nu$CH$_3$</td>
<td>2852(w)</td>
<td>1467(w)</td>
</tr>
<tr>
<td>$\nu$CH$_3$</td>
<td>2904(s)</td>
<td>2904(w)</td>
</tr>
<tr>
<td>$\nu$CH$_3$</td>
<td>2962(w)</td>
<td>2964(vw)</td>
</tr>
<tr>
<td>$\nu$CH$_3$</td>
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<td>2997(s)</td>
</tr>
<tr>
<td>$\nu$CH$_3$</td>
<td>3041(w)</td>
<td>3042(w)</td>
</tr>
</tbody>
</table>
In the Raman spectra (Figure 3.6 (a-c)) changes also occur at 212 cm\(^{-1}\), 300-350 cm\(^{-1}\) and 395-415 cm\(^{-1}\). Again the data here support the conclusions from the FTIR spectra indicating the presence of the cis conformer in the mixtures. Martinelli et al. [20] previously assigned the vibrations at 306, 326, and 333 cm\(^{-1}\) to the cis and 298, 314 and 339 for trans conformers to exist in NTf\(_2\) containing ionic liquids. The observed Raman bands at 277, 298, 313, 341, 402 and 412 cm\(^{-1}\) are associated with the trans conformer in the pure OIPC and a new band in the mixed systems at 329 cm\(^{-1}\), slightly shifted to the red from the NaNTf\(_2\) band corresponds to the cis conformer. Similarly the 356 cm\(^{-1}\) which are in the mixed systems had been observed for both the trans [NTf\(_2\)]\(^+\) and [hmim]\(^+\) [17]. It was also reported [20] that the \(\sim740\) cm\(^{-1}\) intense band (contraction and expansion of NTf\(_2\) ) are assigned to two components, a cis conformer at 738 cm\(^{-1}\) and trans conformer at 741 cm\(^{-1}\). In our case, the mixed systems clearly showed a broader band at \(\sim740\) cm\(^{-1}\) indicates the existence of the cis conformer overlapping with trans conformer. Thus the vibrational spectroscopy showed the bands similar to the OIPC and shifting from the Na[NTf\(_2\)] bands in the mixed systems is consistent with the later which support the presence of additional phase as discussed later in this chapter. Furthermore it appears that the conformation of the anion in this additional phase is likely to be the cis conformer agrees well with the recent report on crystal structure of NaNTf\(_2\) [22]
Previous work [23] suggests that the pure OIPC is disordered at 213K and undergoes rotational motion with some of its cations and anions. At room temperature, more and more cations / anions are involved due to an increase in thermal energy. Previous studies also suggest that the NTf₂⁻ interaction with the pyrrolidinium cation is weaker due to steric shielding of the charge than the coordination with Li⁺ [8, 13].

In the studies related to [hmim][NTf₂], [C₂mim][NTf₂] and [C₃mpyr][NTf₂] [17, 18, 24] ionic liquids, they found that the Raman bands at 277, 299, 315, 340, 402 and 412 cm⁻¹ in the Raman spectra are all associated with the trans conformer of NTf₂ at
room temperature. They suggested these contributions are mainly due to wagging, bending, twisting and rocking modes of SO$_2$. The same work also reported that a characteristic band of the trans conformer occurs at around $\sim$607 cm$^{-1}$ in the FTIR spectra at room temperature. The same study concluded that this band is the dominant conformation of NTf$_2^-$. Our findings on the pure crystal [C$_2$mpryr][NTf$_2$] agrees well with [hmim][NTf$_2$]. The addition of sodium into the ionic plastic crystal brought in the new bands at 600 and 653 cm$^{-1}$, similar to the findings with the increase in temperature of the [hmim][NTf$_2$] and these peaks are correlated to the cis conformer. In their work on pyrrolidinium-N-propanesulfonate zwitterionic compound (PyrZIC) and lithium bis(trifluorosulfonyl)imide, Park et.al [21] found that the conformational changes occur in the cations due to the twisting of pyrrolidinium rings at 1151,1134,1122 cm$^{-1}$. They observed the shoulder in the FTIR spectra, at about 1150 cm$^{-1}$ in the doped system in this work, corresponds to the twisting of pyrrolidinium rings due to different chemical environment as observed in the $^{13}$C NMR spectra presented below.

It was also found that the Na$^+$ interaction at the low frequency region in the Raman spectra at 211 cm$^{-1}$ and at about 540 cm$^{-1}$ and 1150 cm$^{-1}$ in the FTIR spectra, with increased concentration of sodium. Thus, the addition of substitutional cations like Li$^+$, Na$^+$ introduces more defects and volume expansion at higher temperature that could possibly lead to further rotation and thereby to the conformational changes in both cations and anions in the mixtures.
3.2.5. Synchrotron X-ray Diffraction

From the experimental investigation of thermal properties, it is known that the pure OIPC \([C_2\text{mpyr}][\text{NTf}_2]\) and its mixtures with the sodium salt, undergoes several solid-to-solid phase transitions. Typically such transitions are accompanied with a change in the crystal structure when thermodynamic properties such as temperature or pressure variations result in a discontinuous change in material properties. The change in material property such as phase, morphology and conductivity were discussed previously. In this section we present the X-ray powder diffraction patterns for \([C_2\text{mpyr}][\text{NTf}_2]\) plastic crystal and \(\text{Na}_{0.15}[C_2\text{mpyr}]_{0.85}[\text{NTf}_2]\) mixed systems were measured at the Australian Synchrotron at temperatures of 273, 303 and 328K, which correspond to phases III, II and I respectively as shown in Figure 3.7 (a-d). The intensity profile of \([C_2\text{mpyr}][\text{NTf}_2]\) OIPC and the \(\text{Na}_{0.15}[C_2\text{mpyr}]_{0.85}[\text{NTf}_2]\) system were compared separately at 273, 303 and 328K and with each other at 303K. The measurement at 303K was reproducible upon heating and cooling for the purpose of validation. These phases are different from those in previous reported work [23] at 153K (phase IV) and the phases at 213K (phase III) [23] and 273K (phase III) in current work are both triclinic. To investigate the phase changes of the pure and mixed systems at a series of temperatures, a total pattern of synchrotron X-ray data was analyzed using the TOPAS Academic v4.2 Coelho software [25]. On indexing the reflections from the synchrotron X-ray data, it was found that the pure OIPC undergoes subsequent phase changes at different temperatures. The lattice parameters and space groups for the major OIPC phase are presented in Table 3.3. The same lattice parameters were also retained in the \(\text{Na}_{0.15}[C_2\text{mpyr}]_{0.85}[\text{NTf}_2]\) system while the second phase (Table
3.4) was indexed from the peaks left after modeling the [C$_{2m}$pyr][NTf$_2$] phase at each temperature.
Figure 3-7  Indexed synchrotron XRD patterns acquired for (a) [C$_2$mpyr][NTf$_2$] and (b) Na$_{0.15}$[C$_2$mpyr]$_{0.85}$[NTf$_2$] at temperatures of 273, 303 and 328K (i.e., phases III, II and I respectively), (c) compares the [C$_2$mpyr][NTf$_2$], Na[NTf$_2$] and Na$_{0.15}$[C$_2$mpyr]$_{0.85}$[NTf$_2$] patterns at 303K and (d) compares the [C$_2$mpyr][NTf$_2$] and Na$_{0.15}$[C$_2$mpyr]$_{0.85}$[NTf$_2$] patterns at 273K with * indicating mixed phase.
As shown in Table 3.3, the lattice parameters of the pure OIPC undergo crystal structure changes at temperatures of 273, 303 and 328K as evidenced in the XRD patterns shown in Figure 3.7(a-d). The synchrotron powder XRD data for the pure OIPC suggests that phase III (273K) is triclinic P-1, while the phases II (303K) and I (328K) are monoclinic Cc and monoclinic C2, respectively. The lattice parameters for the phase III structure (273K) agree well with the previous study [23] at 213K, with a slight increase in volume/decrease in density which is expected from thermal disorder responsible for the rotational disorder in both the [C2mpyr]+ cation and the [NTf2]- anion. The increase in volume can be seen in the SXRD traces through peak shifts to lower 2θ values. At 303K, in phase II, the SXRD trace is characterised by a general shift of diffraction peaks to lower 2θ values and the disappearance of Bragg peaks is consistent with the change in the crystal structure to high symmetry monoclinic C2. A slight increase in volume was observed in the mixed phase (different from NaNTf2) as shown in Table 3.4. Contrary to the pure OIPC phase in the mixture, there is no change in the space group for the mixed phase at these temperatures; only an elongation of the crystallographic axes. These findings are also supported by the binary phase diagram and SEM micrographs. As shown in the phase diagram (Figure 3.2), the binary systems do not allow for significant solid solutions (~1%) and phase transitions are either of OIPC or mixed phases represented by horizontal isothermal line. They are thermodynamically first order because of the involvement of a change in properties such as volume and crystallographic parameters which could lead to the breaking and/or the forming of bonds.
Table 3.3 Lattice parameters determined for \([C_{2mpyr}][NTf_2]\) OIPC.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>273K</th>
<th>303K</th>
<th>328K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>CC</td>
<td>I222</td>
</tr>
<tr>
<td>(a /\text{Å})</td>
<td>8.5668</td>
<td>15.5696</td>
<td>14.7159</td>
</tr>
<tr>
<td>(b /\text{Å})</td>
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<td>13.9056</td>
</tr>
<tr>
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<td>8.5865</td>
</tr>
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<td>(\alpha/\text{deg})</td>
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<td>90</td>
<td>90</td>
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<tr>
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<td>61.779</td>
<td>90</td>
</tr>
<tr>
<td>(\gamma/\text{deg})</td>
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<td>90</td>
<td>90</td>
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</tr>
<tr>
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<td>1.511</td>
<td>1.490</td>
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<td>(Z)</td>
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<td>4</td>
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<td>(2\theta_{\text{max}}/\text{deg})</td>
<td>83</td>
<td>83</td>
<td>83</td>
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</tbody>
</table>

Table 3.4 Lattice parameters determined for the mixed phase in Na\(_{0.15}\) \([C_{2mpyr}]_{0.85}[NTf_2]\) OIPC.

<table>
<thead>
<tr>
<th>Temperature</th>
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<th>328K</th>
</tr>
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<tbody>
<tr>
<td>Crystal system</td>
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<tr>
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<td>(\gamma/\text{deg})</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(V /\text{Å}^3)</td>
<td>1320.528</td>
<td>1333.544</td>
<td>1343.318</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>(2\theta_{\text{max}}/\text{deg})</td>
<td>83</td>
<td>83</td>
<td>83</td>
</tr>
</tbody>
</table>

Figure 3.7a presents a comparison of the data for the pure OIPC at each of these temperatures, Figure 3.7b compares the SXRD patterns for the 15 mol% Na[NTf\(_2\)] sample at each temperature, and Figure 3.5c compares the XRD pattern at 303K for
the two pure components \([\text{C}_2\text{mpyr}][\text{NTf}_2]\), \(\text{Na}[\text{NTf}_2]\) and the \(\text{Na}_{0.15}[\text{C}_2\text{mpyr}]_{0.85}[\text{NTf}_2]\) mixture. The measurement at 303K was reproduced upon both heating and cooling the samples. In the both pure OIPC and \(\text{Na}_{0.15}[\text{C}_2\text{mpyr}]_{0.85}[\text{NTf}_2]\) materials, as the temperature is increased, the diffraction peaks shift towards the lower 2\(\theta\), split peaks appear to merge and many of the weaker peaks disappear. The shift toward lower 2\(\theta\) values are consistent with an expansion of the lattice parameters and the disappearance of peaks at higher temperatures is attributed to changes in the crystalline phases and/or crystal symmetry. Peak broadening was also observed in these \(\text{Na}^+\) mixture materials, contrary to the pure OIPC at 273K.

The XRD patterns for the mixture shown in Figure 3.7b were significantly more complex than for the pure OIPC. Although the same behaviour in terms of shifts in 2\(\theta\) and the loss of weaker peaks is evident in this mixture, the numerous additional peaks gives a strong indication for the presence of a new second phase. A comparison of the traces for the pure \(\text{Na}[\text{NTf}_2]\) (Figure 3.7c) salt shows that these extra diffraction peaks are not simply insoluble \(\text{Na}[\text{NTf}_2]\) but rather a new compound that incorporates both cations.

From previous studies on the OIPCs it had been known that defects \([11, 14]\) play a vital role in the transport processes. Meanwhile, these materials also undergo plastic deformation due to concentration of defects at their high temperature phases and are built from complex microstructures such as grains, sub-grains, dislocation cells, as has been shown in the SEM micrographs. These microstructural complexities result in crystallite and grain sizes variations. In previous XRD studies \([26]\) on different materials it had been suggested that shifts in Bragg peaks is caused due to internal
stresses, stacking faults, twin boundaries, grain boundaries and chemical heterogeneities, while Bragg peak broadening is due to dislocations, stacking faults, grain boundaries, chemical heterogeneities, crystal size and micro-stresses. The disappearance of Bragg peaks may be due to dislocations, stacking faults, twinning, point defects and precipitates or inclusions. Thus, in line with the correlations between diffraction peaks and elements of microstructures suggested by [26], the shift, disappearance and broadening of the peaks observed in our results may be related to point or line defects inherent in these materials.

It had been suggested [27] that vacancies are associated into pairs or larger clusters and form a nucleus for precipitation of phase/s. There is strong correlation between the Bragg peak broadening and lattice distortion, which could be measured in terms of crystallite size, and strain. Strain broadening is caused by the lattice defects, mainly by dislocations, twinning, stack faults, micro stresses, grain and sub grain boundaries, chemical heterogeneities, point defects or precipitates and inclusions. As shown in our SEM micrographs, precipitates, slip planes, and grains of different sizes were clearly observed. It may be that the differing ionic size of Na⁺ and [C₂mpyr]⁺ facilitates the incorporation of defects and at the same time causes lattice strains in the unit cell. Thus, the peak broadening at the lower temperature phase at 273K may be due to strain from the second phase.

3.2.6. Solid state NMR spectroscopy

Solid-state NMR was used to study the structural and dynamic behavior of the samples in relation to the Na⁺ ion content. The composition of the OIPC allows each component (i.e., Na⁺, [C₂mpyr]⁺ and [NTf₂]⁻) to be specifically probed due to the presence of unique NMR active nuclei. Thus, ¹H NMR is used to study the
[C$_2$mpyr]$^+$ cation, $^{19}$F for the [NTf$_2$]$^-$ anion, and $^{23}$Na for the added Na$^+$ ions. $^{13}$C and $^{15}$N CPMAS spectra were used to study the local environment of both OIPC ions, however $^{15}$N NMR spectra only gave weak signals at very long experiment times and thus were not performed on all samples. First the magic angle spinning (MAS) NMR spectra for different Na$^+$ contents at ambient temperature were compared to investigate the changes in the local environment as shown in Figures 3.8 a-d.
Figure 3-8  $^1$H, $^{19}$F, $^{13}$C, $^{15}$N and $^{23}$Na MAS solid-state NMR spectra (a – e respectively) at ambient temperature (295K) for the binary mixtures from 0 to 100 mol% Na$^+$ content.

The proton NMR did not show significant change apart from little line narrowing and a minor peak observed in the Na$^+$ containing materials at 2.5ppm as shown in Figure 3.8a. All peaks can be assigned to the [C$_2$mpyr]$^+$ as given in [28]. The quite
narrow lines in the proton spectra indicate the high rotational disorder of the molecule which averages the dipolar interactions present in solids and thus decreases the line width in the proton solid-state spectra.

In the $^{19}$F spectra significant changes were observed - the Na[NTf$_2$] spectra exhibited two different peaks with different environments clearly from CF$_3$ groups in the anion NTf$_2$ as shown in Figure 3.8b. The two different peaks, indicating unequal environments are assigned to two conformations of the dihedral angle to the CF$_3$ groups in the anion [NTf$_2$]. The pure [C$_2$mtpyr][NTf$_2$] spectrum however gives one single signal. This means the CF$_3$ groups are in the same environment and move fast enough to average out any conformational or crystallographic differences. For the samples with different sodium contents a series of spectra were recorded which display a continuous transition between the two neat materials with additional signals of increasing intensity for increasing Na$^+$ content (within the studied concentration range). These are assigned to the second phase, in agreement with SXRD measurements, and indicated a different structure of the amide anion in the second phase relative to the structures of the pure components. As discussed in the previous section, the FTIR and Raman measurements clearly indicated the two conformations and are of unequal chemical environments similar to the SXRD and solid-state NMR findings.

The other significant change was in the spectra of $^{13}$C CPMAS spectra (see Figure 3.8c). In the probe of $^{13}$C nuclei, the cation and anion environment were investigated together. Additional signals were observed with increasing Na$^+$ content. More peaks emerged in the mixture materials Na$_{0.04}$[C$_2$mtpyr]$_{0.96}$[NTf$_2$] and Na$_{0.15}$[C$_2$mtpyr]$_{0.85}$[NTf$_2$] whilst some of the peaks overlapped with the pure OIPC
[C₂mpyr][NTf₂]. The neat Na[NTf₂] spectrum shows just one signal for the CF₃ groups of the [NTf₂]⁻, the neat [C₂mpyr][NTf₂] spectrum shows the assigned signals [28] of both the cation and anion. With the addition of Na⁺ to the system, additional peaks can be observed in roughly the ratio of Na⁺ substitution (taking unreliable integration of CPMAS spectra into account) in the second, Na rich phase. This observation confirms that the Na⁺ containing materials exist in two distinct phases – pure [C₂mpyr][NTf₂] phase and a second, Na rich phase which is nevertheless different from Na[NTf₂] evidenced by the SXRD.

The ¹⁵N nuclei did not show any change in the local environment at 295K as shown in Figure 3.8d. For ¹⁵N nuclei, the peaks of central nitrogen in both anion and cation were resolved at 240 ppm and 310ppm respectively and no apparent change was observed with increasing Na⁺ content.

Another interesting variation in the Na⁺ environment in the mixture with [C₂mpyr][NTf₂] OIPC was observed in the ²³Na nuclei (quadrupolar nuclei of spin 3/2). The broad peaks featured in the pure salt NaNTf₂ were narrowed in the mixtures and a change in chemical shift was observed as shown in Figure 3.8e. This indicates that Na⁺ ions in the mixtures occupy a different crystallographic environment than in the neat material. The inability to observe of the additional phase in the ²³Na spectra could either be caused by the low sodium contents in the [C₂mpyr][NTf₂] rich phase, which make it very demanding to get enough signal intensity or alternatively the Na ions are in a very similar environment which would result in a very similar line shape and shift thus becoming indistinguishable from the Na[NTf₂] rich sample. Further studies on the structure and conformation of the additional phase are ongoing.
Figure 3-9 $^1$H static solid-state NMR spectra for the binary mixtures a) $\text{Na}_{0.04}[\text{C}_2\text{mpyr}]_{0.96}[\text{NTf}_2]$ and b) $\text{Na}_{0.15}[\text{C}_2\text{mpyr}]_{0.85}[\text{NTf}_2]$ acquired between 268K (283K) and 349K of Na[NTf$_2$] salt and 15% mol dopèd $\text{Na}_{0.15}[\text{C}_2\text{mpyr}]_{0.85}[\text{NTf}_2]$ show that they belong to one single signal.

Figure 3-10 $^1$H VT-MAS solid-state NMR spectra for the binary mixtures a) $\text{Na}_{0.04}[\text{C}_2\text{mpyr}]_{0.96}[\text{NTf}_2]$ and b) $\text{Na}_{0.15}[\text{C}_2\text{mpyr}]_{0.85}[\text{NTf}_2]$ acquired between 268K
(283K) and 349K of Na[NTf₂] salt and 15% mol doped Na₀.₁₅[C₂mpyr]₀.₈₅ NTf₂ show that they belong to one single signal.

Figure 3-11 ¹⁹F VT-MAS solid-state NMR spectra for the binary mixtures a) Na₀.₀₄[C₂mpyr]₀.₉₆[NTf₂] and b) Na₀.₁₅[C₂mpyr]₀.₈₅[NTf₂] acquired between 268K and 349K.
Variable temperature MAS NMR (VT-MAS) was performed on all materials to study the phase behavior of the cations and the anion using $^1$H, $^{23}$Na and $^{19}$F nuclei as site selective probes. The temperature region studied covers phases III to I (and for 15 mol% Na⁺ also extends into the liquid phase). For the $^1$H nuclei shown in Figure 3.9, the broad peaks observed below 295 K undergo a significant line narrowing at higher temperatures (i.e., at 323K in phase I and at 349K above the eutectic temperature) to a typical two phase spectrum with a liquid-like mobile component and a smaller, broader line width spectrum of a less mobile solid component. This correlates well with the phase behavior in the ‘α + L’ region. At a temperature of 349 K a spectrum of the Na$_{0.15}$[C$_2$mipy]$_{0.85}$[NTf$_2$] melt with narrow signals is measured (see Figure 3.10). The anions were investigated via the $^{19}$F nuclei (Figure 3.11(a,b)) within the same temperature range and showed similar trends as the $^1$H spectra. The broadened signals at lower temperatures narrow
slightly, up to the eutectic temperature, then exhibit the two phase spectrum of the
‘α + L’ region and very narrow signals above the melting temperature. The $^{23}$NaVT-MAS spectra (Figure 3.12) show the quadrupolar line shape, but no significant
line narrowing or change in the line shape or chemical shift could be observed for the phase I or II temperature region. For the melt however, the spectra change significantly to a gaussian broadened isotropic line at $\delta = -10$ ppm. This correlates well with highly mobile Na$^+$ ions in an ionic liquid.

![MQMAS spectra of Na[NTf$_2$] and 15% mol doped Na$_{0.15}$[C$_2$mpyr]$_{0.85}$ NTf$_2$](image)

*Figure 3-13 Observed line shapes MQMAS spectra of Na[NTf$_2$] salt and 15% mol doped Na$_{0.15}$[C$_2$mpyr]$_{0.85}$ NTf$_2$ show that they belong to one single signal*

For further investigation of the Na$^+$ environment, Multiple Quantum MAS NMR spectroscopy was applied for both the pure and doped materials as shown in Figure 3.13. It was confirmed that the Na$^+$ cation sits in a single local environment. It was also observed in Figure 3.3(c) that precipitates form upon addition of Na[NTf$_2$] as evidenced in the SEM micrograph. These precipitates may be a Na rich phase which is being detected by NMR.
3.3. Conclusions

In the phase diagram, it was understood that the two different phases exist below the eutectic line with the [C₂mpyr][NTf₂] rich phase and the other combined phase of [C₂mpyr][NTf₂] / Na[NTf₂] being present. The synchrotron XRD showed the [C₂mpyr][NTf₂] rich phase exists with different phases at different temperatures. The second, Na rich phase was found to be consistently monoclinic P2/1 with volume increasing with increase temperature, similar to the [C₂mpyr][NTf₂] phase. The pure [C₂mpyr][NTf₂] phases continuously undergo change in crystal structure from triclinic P-1 at 273K to monoclinic CC at 328K. This change in crystal structure may be resulted from the rotational disorder at low temperatures and translational mobility of cations and anions at higher temperatures of 328K as was confirmed by the solid state NMR measurements. Another striking difference from the pure OIPC observed in the Raman and FTIR spectra is the presence of cis and trans conformer in the NTf₂ anions of the Na⁺ containing systems at 295K. Conformational changes in the NTf₂ anion was reported in the Raman spectra of Li⁺ doped systems [13] and [hmim][NTf₂] [17] only at temperatures above 273K. In the solid state NMR measurement on Na⁺ containing systems there was no translational mobility detected. Therefore it can be concluded that the conformational flexibility in this system is due to the rotational disorder in the anions. Such conformational transformation or internal rotation in the anion can create defects.

In this work it has been demonstrated that mixtures of [C₂mpyr][NTf₂] OIPC with a sodium salt Na[NTf₂] suitable for solid state electrolyte was presented for the first time and these materials yielded up to 3 orders of magnitude enhancement in ionic conductivities, especially in phase I. Previous studies on OIPCs [1, 2, 12, 13] have
shown that the conductivity mechanism is dominated by defects, mainly vacancies and grain boundaries. The increase in size and concentration of defect results in an increase of ionic conductivity [21] with increasing temperature. In our results, as well as previous studies related to lithium doping in the same plastic crystal, similar trends were observed from between phase III to I for compositions of Na/Li cations lower than the eutectic composition. In the case of Li[NTf₂] mixtures, this eutectic occurred at 33% Li[NTf₂] and at 34°C (when the OIPC is in phase II). It was suggested that the enhancement in conductivity to be attributed to increased mobility of lithium ion in the matrix through a grain boundary phase [4, 13, 29]. The ionic conductivity in the Na⁺ containing materials increases with the concentration higher than eutectic composition at 15% mol Na[NTf₂] (with a eutectic melt occurring at 63±2°C; this is in contrast to the Li⁺ doped system in the same OIPC. Our SEM micrographs have shown the presence of slip planes as evidence of extended defects such as dislocations. Grain boundary or pipe diffusion may also contribute to the enhancement of ionic conductivity in phase I in the Na case presented here. Moreover, from the synchrotron XRD results it had been established that the mixture system has two distinct phases, they undergo volume expansion that would allow more room for vacancy generation, with the increase in thermal energy as the solid-solid transitions proceed to phase I. This finding was also supported by the solid state NMR in which all the nuclei probed showed both the cations (Na⁺ and [C₂mpyr]⁺) and the anion [NTf₂⁻] are mobile at 333K.

It had been suggested that there are large number of vacancies to exist at their melting point in pure [C₂mpyr][NTf₂] plastic crystals [14] and doped with Li[NTf₂] to a concentration in the range of 0.1- 2 mol% [14, 30]. Thus, we propose two...
models of conductivity mechanisms in the Na-doped systems in the phases II and I. The low conductivity compared to the pure OIPC in the phase II and the lower temperature phases was the drainage due to pipe diffusion in the extended defects. The slip planes observed in the micrographs at room temperature (phase II) terminate at the grain boundary. The cause for high conductivity at high concentration of sodium dopant in phase I might be due to the increase of the vacancy volume and the increase concentration of mobile cations and anion.

Both thermal and synchrotron powder XRD studies found two distinct phases to occur in the sodium containing $[\text{C}_2\text{mpyr}][\text{NTf}_2]$. One of them resembles pure OIPC and the second one different from Na[NTf$_2$] phase. The conductivity in sodium doped $[\text{C}_2\text{mpyr}][\text{NTf}_2]$ is enhanced from Phase I and beyond, with increasing concentration of Na$^+$ mainly due to volumetric expansion and vacancy formation as shown in the synchrotron studies. The anion NTf$_2$ in the doped system exist in possible trans and cis conformational states as revealed through Raman and FTIR spectroscopy and the cation interaction with the anion was observed to be weak so that sodium ion mobility brought about three orders of magnitude enhancement in conductivity with the 40% mol Na[NTf$_2$] over the pure plastic crystal as confirmed in the solid state NMR measurements. All these results broadened our basic understanding on the first possible Na- ion solid-state electrolytes to be used in electrochemical devices such as battery, supercapacitors, sensors and fuel cells.
3.4. References


CHAPTER 4. The Influence of Anion on Phase Behaviour and Dynamics of NaX/OIPC Mixtures; X= [BF₄], [N(CN)₂] Anions

4.1. Brief Overview

The experimental characterisation of OIPCs [C₂mpyr][BF₄] and [C₃mpyr][N(CN)₂] mixed with Na[BF₄] and Na[N(CN)₂] salts respectively is presented in the two sub-sections of this chapter. In both mixture systems, the phase behaviour, morphology, conduction mechanisms were analysed through the use of advanced experimental techniques; DSC, SEM, NMR and FTIR/Raman. Results and discussions from measurements investigates the effect of the two anions on the phase behaviour and dynamics of these pyrrolidinium based OIPCs mixed with respective sodium salts followed by the conclusions.

4.2. Thermal, Structural and Transport Properties of Mixtures of NaBF₄ Salt with N-ethyl-N-methylpyrrolidinium tetrafluoroborate [C₂mpyr][BF₄] Solid State OIPC

4.2.1. Phase Behaviour for [C₂mpyr][BF₄] with Na[BF₄]

The DSC traces for the N-ethyl-N-methylpyrrolidinium tetrafluoroborate [C₂mpyr][BF₄] (201.01g/mol, m.p.~280°C) and the binaries with Na[BF₄] (109.79g/mol, m.p. ~384°C) were investigated at different molar concentrations and presented in Figure 4.1 along with a summary of phase behaviour in Table 4.1.
As it can be seen from Figure 4.1 and as reported previously, the DSC traces exhibit multiple solid-solid transitions before melting at \(~280^\circ\text{C}\) [1]. In similar previous studies, the solid-solid phase transitions were assigned for the pyrrolidinium based pure OIPCs of \([\text{BF}_4]\) anion [2-5] and \(\text{Li}^+\) mixed systems [6, 7]. It can be seen from this measurement that the solid-solid transition from IV-III, III-II and II-I occur at \(-36^\circ\text{C}, -24^\circ\text{C}\) and \(65^\circ\text{C}\) respectively. As it has been known from various studies on the OIPCs, the occurrence of several solid-solid transitions is linked to the transformation of the phases from order to disorder state as a result of the rotational motions undergone by the cation and/or anion.

From the DSC traces it can be seen that, the onset temperatures of all solid-solid transitions of the mixed systems remain unchanged although there is an increase of
the enthalpy change with increasing concentration of NaBF₄ for the transitions from phases IV-III and III-II as shown in Table 4.1, in particular for the 10% NaBF₄ sample. This would suggest an increase in order in these lower temperature phases when the NaBF₄ is present, and may have implications for conductivity as discussed later.

Table 4.1 The onset solid-solid transition temperatures (±1°C) of the pure and mixed systems with their corresponding enthalpy change (in J/g within the error margin of ±10%)

<table>
<thead>
<tr>
<th>Na[BF₄] / % mol</th>
<th>Phase IV-III</th>
<th>Phase III-II</th>
<th>Phase II-I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T/ °C</td>
<td>ΔH/Jg⁻¹</td>
<td>T/ °C</td>
</tr>
<tr>
<td>0</td>
<td>-36 42.6</td>
<td>-24 6.5</td>
<td>65 6.1</td>
</tr>
<tr>
<td>1</td>
<td>-36 42.8</td>
<td>-24 6.9</td>
<td>65 5.8</td>
</tr>
<tr>
<td>4</td>
<td>-36 44.5</td>
<td>-24 9.4</td>
<td>65 6.0</td>
</tr>
<tr>
<td>10</td>
<td>-36 33.4</td>
<td>-24 10.5</td>
<td>65 7.4</td>
</tr>
<tr>
<td>20</td>
<td>-36 34.7</td>
<td>-24 7.5</td>
<td>65 5.1</td>
</tr>
</tbody>
</table>

4.2.2. Morphology and topography

The microstructure of the OIPC and the Na mixed systems of [C₂mpyr][BF₄] were probed at ambient temperature using SEM, without sample damage and charging effect through careful experimental choice. Previously, the microstructure of the pure OIPC of alkylpyrrolidinium [BF₄] and their Li⁺ mixed systems was extensively studied [4-6]. These studies have clearly shown the existence of extended defects.
In Figure 4.2, we present the microstructure of the Na\(^+\) mixed \([\text{C}_2\text{mpyr}]\text{[BF}_4]\) systems at different concentrations and at ambient temperature. From the micrographs, we found extended defects such as slip planes and the grain boundaries which emanate from the grains of different sizes and shapes. At the low levels of NaBF\(_4\) addition, e.g. for the Na\(_{0.04}\)[C\(_2\)mpyr]\(_{0.96}\)[BF\(_4\)] system, the precipitates of the new phase appear within the grain surface of the OIPC. Another striking difference was observed at higher concentration of Na\(^+\) dopant, e.g. Na\(_{0.1}\)[C\(_2\)mpyr]\(_{0.9}\) [BF\(_4\)], where the precipitates are embedded as aggregates within the grain boundaries.
Efthimidias et al.[3-5] had studied the effect of the intra-granular and inter-grain boundary segregation of the ionic species in the doping with 2% Li[BF₄] in the same OIPC on the transport properties of the material. They found the correlation between intra-granular and inter-grain boundary segregation of the ionic species and the ionic conductivity. We also previously presented the existence of such precipitates as the occurrence of a new sodium rich phase in our previous work [8] related to Na⁺ doping in [C₂mpyr][NTf₂] and as discussed in Chapter 3. The SEM images in Figure 4.2 suggest that the precipitates could represent a new phase of Na rich species which are segregated to intra-granular regions for low concentration of the Na salt. The other observation was that this second phase is not as clearly aggregated in the grain boundary region for higher doping levels of Na salt, in the Na₀.₄[C₂mpyr]₀.₆[BF₄]. However, for Na₀.₂[C₂mpyr]₀.₈[BF₄] the precipitates no longer appear to be segregated at the grain boundary. From the EDXS elemental

Figure 4-3 EDX elemental map analysis of Na₀.₂[C₂mpyr]₀.₈[BF₄], 25μm showing minor, dispersed Na presence while C and F are clearly the majority.
map analysis shown in the Figure 4.3 there appears to be little segregation of the Na atoms with all elements showing relatively similar dispersion although the Na maps are insignificant.

4.2.3. Ionic conductivity

The ionic conductivity of the samples was determined from the touchdown of the Nyquist semicircle. Variable temperature Nyquist plots of the Na$_{0.04}$[C$_{2}$mpyr]$_{0.96}$[BF$_{4}$] sample shown in Figure 4.4 were used to monitor the stability and reproducibility in the measurement where $Z''$ and $Z'$ are designated as the imaginary and real axes of the impedance respectively. The sample resistance was recorded from the intercept of the real axis (touchdown) point and is inversely proportional to the ionic conductivity.

![Figure 4-4 Nyquist plot of 4%Na$^+$ content in [C$_{2}$mpyr][BF$_{4}$] OIPC](image)

*Figure 4-4 Nyquist plot of 4%Na$^+$ content in [C$_{2}$mpyr][BF$_{4}$] OIPC*
As shown in Figure 4.5, the conductivity of pure OIPC, $[C_{2mpyr}][BF_4]$ is phase dependent, especially at ~65°C. In the understanding of conductivity mechanisms it should be noted that OIPC $[C_{2mpyr}][BF_4]$ has low entropy of fusion and tends to flow under pressure and thus justifies that the material as highly plastic with a high degree of disorder. The conductivity increased linearly from $6.9 \times 10^{-8} \text{S.cm}^{-1}$ at 25°C to $4.6 \times 10^{-7} \text{S.cm}^{-1}$ at 60°C within the phase II and shows that the increase in thermal energy enhances the dynamics of the ionic species. Upon transition from phase II to I (~ 65°C), the conductivity showed a sharp sudden change and jumped by five-fold to $2.2 \times 10^{-6} \text{S.cm}^{-1}$ in both pure and Na salt mixed materials. This jump of conductivity is attributed to the occurrence of the solid-solid transition from phase II-I. Slightly enhanced conductivity was observed in the Na$_{0.04}[C_{2mpyr}]_{0.96}[BF_4]$ mixed samples in contrast to the materials with higher concentrations of NaBF$_4$, Na$_{0.1}[C_{2mpyr}]_{0.9}[BF_4]$ and Na$_{0.2}[C_{2mpyr}]_{0.8}[BF_4]$. In the latter samples, the Na$_{0.2}[C_{2mpyr}]_{0.8}[BF]$ sample presented conductivity similar to pure OIPC, $[C_{2mpyr}][BF_4]$ On the other hand, the conductivity in phase II for Na$_{0.1}[C_{2mpyr}]_{0.9}[BF_4]$ is lower than the pure OIPC. In the Na$_{0.04}[C_{2mpyr}]_{0.96}[BF_4]$ mixed system, the conductivity showed an increase of about 5 times of the OIPC at 25°C and is doubled when it reached the transition from phase II – I at 65°C over the pure OIPC to $\sim 10^{-5} \text{S.cm}^{-1}$. 

- 101 -
In similar previous studies [2, 3, 6, 9-12] a decrease in conductivity was observed in the related [BF$_4$] based OIPC with the addition of nanoparticles and inorganic salts. Jin et al.[6] reported the dependence of conductivity and phase behaviour N,N-dimethyl pyrrolidinium tetrafluoroborate [C$_1$mpr][BF$_4$] mixed with Li[BF$_4$]; a decrease in conductivity in phase II and an increase in phase I was reported with increasing amount of the Li salt. It was suggested an apparent ordering and reduction in ionic mobility following this phase transition could occur within the phases investigated. Similarly, Efthimidias et. al. [2, 3] have shown an increase in conductivity in the binary system composed of 2wt.% Li[BF$_4$]/[C$_3$mpr][BF$_4$] whilst the decrease in conductivity with the high level concentration of mixture with Li[BF$_4$]. They also suggested the conduction mechanisms in the pure [C$_3$mpr][BF$_4$] are facilitated through the grains as well as via the grain boundaries in phase I, but predominantly via grain boundaries in phase II. The addition of
aPEO in the binary system Li[BF$_4$]/[C$_3$mpyr][BF$_4$] was also shown to result in significantly reduced conductivity in phase II as the diffusion pathway is essentially blocked by the polymer, i.e. the polymer acts as a barrier to ion transport via the grain boundaries. It was deduced from the conduction mechanisms in the binary system that the reduction in conductivity correlates with less mobility of the anion and/or cation due to the occurrence of some degree of interaction or aggregation (clustering) with the lithium cation.

Based on a similar argument, the increase in conductivity for 4mol% Na[BF$_4$]/[C$_2$mpyr][BF$_4$] may be mainly due to intragranular ionic transport in phase II (see Figure 4.3) and disordered grain boundaries in phase I. With the increased concentration of Na[BF$_4$], the increased amount of second phase within the binary system may be responsible for the blocking of the transport along the grain boundaries, thereby reducing the conductivity. It is also interesting to note that, the enthalpy of the II $\rightarrow$ I transition actually increases at 10mol% NaBF$_4$. This suggests a stronger degree of ordering in this composition and may explain the lower conductivity measured in this case.

It had been established that the [BF$_4$]$^-$ anion in tetrafluoroborate salts is tetrahedral in shape [13]. The crystal of Na[BF$_4$] salt occurs as orthorhombic [13] with the D$_{2h}$ Space group while a molecular anion of tetrafluoroborate can be considered as a Lewis acid/base complex involving BF$_3$ (Lewis acid) and the fluoride ion (Lewis base) [14]. Moreover the Na[BF$_4$] can form cluster ions (Na[BF$_4$])$_n$Na$^+$ or (NaF)$_n$Na$^+$ and is easily degradable in solution. This salt also favours the mixed fluoride/ tetrafluoroborate cluster over a homogenous salt [15]. Thus, it is also possible that strong ion pairing may effectively trap the mobile cations. Previous reports [16, 17] have shown that the ion-pairing in PEO-Na[BF$_4$] complex
significantly reduce the observed ionic conductivity relative to non-ion-paired complexes of similar structure.

Overall the conductivity properties in this binary systems differ significantly to both the NTf₂ and N(CN)₂ based OIPCs (discussed in the next section) with sodium salt addition. This may be because the pure BF₄ OIPC melts at much higher temperatures and a eutectic is not observed in the accessible temperature range. It is nonetheless interesting that there is still a jump in conductivity at the II -> I transition even when 20% NaBF₄ is present.

BF₄ anion has the least ionic radii and the highest melting points among the anions investigated in this work. The melting point of the sodium salts exceeds the melting point of the pyrrolidinium based OIPCs and ILs of these anions. The larger the size of the cations or with increasing anion radius, the lower the melting point due to the lowering of electrostatic interaction [18]. It was also suggested that the solubility of compounds depends on its melting point and partition coefficient [19], which is determined by the entropy of fusion. Thus, there is correlation between the solubility and melting point of the material. The melting point increases with the increase in enthalpy and lowering of entropy of fusion, which in turn are related to the intermolecular interaction and the geometric factors of the material. This in turn affect the solubility of the mixtures.

AlNashef et.al. [20] found that many sodium salts showed poor solubility in ionic liquids (ILs), and it was found that, among the anions studied, the bis(trifluoromethylsulfonyl) imide anion yielded higher solubilities within the inorganic salt/IL binary mixtures. Given the OIPC materials discussed here are very similar in chemical nature to the ILs discussed in this paper, it is not perhaps
surprising that phase separation is observed in these Na salt/OIPC mixtures. This low solubility could therefore explain the insignificant changes in conductivity observed upon mixing Na[N(CN)₂] / Na[BF₄] into the [C₁mpyr][N(CN)₂]/[C₂mpyr][BF₄] compared to the NTf₂ OIPC materials.

The trend in conductivity in the binary systems differ significantly from anion to anion and in the previous sections we have established that the solubility varies with melting point in the compounds, directly affected by the size of the anion. As the BF₄ anion has higher melting the level of solubility into the binary matrix might markedly lower than other anions. This also explains the lower conductivity in phase I than other binary mixtures containing N(CN)₂ and NTf₂ anions.

**4.2.4. IR/Raman spectroscopy**

To further understand the interactions of the cations and anions within the pure OIPC [C₂mpyr][BF₄] and its mixture with Na[BF₄] salt at different molar concentration room temperature FTIR and Raman spectra were recorded and presented in Figure 4.6 (a-d) and 4.7 (a-d) respectively. The spectra of these samples are rich in vibrational bands with noticeable differences between the mixed and the pure samples. The observed peaks of [BF₄]- anion and [C₂mpyr]⁺cation were assigned and summarized in Table 4.2 based on previous extensive investigations performed by several research groups. Most relevant to this work are investigations on vibrational spectra of imidazolium tetrafluoroborate ionic liquids reported by Heimer et.al [21], combined DFT, Infrared and Raman study alkali [BF₄] crystals by Zavorotynska et al. [22] and the recent work on the mixture ofNa[NTf₂] / [C₂mpyr][NTf₂] and sources therein [8] for the cation [C₂mpyr]⁺.
Table 4.2 Assignment of observed Raman and FTIR bands of \([\text{C}_2\text{mpyr}]\text{[BF}_4\text{]}\) at room temperature based on literature reports [8, 21-23] for related cations and anions.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Raman (\nu / \text{cm}^{-1})</th>
<th>FTIR (\nu / \text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\delta (\text{N-CH}_3), \delta (\text{N-CH}_2))</td>
<td>388</td>
<td>430(vw)</td>
</tr>
<tr>
<td>(\delta (\text{N-CH}_3), \delta (\text{N-CH}_2))</td>
<td>433</td>
<td>476</td>
</tr>
<tr>
<td>(\delta ([\text{BF}_4]), \nu (\text{BF}))</td>
<td>521</td>
<td>520(s)</td>
</tr>
<tr>
<td>(\delta ([\text{BF}_4]))</td>
<td>562</td>
<td></td>
</tr>
<tr>
<td>(\nu (\text{N-CH}_3), \nu (\text{N-CH}_2))</td>
<td>586</td>
<td>584(w)</td>
</tr>
<tr>
<td>(\nu (\text{N-CH}_3), \nu (\text{N-CH}_2))</td>
<td>710</td>
<td></td>
</tr>
<tr>
<td>(\delta_a R, \delta^p R)</td>
<td>718</td>
<td></td>
</tr>
<tr>
<td>(\nu ([\text{BF}_4]))</td>
<td>765</td>
<td>765(vw)</td>
</tr>
<tr>
<td>(\delta (\text{C-C}))</td>
<td></td>
<td>810(m)</td>
</tr>
<tr>
<td>Ring mode</td>
<td>880</td>
<td>878(vw)</td>
</tr>
<tr>
<td>Ring mode</td>
<td>903</td>
<td></td>
</tr>
<tr>
<td>Ring mode</td>
<td>999</td>
<td></td>
</tr>
<tr>
<td>(\nu_a ([\text{BF}_4]), \nu^i \nu R)</td>
<td>1035</td>
<td>1027(vs)</td>
</tr>
<tr>
<td>(\nu_a ([\text{BF}_4]), \nu_a R, \nu (\text{N-CH}_3))</td>
<td>1054</td>
<td>1044(sh)</td>
</tr>
<tr>
<td>(\rho (\text{CH}_3))</td>
<td>1085</td>
<td></td>
</tr>
<tr>
<td>(\nu^i \nu R, \nu (\text{N-CH}_3), \nu (\text{N-CH}_2))</td>
<td>1116</td>
<td></td>
</tr>
<tr>
<td>(\nu_a ([\text{BF}_4]), \nu_a R, \nu (\text{N-CH}_3))</td>
<td>1182</td>
<td></td>
</tr>
<tr>
<td>(\tau \text{CH}_2)</td>
<td>1240</td>
<td></td>
</tr>
<tr>
<td>(\nu^i \nu R, \delta (\text{C-C-C}))</td>
<td>1285(w)</td>
<td></td>
</tr>
<tr>
<td>(\nu^i \nu R, \nu (\text{N-CH}_3), \nu (\text{N-CH}_2))</td>
<td>1325</td>
<td></td>
</tr>
<tr>
<td>(\nu^i \nu R, \delta (\text{CH}_3))</td>
<td>1437(vw)</td>
<td></td>
</tr>
<tr>
<td>(\delta (\text{CH}_3), \delta (\text{CH}_2))</td>
<td>1457</td>
<td></td>
</tr>
<tr>
<td>(\nu (\text{CH}_3), \nu (\text{CH}_2))</td>
<td>1471(m)</td>
<td></td>
</tr>
</tbody>
</table>

Letters representing the vibrational modes: \(\nu\) - stretching, \(\delta\) - bending, \(\tau\) - twisting, \(\rho\) - rocking, \(\omega\) - wagging, \(ip\) - in phase, \(op\) - out of phase, \(s\) - symmetric, \(as\) - asymmetric -letters indicating relative intensities: \(vw\) - very weak, \(w\) - weak, \(m\) - medium, \(s\) - strong, \(vs\) - very strong.

As it can be seen from Table 4.2, the low frequency (300-600 cm\(^{-1}\)) vibrational modes are predominantly from \([\text{C}_2\text{mpyr}]\) cation. In the IR spectra, shown in Figure 4.6 (a), the methyl and ethyl bending and stretching were observed 430 and 586 cm\(^{-1}\) respectively. The 520 cm\(^{-1}\) vibrational band corresponds to the \([\text{BF}_4]\) bending in the OIPC. It can also be seen that the split peaks occur at 520 and 550 cm\(^{-1}\) in a pure salt.
and it exactly coincides with additional peak in the samples of Na salt mixed into the OIPC. The pyrrolidinim ring modes are observed from 880-1050 cm$^{-1}$ (Figure 4.6 (c)). These mode of vibrations are mostly due to the functional groups in the cation $[\text{C}_2\text{mpyr}]^+$. No apparent changes were observed in ring modes occurs within the 880-1050 cm$^{-1}$ frequency range (Figure 4.6 (c)) and the overtones of methyl ethyl stretching between 2900 – 3150cm$^{-1}$ (Figure 4.6 (d)) with the mixing of Na[BF$_4$] with $[\text{C}_2\text{mpyr}][\text{BF}_4]$. Comparison of the IR spectra of $[\text{C}_2\text{mpyr}][\text{BF}_4]$ with $[\text{C}_2\text{mpyr}][\text{NTf}_2]$ shows that the cation vibration dominates in the former while the anion vibration dominates in the later in the region 300-600cm$^{-1}$. Apart from that there is no apparent difference in the cation vibration of both OIPCs in the rest of the spectral regions under study.
Figure 4-6 FTIR spectra of pure [C2mpyr][BF4] and mixture with Na[BF4] salt in the spectral regions of a) 500-600cm⁻¹ b) 800-1200cm⁻¹ c) 1200-1600cm⁻¹ and d) 2800-3100cm⁻¹

The Raman spectra in the pure [C2mpyr][BF4] and mixture with Na[BF4] salt presented in Figure 4.7 a-d show similar trend to the FTIR study of these materials. However, in the 300-600cm⁻¹ an extra vibrational band at ~475cm⁻¹ was assigned to the bending of [BF₄]⁻ anion and stretching of the B-F bond. The most intense Raman spectra at ~ 765cm⁻¹ in the OIPC and mixtures corresponds to the symmetric stretching vibration of the [BF₄]⁻ anion. In the Na[BF₄] salt this vibration was shifted by ~10cm⁻¹ to the higher frequency. The new peak observed at ~785cm⁻¹ in the [C2mpyr]₀.₈Na₀.₂[BF₄] heralds possible co-ordination with the Na⁺ cation. The Raman spectra (Figure 4.7 (c)) did not show apparent variation with the concentration of Na⁺ in the OIPC in the vibrational modes of the pyrrolidinium ring within the 880-1050 cm⁻¹ frequency range. Similarly, the overtones of methyl ethyl stretching to occur in the frequency range of 2900 – 3150cm⁻¹ (Figure 4.7 (d)) were
unaffected with the mixing of Na[BF₄] in [C₂mpyr][BF₄]. The “ring breathing”
vibration of the cation at 903 cm⁻¹ in [C₂mpyr][BF₄] was observed shifted to the
lower frequency by 6 cm⁻¹ at 897 cm⁻¹ [9, 24, 25] in [C₁mpyr][BF₄]. The umbrella-
like bending around the quaternary nitrogen atom of the cation at 580 cm⁻¹ observed
in [C₁mpyr][BF₄] [30] was shifted to the higher frequency by 6 cm⁻¹ in the
[C₂mpyr][BF₄] to 586 cm⁻¹. We did not observe change in the peak position as
compared to the [C₁mpyr][BF₄] symmetric stretching vibration of the [BF₄]⁻ anion.
Comparison with [C₂mpyr][NTf₂] did not show any significance difference apart
from what had been already discussed in the FTIR spectra.
It had been previously [13,19] reported that free $[\text{BF}_4^-]$ anion (free from coordination with cation and/or molecules of solvent) species belong to $T_d$ symmetry group with four normal modes of vibration $\nu_1$, $\nu_2$, $\nu_3$ and $\nu_4$ which are all Raman active and only $\nu_3$ and $\nu_4$ are IR active, in a solid state alkali tetrafluoroborate salts. The $[\text{BF}_4^-]$ vibrational bands ($\nu_1$, $\nu_3$ and $\nu_2$, $\nu_4$) lie within the range of frequency of 1100 - 700 cm$^{-1}$ and 600 - 300 cm$^{-1}$. In our measured infrared spectra for Na$[\text{BF}_4]$ (Figure 4.6), the doubly degenerate asymmetric band in the anion $\nu_2$ at $\sim$ 360cm$^{-1}$ and the fully symmetric stretching band $\nu_1$ of the free anion at $\sim$760cm$^{-1}$ were not observed in the Na salt and pure OIPC. However, only the IR active peaks at $\sim$1000 cm$^{-1}$ and $\sim$520 cm$^{-1}$ correspond to the triply degenerate asymmetric bending $\nu_3$ and $\nu_4$ bending bands respectively were found. Zavorotynska et al. [38] had previously reported the stretching of $\sim\nu_3$ mode split in all the tetrafluorides. The other weak peaks which appear as shoulders in this spectral region comprise the overtones of the $\sim\nu_4$ bending mode of the anion. The weak peaks in the range 1300-1340 cm$^{-1}$ are assigned to the combination of $\nu_1+\nu_4$ of different transitions respectively.

Numerous absorptions bands exceeding that of free anion were observed to show that the interaction of $[\text{BF}_4^-]$ with a cation lowers the symmetry by removing the degeneracy and selection rules forbidding vibrational transitions. In case one fluorine atom interacts with a cation, the symmetry lowers to $C_{3v}$ from the $C_{2v}$,
whereas additional fluorine transforms the symmetry to the lower $C_{4v}$ symmetry by increasing the absorptions bands further [26, 27].

As the mixture of $[\text{C}2\text{mpyr}]\text{[BF}_4]\text{]}$ and $\text{Na[BF}_4]\text{]}$ were prepared in dry acetonitrile under nitrogen atmosphere for this experiment we also investigated previous studies. The IR/ Raman studies of $\text{Li[BF}_4]\text{]}$ in acetonitrile and $\text{Na[BF}_4]\text{]}$ in N-N-dimethylformamide (MF) were previously reported by Xuan et. al. [28, 29]. In the former case, strong interactions between $\text{Li}^+$ and the $N$ atoms of the C-N groups affects the C-N stretching mode and results in the transfer of an electron from the $N$ atom of the CN group to $\text{Li}^+$, thereby causes the decrease of cation charge with increasing cluster size. They also suggested that $\text{Li}^+\text{[BF}_4]\text{]}^-$ contact ion pairs possibly exist as monodenate with a $C_{3V}$ symmetry, bidenate $C_{2V}$ and tridenate $C_{3V}$ structures while $\text{Na}^+\text{[BF}_4]\text{]}^-$ contact ion pairs exist only as bidenate $C_{2V}$ and tridenate $C_{3V}$ structures in DMF as well as in vacuum [30]. Ion association was also found to occur at medium and high salt concentrations as deduced from the changes in the vibrational band of the B-F symmetric stretch in $\text{[BF}_4]\text{]}^-$ anions. A broad spectrum around $\sim 765 \text{ cm}^{-1}$ was assigned to free anions $\text{[BF}_4]\text{]}^-$ ($763 \text{ cm}^{-1}$), contact ion pairs $\text{Li}^+\text{[BF}_4]\text{]}^-$ ($771 \text{ cm}^{-1}$), and dimers ($\text{Li}^+\text{[BF}_4]\text{]}^-$)$_2$ ($780 \text{ cm}^{-1}$). The band at $\sim 550 \text{ cm}^{-1}$ in the IR spectra and $\sim 785 \text{ cm}^{-1}$ in the Raman spectra in our work therefore reflect the interaction of $\text{Na}^+$ with the $\text{[BF}_4]\text{]}^-$ anion, possibly due to ion-pairing with sodium cation.
4.2. Thermal, Structural and Transport Properties of Mixtures of Sodium Dicyanamide Salt with N,N-Dimethylpyrrolidinium Dicyanamide Solid State OIPC

4.3.1. Phase behaviour of C1mpyr][N(CN)2] and its binaries with Na[N(CN)2]

The DSC traces for [C1mpyr][N(CN)2] and the binaries with Na[N(CN)2] at concentrations ≤50 mol% Na[N(CN)2] are presented in Figure 4.8, and the phase behaviour is summarized in Table 4.3. The melting temperatures of pure [C1mpyr][N(CN)2] and Na[N(CN)2] were ~117°C and ~300°C, respectively. No evidence of a glass transition was observed in the investigated temperature range. As shown for other OIPCs in several previous studies [31, 32] [C1mpyr][N(CN)2] undergoes several solid-solid phase transitions. The transition from phase III to II occurs at -2 ± 1°C, followed by the phase II to I transition at 91 ± 2°C, before final melting at 117 ± 1°C. Again, as with previous studies on pyrrolidinium-based OIPCs [2-5, 31, 33], we have several solid-solid transitions which probably reflect the transition from ordered to more disordered phases.

Upon addition of Na[N(CN)2] the solid-solid transition temperatures from phases III-II and II-I (dashed lines in Figure 4.8) of the binary systems appear to be little altered occurring at approximately the same temperature as in the pure OIPC. However, an extra peak was observed at 88±1°C in the binary systems containing Na[N(CN)2] and the enthalpy (i.e. area) of this peak increased relative to that of the final melting peak as the Na[N(CN)2] concentration increased, as shown in Table 4.3. This effect was also seen in mixtures of Na[NTf2] and [C2mpyr][NTf2] [8]. This
transition in the binary system is most likely the eutectic transition, which grows in intensity until 20mol% Na[N(CN)_2]. As previous studies on Na\(^+\) [8] and Li\(^+\) salt [6, 31, 33, 34] mixed systems confirmed, mixing of these salts into the OIPC usually leaves the solid-solid phase transitions unaltered, but lowers and broadens the final melting point of the compound, consistent with liquidus behavior. With increasing salt concentration in the binary mixture, the appearance of extra transition(s) suggests eutectic melting, and the presence of a new sodium- or lithium-rich phase.

Figure 4-8 DSC traces of pure \([\text{C1mpyr}\][\text{N(CN)}_2]\) and mixtures (0–50 mol%) of Na\([\text{N(CN)}_2]\] with \([\text{C1mpyr}\][\text{N(CN)}_2]\].
Table 4.3 Peak solid-solid transition temperatures (±1°C) of the pure and mixed systems with their corresponding enthalpy changes (in J/g within an error margin of ±10%)

<table>
<thead>
<tr>
<th>NaN(CN)_2 / % mol</th>
<th>III -&gt; II</th>
<th>II -&gt; I / eutectic</th>
<th>melt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T/ °C</td>
<td>ΔH /Jg⁻¹ T/ °C</td>
<td>ΔH /Jg⁻¹</td>
</tr>
<tr>
<td>0</td>
<td>-2.7</td>
<td>53.3</td>
<td>91</td>
</tr>
<tr>
<td>5</td>
<td>-2.0</td>
<td>54.6</td>
<td>89</td>
</tr>
<tr>
<td>10</td>
<td>-2.5</td>
<td>49.8</td>
<td>89</td>
</tr>
<tr>
<td>15</td>
<td>-2.1</td>
<td>39.6</td>
<td>89</td>
</tr>
<tr>
<td>20</td>
<td>-1.8</td>
<td>42.0</td>
<td>88</td>
</tr>
<tr>
<td>25</td>
<td>-1.7</td>
<td>39.3</td>
<td>88</td>
</tr>
<tr>
<td>30</td>
<td>-2.4</td>
<td>38.0</td>
<td>88</td>
</tr>
<tr>
<td>40</td>
<td>-3.0</td>
<td>36.1</td>
<td>88</td>
</tr>
<tr>
<td>50</td>
<td>-3.2</td>
<td>32.7</td>
<td>88</td>
</tr>
</tbody>
</table>

The 20 mol% Na[N(CN)_2] / C1mpyr[N(CN)_2] binary mixture showed only a sharp peak at 88±1°C, but no separate melting transition. A similar sharp peak has previously been reported at 63±2°C for binary systems containing 15 mol% Na[NTf_2] in [C2mpyr][NTf_2][8]. It had also been reported that mixing 2 mol% Li[N(CN)_2] with [C1mpyr][N(CN)_2] results in an isothermal peak at 32°C [31]. The invariance of this peak temperature with salt concentration is indicative of the formation of a eutectic phase. Similarly, when Li[NTf_2] was mixed into [C2mpyr][NTf_2] OIPC, the eutectic temperature, T_E, was approximately 30°C [35]. In the Na[N(CN)_2] / [C1mpyr][N(CN)_2] binary system, when we examine the shapes of the transitions at 15 and 25 mol% salt, we see “tails” or “shoulders”, which are indicative of two separate peak positions. This behavior implies that the eutectic
composition is around 20 mol% salt, and that the 20 mol% mixture melts at the eutectic temperature, $T_E$. Therefore, above $T_E$, the material is completely liquid and it solidifies into two distinct phases below this temperature, as shown in the partial binary phase diagram for Na[$N(CN)_2$] / [C$_{1}$mpyr][N(CN)$_2$] presented in Figure 4.9.

\[ \text{Figure 4-9 Partial phase diagram for Na}[N(CN)_2] \text{ mixed with [C}_{1}\text{mpyr}][N(CN)_2] \]

Further evidence for this interpretation of the DSC data is the observation that the enthalpy of the melting transition associated with the pure OIPC phase (see Table 4.3) decreases with increasing Na$^+$ concentration until it reaches the eutectic composition of $\sim$20 mol% Na[$N(CN)_2$]. Beyond the eutectic composition, slight decreases in enthalpy of the eutectic transition at 88°C were observed whilst a new melting transition (liquidus) associated with a second solid ($\beta$) phase appeared. The
phase diagram for this binary mixture is very similar in appearance to those of Li[NTf₂]/[C₆mepy][NTf₂] [35] and Na[NTf₂]/[C₂mepy][NTf₂] mixtures [8]. Furthermore, Table 4.3 shows that the enthalpy of the III $\rightarrow$ II transition first decreases and then increases again at 20mol% before decreasing again. It is likely that this peak is overlapped with two closely related transitions where the phases are only slightly different structurally. The asymmetric shape of the peak in the mixed systems also suggests this overlap.

4.3.2. Morphology

SEM was used to analyse the microstructure of the pure [C₆mepy][N(CN)₂] and its mixtures with Na[N(CN)₂] at ambient temperature. Because of the hygroscopic nature of these samples, they were transferred into the vacuum chamber of the SEM without exposure to air; the charging effect was controlled by limiting the applied accelerating voltage to the maximum of 1kV.

Figure 4.10 presents SEM images of the [C₆mepy][N(CN)₂] OIPC and the binary mixtures with up to 20 mol% Na[N(CN)₂] at ambient temperature. The micrographs clearly show the higher plasticity of the pure OIPC, with slip planes (which demonstrate the existence of dislocations) seen in images a) and b). Grain boundaries emanating from grains of different sizes and shapes were also observed in both pure OIPC and in the binary mixture with Na[N(CN)₂], see images b) and c). Precipitates were also observed on the grain surfaces of the binary system. In previous studies, periodic slip planes were consistently observed in different OIPCs and their binary mixtures with Na salts [8]. Small particles appear to be dispersed throughout the matrix of the binary mixture of Naₓ[C₆mepy]₁₋ₓ[N(CN)₂]; these were
similar to those seen in Na$_x$[C$_2$mpyr]$_{1-x}$[NTf$_2$], and differ from the morphology of 1 mol% Li[NTf$_2$] in [C$_2$mpyr][NTf$_2$], in which the grain boundaries appear to be coarsened [11]. In the Na$_x$[C$_2$mpyr]$_{1-x}$[NTf$_2$] binary mixture, the dispersed particles were found to be a second, Na$^+$-rich phase. The phase diagram for Na$_x$[C$_1$mpyr]$_{1-x}$[N(CN)$_2$] (see Figure 4.9) also indicates the formation of a minority Na$^+$-rich phase in these mixtures.

![Micrographs of [C$_1$mpyr]/N(CN)$_2$ OIPCs. a) pure (scale bar 25 µm); b) pure (scale bar 10 µm); c) containing 5 mol% Na[N(CN)$_2$] (scale bar 25 µm) and d) containing 20 mol% Na[N(CN)$_2$] (scale bar 25 µm).](image)

We have previously found a correlation between the existence of such precipitates as shown in Figure 4.10 (i.e. the formation of sodium-rich phase) in Na$^+$-doped [C$_2$mpyr][NTf$_2$] and the transport properties of the constituent ionic species. The
next section of this work will detail the effect of these precipitates on ionic conductivity in relation to the addition of Na[N(CN)₂] and its solubility in [C₁mpyr][N(CN)₂] OIPC.

4.3.3. Ionic conductivity

The ionic conductivities of the pure OIPC [C₁mpyr][N(CN)₂] and mixed Na[N(CN)₂] systems were determined from the resistances at the touchdowns (i.e. real-axis intercepts) of the semicircles in the Nyquist plots. For example, the Nyquist plots of the Na₀.₀₅[C₁mpyr]₀.₉₅[N(CN)₂] system at various temperatures are presented in Figure 4.11.

![Figure 4-11 Nyquist plots of Na₀.₀₅[C₁mpyr]₀.₉₅[N(CN)₂] from 25–40°C, showing an increase in ionic conductivity](image)
Figure 4.12 presents the ionic conductivity of pure OIPC [C_{1mpyr}][N(CN)_{2}] and 5, 15, 20, 30 and 50 mol% Na[N(CN)_{2}] binary systems as a function of temperature (from 25–80°C). In the pure OIPC, the conductivity increased linearly from \(3 \times 10^{-8}\) S.cm\(^{-1}\) at 25°C to \(3 \times 10^{-4}\) S.cm\(^{-1}\) at 80°C within phase II.

In comparison with the pure OIPC, the conductivity in the Na\(_{x}\) [C_{1mpyr}\(_{1-x}\)][N(CN)\(_{2}\)] binary system was not significantly enhanced. This observation is in contrast to the behaviour of the Li\(_{x}\)[C_{1mpyr}\(_{1-x}\)][N(CN)\(_{2}\)] binary system, in which the addition of 2 mol% Li[N(CN)\(_{2}\)] resulted in a two orders of magnitude conductivity jump to \(10^{-2}\) S.cm\(^{-1}\) at \(80°C\) [31]. However, in the lithium containing system, at
80°C there is a significant liquid component since the eutectic temperature is around 30°C. At concentrations above 20 mol% Li[N(CN)2], the conductivity did not show an increase over that of the OIPC for temperatures below 40°C, but a two orders of magnitude increase was seen above 40°C. Again, the previous observation [31, 36-38] that the eutectic temperatures of mixtures of Li salts and pyrrolidinium-based OIPCs typically occur at ~30°C is consistent with an enhancement in conductivity caused by formation of a Li⁺-rich, liquid phase in the material above this temperature. Similarly, in LiI-doped [C1m pyr][N(CN)2], a three orders of magnitude enhancement in conductivity resulted from the increase in the mobility of the matrix and the Li⁺ cation [24] In contrast, the similarity in conductivities of the Na[N(CN)2] binary systems and the base OIPC in the present system suggests that the dispersed particles or Na⁺-rich phase do not contribute to the conduction process and there is likely very little solid solution behaviour of Na⁺ ions in the OIPC lattice; thus conduction in this system arises mostly from the OIPC. This is contrary to the behaviour of the Na[NTf2] binary systems at temperatures above 40°C. Thus, while the enhanced conductivity in the Liₙ[C₁mpyr]₁₋ₙ[N(CN)₂] binary system demonstrated the formation of a solid solution, the dispersed particles here in the Na analogue may not be participating in conduction.

It is interesting to reflect on the solubility of Na salts in OIPCs in contrast to the Li salts in the same systems. Prior work in related ionic liquids, for example, [36] has found that the [NTf₂] anion led to higher solubilities of the inorganic salts within the binary mixtures studied, whilst larger alkyl chain cations within the ionic liquid hindered the solubility of inorganic salts in ionic liquids. On the other hand, when specifically considering Na salt solubility, AlNASHEF et al. [20] found that the solubility of NaCl in ionic liquids containing [NTf₂] was low. Therefore, it is
evident that, solubility depends on the chemical nature of cation and anion. As the concentration of inorganic salt in the ionic liquid is increased, the lack of solubility will be exacerbated until phase separation (either of the pure inorganic salt or a new sodium ion rich precipitate) eventuates. Interestingly, this prior work in Ionic Liquids also suggests that BF$_4$ based salts are likely to be less soluble whereas the [NTf$_2$] type salts are most soluble [27].

Another important factor related to the ionic conductivity is the association of ions as ion pairs or other charged/non-charged aggregates. Na[N(CN)$_2$] has been reported to undergo a range of such transformations [39]. Juergens et al. [39] found that Na[N(CN)$_2$] salt could exist in two different phases, and could also trimerize to form Na$^+$-containing tricyanomelamines ([N(CN)$_2$])$_3^-$ under heating in the solid state, without melting and without forming intermediate aggregates such as dimers ([N(CN)$_2$])$_2^2$. However, given the similarity in ionic conductivity of the OIPC and Na$_x$ [C$_1$mpyr]$_{1-x}$[N(CN)$_2$] mixtures, the effect of trimerization and ionic pair formation is insignificant.

### 4.3.4. IR/Raman spectroscopy

Room temperature FTIR and Raman spectra were recorded to investigate interactions between cations and anions within the pure OIPC [C$_1$mpyr][N(CN)$_2$] and different Na$_x$[C$_1$mpyr]$_{1-x}$[N(CN)$_2$] binary mixtures. The FTIR and Raman spectra of both the pure OIPC and binary mixtures are presented in Figures 4.13(a–d) and 5.15(a–d), respectively. The observed IR and Raman peaks from the [N(CN)$_2$]$^-$ anion and [C$_1$mpyr]$^+$ cation were assigned based on previous studies [24, 39, 40] of the IR and Raman vibrational modes of inorganic salts of dicyanamide.
such as Ba[N(CN)₂], Pb[N(CN)₂] and NH₄[N(CN)₂]. Recent works [8] on a mixture of Na[NTf₂][C2mpyr][NTf₂] (and sources cited therein) and on [C1mpyr][I][24] were used for the assignment of cation C₁mpyr⁺ vibrational modes. The assignments of the vibrational modes are summarized in Table 4.4.

Table 4.4 Assignment of observed Raman and FTIR bands of [C₁mpyr][N(CN)₂] at room temperature based on literature reports [24, 39, 40] for related cations and anions.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>FTIR /cm⁻¹</th>
<th>Raman /cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ (N-CH₃), δ (N-CH₂)</td>
<td>436</td>
<td></td>
</tr>
<tr>
<td>δ₁ N–C≡N</td>
<td>507(w)</td>
<td></td>
</tr>
<tr>
<td>ɣ₁ N–C≡N</td>
<td>523(s)</td>
<td></td>
</tr>
<tr>
<td>ɣ₂ N–C≡N</td>
<td>544(w)</td>
<td></td>
</tr>
<tr>
<td>ν (N-CH₂), ν (N-CH₂)</td>
<td>582 (w)</td>
<td>582(w)</td>
</tr>
<tr>
<td>δ₁ N–C≡N</td>
<td>666 (w)</td>
<td>670</td>
</tr>
<tr>
<td>ν₈ N–C</td>
<td>936</td>
<td>930/903</td>
</tr>
<tr>
<td>ν₈ N–C</td>
<td>1301/1342</td>
<td></td>
</tr>
<tr>
<td>ν (CH₃), ν (CH₂)</td>
<td>1469/1475</td>
<td></td>
</tr>
<tr>
<td>ν₂₈ N–C + ν₈ N–C</td>
<td>2226</td>
<td>2225</td>
</tr>
<tr>
<td>ν₅ C≡N</td>
<td>2899/2979/301</td>
<td>2970/2998</td>
</tr>
<tr>
<td>ν₅ C≡N+ ν₈ N–C</td>
<td>3028</td>
<td>3036</td>
</tr>
</tbody>
</table>

Letters representing the vibrational modes: v –stretching, δ – bending, ɣ – deformation, s - symmetric, as- asymmetric and indicating relative intensities: vw - very weak, w - weak, m - medium, s - strong, vs - very strong

As can be seen from figure 4.13(a–d), the vibrational modes of the pure and binary mixtures are dominated by the [N(CN)₂]⁻ anion deformations and stretching. The ~520 cm⁻¹ and ~544cm⁻¹ vibrational bands observed in the IR spectra correspond to the N(CN)₂ bending in the OIPC and the salt. The shift in the vibrational bands of sodium salt and OIPC indicate different crystallographic environments of the anion. Splitting of the IR spectra resulting from different crystallographic environments were reported for the [N(CN)₂]⁻ ions in M[N(CN)₂]₂ (M = Ba, Pb). In our findings,
split IR peaks (strong peaks with shoulders) were also observed at 507/523, 1254/1301, and 2098/2127 cm\(^{-1}\) in the OIPC, but not in the Na\([N(CN)\text{2}]\) salt. The bands from K\([N(CN)\text{2}]\), previously reported to be at 662, 910, 1316, and 1339 cm\(^{-1}\), are consistent with the 666, 903, 1301 and 1342 cm\(^{-1}\) bands in Na\([N(CN)\text{2}]\). The nitrile stretching region at 2102, 2163, 2190, and 2227 cm\(^{-1}\) is a doublet from the combination of vibrational modes from the asymmetric and symmetric stretching in the anion.

The methyl and ethyl bending and stretching of the \([C_{\text{1mpyr}}]^+\) cation were observed at \(~430\) and \(~582\) cm\(^{-1}\), respectively, consistent with previous reports [9, 24]. Some of the pyrrolidinium ring modes observed within the 880–1050 cm\(^{-1}\) region in \([C_{\text{2mpyr}}][\text{NTf}_2]\) and \([C_{\text{2mpyr}}][\text{BF}_4]\) were also observed in this OIPC.
Figure 4-13  FTIR spectra of pure and mixed materials at different frequencies a) 400 – 700cm\(^{-1}\), b) 1200–1600cm\(^{-1}\) and c) 1900–2400cm\(^{-1}\) d) 2850–3250cm\(^{-1}\) for \([C\text{mpyr}][N(CN)_{2}]\) and binary mixtures with Na\([N(CN)_{2}]\) salt

The FTIR spectral regions of 475-560cm\(^{-1}\) and 1220-1375cm\(^{-1}\) were deconvoluted to the mixtures of Lorentzian and Gaussian line shapes to analyze the effect of mixing with a sodium salt on the vibration of anion and cation species. The whereabouts of the peaks were identified by the peak-picking procedure of OPUS software. The variations in the peak positions are reported for the comparison. The \(\delta_{\text{as}}\) N–C≡N (505cm\(^{-1}\)) band in C\text{mpyr} [N(CN)\(_{2}\)] OIPC is blue-shifted by 2cm\(^{-1}\) upon addition of the 20%Na salt towards Na\([N(CN)_{2}]\) band at 508cm\(^{-1}\). The 523cm\(^{-1}\) band (\(\gamma_{\text{as}}\) N–C≡N) is unaffected by the mixture of Na salt. The unassigned 518cm\(^{-1}\) in the OIPC is red shifted by about 3cm\(^{-1}\) towards the Na salt peak at 515cm\(^{-1}\) upon mixing with 20%Na and the same peak disappears with the addition of 5%Na salt. Similarly, the unassigned 526cm\(^{-1}\) band is red-shifted with the addition of the salt. Evidences show that the different chemical environment within the anion can cause the shift in the spectral peak. The appearance of 544cm\(^{-1}\) in the 20%Na mixture clearly
correlates with the co-ordination of Na cation via the deformation of N–C≡N bonds. This indicates the presence of Na coordination in the system and could be the Na rich phase.

In the region 1220-1375cm⁻¹, the 1248, 1278 and 1300cm⁻¹ bands were unaffected and appear in the mixed systems. However, there were new weak bands emerge in the 20%Na mixed system at 1235 and 1341cm⁻¹ is consistent with the presence of Na rich phase. The 1317 cm⁻¹ band in the OIPC was shifted to 1321 cm⁻¹ in the 20% Na system. Figures and tables below (figure 4.14a-c) show the fitted curves and the peaks evaluated from the fits to selected regions.

a) Fitted FTIR spectrum for 0% Na (pure OIPC) 475 – 560cm⁻¹

![Fitted FTIR spectrum for 0% Na](image)

b) Fitted FTIR spectrum for 20% Na (475–560 cm⁻¹)
c) Fitted FTIR spectrum for 0% Na (1220–1375 cm⁻¹)
d) Fitted FTIR spectrum for 20% Na (1220–1375 cm$^{-1}$)

![Deconvoluted FTIR spectrum](image)

Figure 4-14 Deconvoluted FTIR spectrum for a) 0% Na (pure OIPC) in 475–560 cm$^{-1}$, b) 20% Na (475–560 cm$^{-1}$), c) 0% Na (pure OIPC) in 1220–1375 cm$^{-1}$ and d) 20% Na in 1220–1375 cm$^{-1}$ spectral regions

Table 4.5 Summary of the fit parameters in the FTIR region of 475–560 cm$^{-1}$

<table>
<thead>
<tr>
<th>NaN(CN)$_2$ / % mol</th>
<th>Peak position / cm$^{-1}$</th>
<th>Normalised intensity</th>
<th>Width / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>505</td>
<td>0.08</td>
<td>22.0</td>
</tr>
<tr>
<td></td>
<td>518</td>
<td>0.04</td>
<td>25.5</td>
</tr>
<tr>
<td></td>
<td>523</td>
<td>0.14</td>
<td>11.1</td>
</tr>
<tr>
<td></td>
<td>529</td>
<td>0.04</td>
<td>24.7</td>
</tr>
<tr>
<td>5</td>
<td>507</td>
<td>0.10</td>
<td>22.7</td>
</tr>
<tr>
<td></td>
<td>523</td>
<td>0.18</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>530</td>
<td>0.04</td>
<td>21.9</td>
</tr>
<tr>
<td>20</td>
<td>507</td>
<td>0.09</td>
<td>26.7</td>
</tr>
<tr>
<td></td>
<td>515</td>
<td>0.08</td>
<td>21.6</td>
</tr>
<tr>
<td></td>
<td>523</td>
<td>0.17</td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>0.03</td>
<td>23.7</td>
</tr>
<tr>
<td>NaN(CN)$_2$ / % mol</td>
<td>Peak position / cm$^{-1}$</td>
<td>Normalised intensity</td>
<td>Width / cm$^{-1}$</td>
</tr>
<tr>
<td>--------------------</td>
<td>--------------------------</td>
<td>---------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>0</td>
<td>1248</td>
<td>0.04</td>
<td>26.3</td>
</tr>
<tr>
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<tr>
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<td>0.31</td>
<td>22.0</td>
</tr>
<tr>
<td></td>
<td>1317</td>
<td>0.05</td>
<td>21.1</td>
</tr>
<tr>
<td>5</td>
<td>1248</td>
<td>0.04</td>
<td>25.6</td>
</tr>
<tr>
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<td>1279</td>
<td>0.08</td>
<td>25.5</td>
</tr>
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<td>0.30</td>
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<td>0.04</td>
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<td>1276</td>
<td>0.05</td>
<td>21.1</td>
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<tr>
<td></td>
<td>1300</td>
<td>0.29</td>
<td>23.3</td>
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<td></td>
<td>1321</td>
<td>0.08</td>
<td>29.4</td>
</tr>
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<td></td>
<td>1341</td>
<td>0.04</td>
<td>19.8</td>
</tr>
<tr>
<td>100</td>
<td>508</td>
<td>0.08</td>
<td>26.0</td>
</tr>
<tr>
<td></td>
<td>515</td>
<td>0.13</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>526</td>
<td>0.14</td>
<td>15.5</td>
</tr>
<tr>
<td></td>
<td>544</td>
<td>0.05</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Table 4.6 Summary of the fit parameters in the FTIR region of 1220-1375cm$^{-1}$
As shown in the Raman spectra (Figure 4.15a-d) the binary mixtures of different compositions undergo changes in intensity compared to pure plastic crystal [C1mpyr][N(CN)2]. An increase in intensity was observed in the bands at ~ 582, 903, 2195, 2970 cm\(^{-1}\) which were assigned to the stretching of \(\nu\) (N-CH\(_3\)), \(\nu\) (N-CH\(_2\)) in the [C1mpyr]\(^+\) cation N–C and C≡N bonds in the [N(CN)\(_2\)]\(^-\) anion. This observation might be due to structural changes resulting from orientational/rotational disorder and/or new chemical composition yet to be confirmed and investigated further below using solid state NMR. In our previous study [8] we have shown that when different phases are co-existing in the binary mixtures new Raman peaks are observed. For example, in the Na\(_x\) [C2mpyr]\(_{1-x}\) [NTf\(_2\)] binary mixtures we observed different Raman bands which correlated to different structures observed in the synchrotron X-ray diffraction studies. The frequency shift observed in the Raman spectra of Na[N(CN)\(_2\)] here, compared to the pure and binary mixtures, also indicate different anionic environments. The presence of an additional peak in the 20% Na[N(CN)\(_2\)] mixture at a frequency of ~2225 cm\(^{-1}\) provides some evidence of the existence of an additional phase, likely involving a different co-ordination of the dicyanamide anion with the sodium, however the spectra do not suggest simple addition of pure Na[N(CN)2] with pure OIPC components, since other bands in the sodium salt are completely absent in the Raman spectra in addition to others being shifted relative to the pure components. Certainly the vibrational spectroscopy associated with the dicyanamide anion suggests the presence of a new phase, although the bands associated primarily with the organic cation are not significantly perturbed.
Figure 4-15  Raman spectra of [Cimpyr][N(CN)2] and binary mixtures with Na[N(CN)2] salt. a) 500–780 cm\(^{-1}\), b) 870–1100 cm\(^{-1}\), c) 2100–2300 cm\(^{-1}\) and d) 2800–3200 cm\(^{-1}\)
4.3.5. Solid state NMR

Room temperature solid-state NMR was used to study the structural and dynamic behavior in the pure OIPC and Na salt mixed samples. The OIPC and samples of Na\(^+\) ion content were probed through NMR active nuclei: \(^1\)H to study the [C\(_{1}\)mpyr]\(^+\) cation, and \(^{23}\)Na for the Na\(^+\) in the mixed system. Furthermore, \(^{13}\)C CPMAS spectra were used to study the local environments of the cation in the OIPC and binary mixtures.

The proton NMR spectra (Figure 4.16) show very small amounts of water at 4.75 ppm (as it is very difficult to keep these samples completely dry when handling to pack the NMR rotor, and slight variations in terms of different line widths for mixtures of varying Na\(^+\) content. The narrow lines in the proton spectra indicate higher rotational disorder of the molecules, which averages the dipolar interactions present in solids. This observation is consistent with the weakening of the peaks in the Raman spectra at \(\sim582\text{cm}^{-1}\) (assigned to the CH\(_2\) and CH\(_3\) stretching vibration in the [C\(_{1}\)mpyr]\(^+\) cation) upon addition of salt. The \(^{13}\)C CPMAS spectrum of Na[N(CN)\(_2\)] (Figure 4.17) did not show any cross-polarization transfer, this is because there were no protons in the Na[N(CN)\(_2\)] to excite polarization and thus no [N(CN)\(_2\)]\(^-\) anion carbon signal detected.
Figure 4-16  $^1$H RT - MAS solid-state NMR spectra of pure Na[$\text{N(CN)}_2$] (blue) and mixtures Na$_{0.05}$[C$_{\text{mpyr}}$]$_{0.95}$[$\text{N(CN)}_2$] (red) and Na$_{0.2}$[C$_{\text{mpyr}}$]$_{0.8}$[$\text{N(CN)}_2$] (green).

Figure 4-17  $^{13}$C RT - CP MAS solid-state NMR spectra of pure Na[$\text{N(CN)}_2$] (blue) and Na$_{0.05}$[C$_{\text{mpyr}}$]$_{0.95}$[$\text{N(CN)}_2$] (red) and Na$_{0.2}$[C$_{\text{mpyr}}$]$_{0.8}$[$\text{N(CN)}_2$] (green) mixtures.
Figure 4-18 $^{23}$Na RT-static (upper) and MAS (lower) solid-state NMR spectra of pure Na[N(CN)$_2$] (blue) and Na$_{0.05}$[C$_{1}$mpyr]$_{0.95}$[N(CN)$_2$] (red) and Na$_{0.2}$[C$_{1}$mpyr]$_{0.8}$[N(CN)$_2$] (green) mixtures.
Differences are seen in the $^{23}$Na room temperature static NMR spectra (see Figure 4.18). The spectrum of Na[N(CN)$_2$] shows a single signal, indicating a unique environment. For the mixtures of Na$^+$ with the OIPC, two signals (with shoulders) show differing environments in the materials. Investigation with $^{23}$Na MAS NMR also showed more complicated signal(s); at 20 mol% Na$^+$ sample had a single, narrow signal, similar to that seen for the pure sodium salt; in contrast, two quadrupolar signals (which can be attributed to two different Na$^+$ sites with significantly different chemical environments) were seen for the mixture containing 5% Na$^+$. Understanding this unusual trend will require further studies on the structure of the mixtures. Thus, future work will use VT MAS and X-ray diffraction and VT Raman techniques are required to further understand dynamic and structural properties in these materials.

4.3. Conclusions

4.4.1. Na[BF$_4$]/[C$_2$mpyr][BF$_4$] binary mixtures

The effect of mixing of Na[BF$_4$] with the OIPC [C$_2$mpyr][BF$_4$] on thermal, structural and transport properties has been investigated using different experimental techniques: DSC, conductivity, SEM, FTIR/ Raman and solid state NMR. In the DSC traces, the solid-solid transitions were not affected by the addition of Na[BF$_4$] up to the temperature of 140 °C in phase I. We could not find any evidence that the solid solution is formed in the mixtures up to 20 mol % of Na$^+$ content. The SEM micrographs showed the precipitates which occupy the inter-grain surface of the OIPC at low level of concentration and embedded as aggregates within the grain boundaries at high level of concentration, may be an additional Na
rich phase as observed in Na[NTf2] / [C2mpyr][NTf2] mixtures. The existence of this new phase is yet to be elucidated by XRD.

The conductivity of the mixture of Na[BF4] and [C2mpyr][BF4] did not show a dramatic increase in lower temperature phases with increasing the Na+ content. A slight increase in conductivity for 4 mol % Na[BF4]/[C2mpyr][BF4] may be mainly due to intra-granular ionic transport in phase II and disordered grains in phase I. With the increased level of concentration in the mixing with Na[BF4], the aggregations /dissociations within the binary system were responsible for the blocking of the grain boundaries, thereby reducing the conductivity. Interestingly, the DSC data show that the enthalpy of transition for III→II and II→I are higher for 10% NaBF4, which suggests more ordering and may be responsible for the lower conductivity.

### 4.4.2. Na[N(CN)2]/ [C1mpyr][N(CN)2] binary mixtures

In this work, we investigated thermal, dynamic and spectroscopic properties of the OIPC [C1mpyr][N(CN)2] mixed with the sodium salt Na[N(CN)2]. We employed DSC to study the thermal properties and phase behavior. The solid-solid transition from phase II to I occurs at ~89°C, as does a eutectic point at 20% Na+ content. The microstructure of the mixed system showed regions where precipitates occur, as was previously seen for binary mixtures of Na[NTf2] with [C2mpyr][NTf2] OIPC. In the latter case, the precipitates were suggested to be a Na-rich second phase. By analogy, it can be deduced that a Na-rich second phase exists. Further evidence of this is a Raman peak at 2225cm⁻¹, which implies increasing coordination of the anion with increasing Na+ content. At this stage, it is difficult to determine the nature of this second phase without further evidence from X-ray diffraction and VT-NMR studies. In the same OIPC mixed with Li[N(CN)2], enhanced conductivity
was observed and a eutectic point occurred at ~30°C and 33% salt. In the present system, the line narrowing in $^1$H and $^{23}$Na NMR spectra and $^{23}$Na line shape changes suggest that both cations may be mobile. However, the addition of sodium cations did not lead to an increased conductivity in these materials, since the conductivities of the mixtures and the pure OIPC are similar and so we cannot yet determine if in fact the Na ion is contributing to the conduction in these systems. Further work is required to determine the mobility of the Na ion, especially in the mixtures with higher Na content.

4.4. References


CHAPTER 5. Molecular dynamics simulation of OIPCs

5.1. Overview

Pyrrolidinium and ammonium containing OIPCs were extensively investigated either for their plastic behaviour or as ionic liquids in the last two decades. The MacFarlane and Forsyth groups [1-19] have extensively reported and studied different pyrrolidinium cations with different anions. [C2mpyr][NTf2] (see Figure 1.2, in chapter 1) has been of interest for its rich solid-solid phase transitions and being one of the original OIPCs reported with relatively high solid state conductivity [1]. Henderson et al.[20] reported the crystal structure of [C2mpyr][NTf2] using x-ray diffraction technique in two different phases at -120°C and -60°C as ordered (Phase IV) and disordered (Phase III). They found an ordered-disordered ionic orientation transition from phase IV to Phase III. The structures of both the cation and anion sublattices are less symmetric in the higher temperature phases. It is shown in both phases III and IV that the NTf2- anions adopt a C2 conformation (trans) [21] while the [C2mpyr] + cations adopt an envelope (Cs) conformation.

Numerous previous studies have also shown that the pure sample of [C2mpyr][NTf2] undergoes several solid-solid transitions [19, 20, 22-24]. Thus, the transition from ordered phase IV to disordered phase III was observed at -85 °C, followed by two solid-solid phase transitions at 17 °C and 45 °C, respectively, and a melting transition at 91°C. The melting curve (peak) of the material is characterized by a sharp narrow peak, which indicates much faster transformation rate than the
other solid-solid transitions. For example the transition peak from phase IV- III is broader than the melting peak.

Prior work has shown that [C$_2$mpyr][NTf$_2$] has significant ionic diffusivity even in the solid state, particularly in the high temperature phases [25]. This leads to a high ionic conductivity of this material, which is enhanced upon doping (or mixing) with a second component, such as Li[NTf$_2$] [19, 26]. Recently, the mixed [C$_2$mpyr][NTf$_2$] / Li[NTf$_2$] solid electrolyte has shown promising behaviour in the Li-ion batteries [27]. In general, experimental studies have established that, the addition of Li$^+$ and Na$^+$ into an OIPC can enhance its transport properties, and hence the ionic conductivity of the mixture. The enhanced ionic conductivity in these solid OIPCs and the doped complexes qualify them for solid state electrolyte to be used in electrochemical cells. Despite the potential application prospect of this material, our understanding towards the structure, phase behaviour and transport mechanisms at the atomic level is still in its infancy [17]. The fundamental understanding of these ionic motions thus requires a thorough and careful investigation at an atomic level.

Molecular dynamics (MD) simulation provides detailed information about time evolution or motions of molecules by solving Newton’s laws of motion. It is the best available method to study dynamical processes in molecules at the atomic level of detail. The size and time-scales of MD simulation become advanced with the speed of contemporary computers, however, despite the advancement of the computational technology with each passing year, there are still limitations that need to be considered with the use of MD simulations for studying complex
systems. The results from MD simulation mainly depend on the choice of accurate
molecular model, force field, ensembles and the time of simulation.

It is often used to extract and predict the results for the properties of a material in
order to compare with the experiment. This in turn helps to understand and interpret
observations from the experiments. In the case of OIPCs there were several
experimental results which were not validated and well understood, mainly in the
area of the structural and dynamical properties. Thus, the use of MD simulation is
vital to validate these experimental observations and helps to understand those
observations by correlating details on microscopic scale (in atomic and molecular
level) to the macroscopic properties.

In principle, thermodynamic, structural, mechanical, and dynamical properties of a
system of particles can be obtained from ensemble averages, fluctuations,
distribution functions and correlation functions of MD simulations. An
understanding on the structural properties such as crystal structure, phase change,
radial distribution function (RDF), defects (vacancies and interstitials, dislocations,
grain boundaries) can be made possible. From thermodynamic point of view, the
equation of state, heat capacities, thermal expansion etc. can be obtained from the
averages and fluctuations. Mechanical properties such as elastic constants, elastic
and plastic deformation and cohesive and shear strength etc. can be calculated.
Phonon dispersion curves, and vibrational frequency spectra can be obtained from
the Fourier transform of perturbation of the harmonic terms in the potential
function. Dynamics and transport properties such as rotational or orientation
relaxation times, diffusion coefficients, viscosity, conductivity etc. can be extracted
from the time correlation functions.
In recent years this method has been widely adopted to study the structural and dynamical behavior of many ionic species in depth [28-32]. Such relevant molecular dynamics simulation studies include the work in references [28-30] on pure [Me₄N][N(CN)₂] OIPC and on Li⁺ doped [Me₄N][N(CN)₂] OIPC [31] as well as the numerous MD simulations work published on the ionic liquids (ILs) [33-40]. To our knowledge, there have been only few molecular dynamics studies in the area of OIPCs [22, 29, 30], namely N,N,N,N-tetramethylammonium dicyanamide and diethyl(methyl)(isobutyl)-phosphonium hexafluorophosphate plastic crystals have been carried out, and none are in relation to the OIPC [C₂mpyr][NTf₂] phases and a Na⁺ doped tetramethylammonium dicyanamide [Me₄N][N(CN)₂] OIPC system. Therefore, molecular dynamics simulation studies conducted on these materials contributes towards full understanding of the structure and dynamic properties of the OIPCs and the design of novel solid-state electrolytes.

In this chapter, the structural and dynamical properties of N-ethyl-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide–[C₂mpyr][NTf₂] OIPC and [Me₄N][N(CN)₂] OIPC doped with Na[N(CN)₂] salt are presented. For the [C₂mpyr][NTf₂] OIPC, the lattice parameters (crystal structure) at different phases/temperatures were discussed along with the radial distribution function (RDF) to elucidate the structural properties. The dihedral distribution, the rotational autocorrelation functions and the self-diffusion coefficients of the ionic species were scanned to understand the dynamical properties of this material. Furthermore, the effect of vacancies on the dynamical properties was also studied at 333K, in phase I of the OIPC, in this work. The MD theoretical results were compared with the synchrotron X-ray, NMR and spectroscopic experimental data. In the MD work
related to the [Me₄N][N(CN)₂] OIPC doped with Na[N(CN)₂] salt, the structural properties - radial distribution function (RDF) and the dynamical properties - the rotational autocorrelation functions and the self-diffusion coefficients of the ionic species were studied.

5.2. Simulation Procedures

5.2.1. [C₂mpyr][NTf₂] OIPC

The starting structure of [C₂mpyr][NTf₂] for the MD simulation was the crystalline structure obtained from the experimental work at 153K [20]. The structure in the higher temperature phases above 213 K has been reported [41]. Therefore, we include the unit cell parameters determined from the synchrotron powder XRD at 273K (phase III), 303K (phase II) and 328K (phase I) for the purpose of the validation of our MD results with the x-ray diffraction data. In all simulations, 512 ion pairs consisting of 19968 atoms in the system (64 unit cells) were used to represent the monoclinic phases of the crystal. Each unit cell in the monoclinic phase was composed of 8 ion pairs. Periodic boundary conditions were set fixed in all simulations to wrap all the coordinates into the box of dimensions of 52.4, 57.82, 67.95Å for monoclinic phase.

The force field in this work is in the CHARMM format (The Chemistry at HARvard Macromolecular Mechanics) [42-44]. The parameters for the force field of the anion and cation are obtained from the literature [36, 38, 39, 45], which were proved to provide consistent prediction of structures, thermodynamic and transport properties.
of related ionic liquids [33-35, 38-40]. The detailed force field parameters are given in the appendix A.II.

The description of the CHARMM force field is given in equation 5.1. The first three terms describe the bonded interactions including bond stretching, angle bending, and torsion angle motions; the last two terms describe non-bonded electrostatic potential and van-der-Waals interaction, respectively

\[
V = \sum_{\text{bonds}} K_l (l - l_0)^2 + \sum_{\text{angles}} K_\theta (\theta - \theta_0)^2 + \sum_{\text{torsions}} K_\phi \left[ 1 + \cos \left( n\phi - \delta \right) \right] + \sum_{ij} \frac{q_i q_j}{4\pi\epsilon r_{ij}}
\]

\[
\sum_{\text{vdw}} \varepsilon_{ij} \left( \frac{r_{ij}^{\min}}{r_{ij}} \right)^{12} - \left( \frac{r_{ij}^{\min}}{r_{ij}} \right)^{6}
\]

\text{Equation 5-1}

The van der Waal’s interaction is taken a Lennard–Jones (LJ) potential format composing a sum of repulsive and attractive potential terms, which are a function of the distance \(r_{ij}\) between two atoms \(i\) and \(j\). The cutoff distance \(r_c\) of 12Å and the switching distance \(r_s\) of 10Å had been applied to the Lennard-Jones interactions. For the LJ interaction with different atom types the use of combining rules is mandatory. As an integral part of a force field, either the Geometric or Lorentz-Berthelot combining rules can be used. Lorentz-Berthelot combination rules were adopted [46] in this work. Long range electrostatic forces were treated using the Ewald summation method [47, 48]. The bond lengths were constrained using the SHAKE [49] with Verlet algorithm [50, 51] allowed to run a maximum of 500 iterations within the desired accuracy of \(10^{-6}\) Å. All MD simulations were conducted using DLPOLY package [52, 53]. The Nosé-Hoover thermostat [54-56] was employed to control temperatures and the Melchionna modification of the Hoover
algorithm [57] was applied to control the pressure as it allows both the cell size and the cell shape to change. The desired pressure was set to 1 atm with the oscillation and decay times of the barostat piston each 0.5 ps each respectively.

The conjugate gradients method was applied to minimize and relax the system. Heat bath was coupled to the system to rescale the velocities in the system to be set to the desired temperature; thereby allowing the equilibration calculation for 1.0 ns with a timestep of 2 fs at temperatures of 153, 213, 273, 303, 333, 363 and 383 K, and followed by up to 5 ns NPT data production. The NPT ensemble was utilized to collect data with a time step of 2 fs. The trajectory file was recorded every 1 ps. The calculation starts with a monoclinic crystalline structure [20] at 153 K. Similarly, the NST ensemble was employed to collect data with a time step of 2 fs at 273 and 383 K to investigate the changes in the box shape and size.

5.2.2. [Me₄N][N(CN)₂] OIPC Doped with Na[N(CN)₂] Salt

In this section, the effect of the doping sodium dicyanamide Na[N(CN)₂] salt on the structure and dynamics of tetramethylammonium dicyanamide [Me₄N][N(CN)₂] OIPC shown in Figure 5.1 has been investigated through molecular dynamics simulations. MD simulation of the [Me₄N][N(CN)₂] doped with Na[N(CN)₂] is of significant importance due to the availability of the crystal structure; compare with the Li doped system and better understand the structure and dynamics of the N(CN)₂ and Na ionic species in the mixtures.
In the MD simulation of this material, the DL_POLY 2.2 Classic software package was used for all MD simulations. The force field parameters for [Me₄N][N(CN)₂] OIPC and Na⁺ ion were extracted from the previous studies [28, 31] and CHARMM files [42] which is given in appendix A.III. The force field used in this work takes a CHARMM format, as described in a previous section of this chapter. The simulation box was constructed to a 4 x 2 x 2 super-cell consisting 128 ion pairs with a total of 2736 and 2576 atoms in the concentration of 5% and 15% [Me₄N]⁺ cations were randomly replaced with Na⁺ cations for the investigation. MD simulations were conducted using an NPT-ensemble with Hoover thermostat/barostat for temperature control. The system was equilibrated for 1ns, followed by a production run of 3 ns which is enough to study the both structure and dynamics based on past experiences on the this material, with a timestep of 2 fs.
5.3. Structural Properties of [C$_2$mpyr][NTf$_2$] OIPC

5.3.1. Unit Cell Parameters

Table 5.1 compares the simulation results of the crystalline structure of a unit cell with the X-ray diffraction experimental results in an ordered monoclinic phase IV at 153 K. The predicted unit cell parameters, volume and density were in excellent agreement with the experiment results.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Exp.</th>
<th>Sim in NST</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Å)</td>
<td>13.099</td>
<td>13.096±0.017</td>
</tr>
<tr>
<td>B (Å)</td>
<td>14.454</td>
<td>14.451±0.019</td>
</tr>
<tr>
<td>C (Å)</td>
<td>16.987</td>
<td>16.983±0.023</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>97.546</td>
<td>97.546</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>3188.5</td>
<td>3186.25±3.19</td>
</tr>
<tr>
<td>ρ (g cm$^{-3}$)</td>
<td>1.643</td>
<td>1.644±0.002</td>
</tr>
</tbody>
</table>

The equilibrated structure of monoclinic phase at 153K [20] was used and rescaled to the higher temperature for further simulations for comparisons in the phases III (273K), phase II (303K) and I (328K). The simulation results were compared with our recent synchrotron powder XRD data [41]. The simulated unit cell parameter
agrees well with the experimental result at 153K (see table 5.1). The changes in $\beta$ from $97.546^\circ$ to $(90.012\pm0.325)^\circ$ while $\alpha = (89.942\pm0.246)^\circ$ and $\gamma = (90.116\pm0.807)^\circ$ in the NST simulation at 383K clearly shows the change in shape of the simulation box with increasing temperature. The experimental data in fact suggests that the phase III is triclinic $P-\overline{1}$, while the phase II and I are monoclinic $CC$ and Orthorhombic $I\overline{2}22$ respectively. This makes simulation of this material very challenging.

5.3.2. Volume Changes

Figure 5.2. shows that the simulation volume changes as a function of temperature / phase. The available experimental data [20] are also given as a comparison in Table 5.1. The volume increases (density decreases) with the increase in temperature over the ranges covered in the simulation. As shown in Table 5.2, the simulation volume (density) per ion pair of the OIPC system increased (decreased) by 7.1% while the experimental volume increased by the 10.7% as temperature increased from 153K to 333K, which is within the margin of the experimental error. In the temperature range of our investigation there was no discontinuity identified in the unit cell parameters apart from the increase (decrease) in volume (density). As expected, the OIPC undergoes change from ordered to disordered phase with increasing temperature.
Figure 5-2 Volume of the simulated box as a function of temperature, starting from the crystallographic data of monoclinic phase at 153K

Table 5-2 Comparison of simulated and experimental occupied volumes per pair of ions at different temperatures

<table>
<thead>
<tr>
<th>T / K</th>
<th>Experiment / Å³</th>
<th>Simulation / Å³</th>
<th>Difference / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>153</td>
<td>398.6</td>
<td>398.3</td>
<td>0.07</td>
</tr>
<tr>
<td>213</td>
<td>411.6</td>
<td>408.4</td>
<td>0.79</td>
</tr>
<tr>
<td>273</td>
<td>422.4</td>
<td>419.7</td>
<td>0.64</td>
</tr>
<tr>
<td>303</td>
<td>431.6</td>
<td>423.9</td>
<td>1.81</td>
</tr>
<tr>
<td>333*</td>
<td>445.5</td>
<td>429</td>
<td>3.71</td>
</tr>
</tbody>
</table>

* Experimental volume determined at 328K
5.3.3. Radial Distribution Function (RDF) and the Co-ordination Number

The RDFs for atomic pair of the central nitrogens of the cation N1 and the anion N3 are generated in Figure 5.3 with their corresponding co-ordination numbers. The heights and breadth of the peaks in the RDF provide ample information on the lattice structure. At short distances the RDF is zero. This indicates the repulsive force makes the atoms not to approach each other. At 153 K, the appearance of sharp peaks representing different shells occur at around 6.9Å, 8.3Å (split at 8.9Å), 10.2Å (shoulder at 11.1 Å), 14.4Å for cation-cation ([C2mpyr]^+-[C2mpyr]^+) as shown in Figure 5.3a, 4.6Å (shoulder at 4.1Å), 5.7Å (split at 6.1Å), 7.9Å, 12.0Å and 13.6Å for cation-anion ([C2mpyr]^+-[NTf2]^-) as shown in Figure 5.3c, and at 5.9Å, 7.6Å (shoulder at 8.2 Å), 10.1Å, 11.5Å and 14.5Å for anion-anion ([NTf2]^-[NTf2]^+) as shown in Figure 5.3e. The appearance of sharp peaks indicates that the atoms pack with a high degree of ordering at both short and long ranges due to strong confinement of atoms in their positions at lower temperatures. The presence of the shoulder and split peak is attributed to the two central nitrogens in the asymmetrical unit of the ionic species. The split peaks between 7 and 9 Å start to merge from 273 K as shown in Figure 5.3a. In general, at low temperatures, the radial distribution functions are characterised by sharp peaks even beyond the first two solvation shells. At high temperatures, the RDF display broad, structure-less peaks in the furthest solvation shells.
Figure 5-3 The plots of the radial distribution function (RDF) as a function of interatomic distance $r$ of the central nitrogens of the cation $N_1$ and the anion $N_3$ with their corresponding co-ordination number in $a$, $b$ - cation-cation; $c$, $d$ - cation-anion and $e$, $f$ - anion-anion interactions obtained at different temperatures from NPT simulation.
The cation-cation RDF is characterized by sharp peaks at 153K and 213K. The peaks broaden at 273K which shows that the system starts to lose its short-range order. It appears that, from 153-273K, 3 cations exist as first nearest cation-cation neighbours within 6-8 Å while the number decrease to 2 for temperatures above 333K and is more smeared over 6-10 Å. In total up to 10 cations exist within a 15 Å radius of any given cation. Moreover, in the cation-cation interaction there is no significant change observed at 213K except spectral shift of 0.2Å in the outer solvation shell. This might be the due to the volume expansion that the system starts to undergo. However, the RDF undergoes significant changes in height, width and peak position as temperature increases above 273K and at all temperatures above 273K, the height of the RDF decreases and the peak position shifts as it is immensely broadened.

In the cation–anion RDF at the temperature of 153K, the peaks are sharper and narrower than at 213K. The 213K broadening peaks herald the onset of disorder as also occurs for 273K. The temperatures above 333K show a more significant change in the structure; up to 6 anions exist in the first coordination sphere of the cation within 4-7 Å for all temperatures. Up to 12 anions exist next to a cation within 15 Å. For the next higher temperature, at 213K, the RDF of the first shell becomes broadened without considerable change in height or shift of peak position for cation-anion species. The disappearance of double peaks and the broadening of the spectra herald the beginning of disorder in the system. As temperature increases, the peaks tend to be broad due to the occurrence of thermal motion possibly reflecting the onset of rotations.
At 153K and 213K the anion-anion RDF is characterized by sharper and narrower peaks than at 273K similar to the trend in cation-cation RDF. The shift in the second peak at 273K shows different anion-anion restructuring. The temperatures above 333K show the short range disorder that accompanies an apparently rather new structural rearrangement. Only up to 2 anions exist next to each other within 6-8 Å for all temperatures. Up to 10 anions exist next to a cation within 15 Å. The second solvation peaks appear to split and broaden and occur at around 7.5Å at lower temperatures in the cation-cation and anion-anion interactions. The split can be the result of superposition of two separate peaks which could be resolved to two separate peaks one for the cation-cations and the other for anion-anions next to each other. These splits may have been facilitated by induced sequential ordering from cation-anion pairs and the weak ordering due to long range coulombic interactions [29, 30].

The sharp peaks observed in the lower temperature phase IV at 153K is consistent with the x-ray studies [20] and thus both the cations and anions in the OIPC are ordered. It had also been reported that the cations and anions undergo disorder in phase III at 213K and the crystal structure is triclinic. In our simulation there was clear indication that the cation-anion RDF at 213K undergoes broadening which is consistent with a major change. However, at all temperatures at 273K and above, the RDF decreases in height and the peak position shifts while immensely broadened in all cation-cation, cation-anion and anion-anion RDFs indicate the OIPC is more disordered in phase II and I agrees well with several phase changes of differing lattice structure observed from the synchrotron XRD experiment. It had been reported that the vacancy number and size increases substantially with temperature for this OIPC from the Positron Annihilation Lifetime Spectroscopy.
(PALS) and the link between the vacancies and rotational/orientational disorder in plastic crystal phases of \([\text{C}_{2}\text{mpyr}]\text{[NTf}_2]\) was established [58]. The difference observed at 213K and 273K both in phase III is actually due to the increased rotational motions of ions, which would be explained in a later section. Further broadening and disappearance of RDF peaks at 303K in phase II and 333K in phase I correlates with the high symmetry lattice structures monoclinic \(CC\) and Orthorhombic \(I222\) correlates with the SXRD observation in which split peaks appear to merge and many of the weaker peaks disappear at higher temperatures and with the shift in Bragg peaks towards the lower 20 attributed to changes in the crystalline phases and/or crystal symmetry [41]. It had been further suggested that shifts in Bragg peaks and broadening of the peaks are caused by defects such as internal stresses, stacking faults, twin boundaries, grain boundaries and chemical heterogeneities [59] which may have resulted in the increased plasticity and hence enhanced conductivity in the OIPC in phases II and I. Thus, in the phase II and I of this OIPC, the defects continue to expand with the increase in temperature agrees well with the disappearance of long-range order.

![Graph](image1.png)

![Graph](image2.png)
Upon addition of 1% and 2% vacancies on the OIPC at 333K (phase I), there was no change observed in all cation-cation, cation-anion and anion-anion RDFs (see Figure 5.4(a,c,e)) and the co-ordination number (see Figure 5.4(b,d,f)). This may be attributed to the insignificant increase in size and concentration of defects at this temperature that did not affect the crystal restructuring and the plasticity in the OIPC. Further study is required to conclude the effect of vacancies on the RDF. This is in contrast to the behavior recently reported [32] for the phosphonium PF$_6$ OIPC system where the addition of vacancies had significant effect on the dynamics and structure in that OIPC.

**Figure 5-4** Variation of radial distribution function (RDF) as a function of vacancy and their corresponding co-ordination number in a, b - cation-cation ; c, d - cation-anion and e, f - anion-anion interactions.
5.4. Dynamical properties of [C$_2$mpyr][NTf$_2$] OIPC

5.4.1. Brief overview

As discussed in the previous section, the evolution of the dynamics of the ionic species in each phase involves the onset of rotational motions and lattice transformations and restructuring which is predominant in this OIPC. Thus, the investigation of spectroscopic and transport properties on the material using the Raman/FTIR spectroscopy and nuclear magnetic resonance (NMR) techniques is very essential to further understand the dihedral distribution and the rotational dynamics from the simulation in [C$_2$mpyr] [NTf$_2$] OIPC with and without the inclusion of vacancy. To this end we employ the power of MD and FTIR/Raman techniques in the following sections mainly in the understanding of conformational and rotational studies of the cation and the anion.

5.4.2. Dihedral Distribution in [NTf$_2$]$^-$ Anion and [C$_2$mpyr]$^+$ Cation

In a previous report [21], it is shown that the NTf$_2^-$ anions exist in two pairs of asymmetric units in both low temperature phases IV and III, and adopt a C$_2$ trans conformation while [C$_2$mpyr]$^+$ cations adopt an envelope (C$_S$) conformation [21]. However, the quantum chemistry simulations of NTf$_2^-$ anions [60, 61] showed that it could exist in both a trans (favoured) and cis conformations, in which two CF$_3$ groups orientate towards the opposite or the same side of the S–N–S plane,
respectively. It is also reported in many metal NTf$_2$ salts that the *cis* conformation is favoured over the *trans* conformation [60]. The evidences of coexisting of both *trans* and *cis* conformation of NTf$_2$ have also been given in the pyrrolidinium and imidiazolium [21, 34, 39, 40, 62-67] based ionic liquids, as well the Na doped ionic plastic crystals [41]. Therefore, in this ionic plastic crystal, it would be expected that both rotational and translational motion of the whole cation and anion, as well as the intramolecular rotation of its constituent functional groups CF$_3$ and CH$_3$, occurred in the high temperature phases. These motions would help us better understand the origin of the complicated phase behaviour in this material and so here we investigate the conformation of NTf$_2$ anion at different phase temperatures.

The dihedral distributions of free NTf$_2$ anion in [C$_2$mipy][NTf$_2$] plastic crystal was studied by several researchers using DFT and ab-initio methods [21, 39, 62-66]. To our knowledge the simulation study of the rotational and translational motion in the pure [C$_2$mipy][NTf$_2$] plastic crystal has not been undertaken. The understanding of prevalent types of motions at different temperatures enables to thread the interrelationship between the structural, thermal and transport properties in the material. In the current study, we employ the power of molecular dynamics (MD) simulation to gain insight into the dihedral distribution function of the anion, the rotational autocorrelation of [C$_2$mipy][NTf$_2$] plastic crystal at different temperatures.

In the anion, the two dihedral vectors, defined by the set of bond vectors C15→S1→N3→S2 and S1←N3←S2←C16 shown in Figure 5.5, were chosen and investigated as a function of time. The two equivalent CSNS and SNSC dihedrals were defined by the orientation of S–C bonds. As shown in Figure 5.5, in the *cis*
orientations the two CF$_3$ groups in CF$_3$–SO$_2$–N–SO$_2$–CF$_3$ are on the same side of the S–N–S plane while in trans the CF$_3$ groups are oriented on opposite sides of the plane [39, 62, 65].

![Figure 5-5 The dihedral angle of the anion NTf$_2$ defined by CSNS-SNSC dihedrals with the orientation of S–C bonds in the two planes a) C$_1$ (cis) conformation and b) C$_2$ (trans) conformation adopted from [63]](image)

The conformational analysis of the dihedral CSNS in the NTf$_2$ anion has been conducted at different temperatures of 153, 213, 273 and 333K, as shown in Figure 5.6. Two types of dihedral CSNS with dominant populations shown at around $\pm 90^\circ$ and $\pm 180^\circ$ were related to a trans and cis conformation respectively. At 153K, there were only trans conformations observed. As temperature increases to 213K, there was slight presence of cis conformation in addition to the predominant trans conformation. With further increase in temperature, the trans conformation decreased and the cis conformation increased. For example, at temperatures above 303K in both phase II and I of this OIPC, the predominant conformation was cis conformation.
The geometry changes due to the rotation in the dihedral angle reflects the flexibility and plastic behaviour in the NTf₂ anion which is shown in Figure 5.6 as temperature increases from 153K to 333K. For the torsional distribution at 273 and 333K, the positions of the peak and minima did not change apart from the barrier height that considerably decreases with increasing temperature. The changes of the conformation of NTf₂ reported in this work are actually supported by the FTIR experiments [41].

In FTIR studies [68], the presence of dominant trans conformation of the NTf₂ were reported in the solid state, with a characteristic band observed at 607 cm⁻¹ that is assigned to the bending of SNS and out of phase asymmetric bending of SO₂ bonds. The bands observed at 600 cm⁻¹ and 653 cm⁻¹ are assigned to the bending of SNS and in-phase asymmetric bends of SO₂ bonds, which correspond to the presence of
cis conformers. It was also suggested that both cis and trans conformers coexist in the molten state of NTf₂ [66].

In our simulation work, two main peaks are observed in the dihedral angle probability plot consistent with proper dihedral of 90° (trans) and 180° (cis) conformers between 213K and 333K. The trans conformer decreases as temperature increases. A dramatic change is found to occur from 303K, which represents plastic crystal phase II of this material. Thus, a mixture of both trans and cis isomers co-exist in high temperature phases. The significant increase of cis conformers in high temperature phases is consistent with the experimental observations for the C₁mpyr NTf₂ system, in which the Raman results reported 60% cis and 40% trans conformation in the solid-state at 326K [66]. Further MD investigations were also made with the inclusion of vacancies, as shown in Figure 5.7. It is found that the addition 2% vacancies to this structure led to a further reduction of the trans conformer at 333 K, thus the cis conformer dominates in the more disordered material.
Similarly, the conformational analysis of the ethyl-methyl pyrrolidinium \([\text{C}_2\text{mpyr}]^+\) cation had been carried out using MD simulation as a function of temperature. The simulation analysis on the pyrrolidinium ring, based on the bonds \(C_1 \rightarrow N_1 \rightarrow C_4 \rightarrow C_3\) and \(C_4 \rightarrow N_1 \rightarrow C_1 \rightarrow C_2\) (see Figure 5.9) that form the dihedral angle, was undertaken in order to understand the changes of the conformation of pyrrolidinium ring. It is expected that the alkyl chain and the pyrrolidinium ring undergo conformational changes. For this investigation we scanned the average of the distribution of \(CNCC\) dihedral angles as shown in Figure 5.8. As it can be seen from Figure 5.8, the dihedral probability at temperature of 153K in phase IV shows that a single conformer exists at the torsional angle of -60 and 60°. As temperature increases from 213K to 333K (phase III to I), the dihedral distribution changes and numerous conformers appear. At 213K, the distribution peaks were observed at -70°, -35°, 10°, 125°, 160° changed to -60°, -20°, 165° at 273K and -60°, -30°, 120° at 333K respectively. As shown in Figure 5.8, the distribution probabilities were almost equal (except at 153K) and the trend in the dihedral distribution of the \([\text{C}_2\text{mpyr}]^+\) is linked to the possibility of the existence of the envelope (-60° and 60°) and the twist type conformers in the alkyl chains, in addition to pseudo-type rotations in the pyrrolidinium ring as previously observed in the pyrrolidinium containing ILs and crystals. At this stage we are not able to identify and assign the distribution corresponding to the twist type conformers in the alkyl chains and pseudotype rotations in the pyrrolidinium ring. Thus, our further discussions on these conformers will be based on the comparison with the DFT and Raman studies.
Adebahr et al. [4], reported that the [C_1mpyr]^+ ion has both twist and envelope ring structures as an isolated [C_1mpyr]^+ cation and in an ion-pair of [C_1mpyr]^+ \Gamma. As shown in Figure 5.9, in the eq- envelope, the central N atom is above the plane formed by four carbon atoms in the pyrrolidinium ring C2\rightarrow C3\rightarrow C4\rightarrow C5 (N-envelope with dihedral to be fixed at 0°) and the ethyl group lies in an equatorial position with respect this plane. On the other hand, in an ax- envelope, the N-envelope with the ethyl group is in an axial position with respect to the ring plane whereas in the twist isomer mode the pyrrolidinium ring is twisted. Umebayashi et
al [64, 69], studied possible conformers in the [C₃mpyr]⁺, [C₄mpyr]⁺ cations in NTf₂ anion ILs to be the ax-envelope and eq-envelope whilst the alkyl groups favor trans conformation with the carbon atoms next to central N atom.

![Schematic representation of [C₂mpyr]⁺ conformers adopted from the crystal structure at 153K (64, 69)](image)

**Figure 5-9** Schematic representation of [C₂mpyr]⁺ conformers adopted from the crystal structure at 153K (64, 69)

In most pyrroloidinium crystalline solids, trans conformation was suggested to be favorable [69]. It was concluded from the Raman measurement that the C₄mpyr⁺ ion involves the eq-envelope conformation in the C₄mpyrBr crystals. In line with this argument the completely ordered, monoclinic phase in [C₂mpyr]⁺ obtained from the x-ray structure is in an eq-envelope trans conformational state as shown in Figure 5.10a. The combinations or the inter-conversion of these pseudo-rotations were also reported for the ILs and gave rise to different dihedral distributions, or the occurrence of numerous conformational states with increasing temperature [64,69].

- 166 -
The coexistence of C₁ and C₂ conformers were previously reported in the NTf₂ anion of the same OIPC with increasing temperature as well. In line with this, the variations in the dihedral distribution of [C₂mpyr]⁺ arise from the disorder in the plastic crystal from the phase III. Therefore, the conformational states of ax-envelope and/or twist conformations could be triggered by the onset of rotation at 213K (in phase III) and beyond.

![Schematic representation of trans a) eq-envelope trans at 153K b) ax-envelope of \([C2mpyr]^+\) conformers extracted from the trajectory of \([C2mpyr]^+\)[NTf2]^− at 333K](image)

In the Raman spectra at room temperature for this OIPC [41] in phase and out of phase bending of the pyrrolidinium ring observed at ~570 cm⁻¹ and 590 cm⁻¹ respectively confirm the possibility of both ax and eq-envelope. The stretching of the ring (both symmetric and anti-symmetric) in the spectral region ~1050-1350 cm⁻¹ accompanied by twisting, bending and stretching of N-CH₃ and N-CH₂ clearly indicate the twist conformational modes in ring. Thus, the observed variation in the dihedral distribution could be further understood in light of the variation of these bands. However, careful observation of the cations from dynamical trajectories (see Figure 5.14) in the molecular dynamics calculations, show that they undergo
various conformations at 333K in phase I. More detailed variable temperature Raman spectroscopy, together with the MD simulations, could be instrumental to get a better understanding.

5.4.3. Rotational Autocorrelation Functions

Figure 5-11 Vectors in cation and anion defined for rotational autocorrelation function calculations. a) vector \( u_{t1pp} \) describes an axis perpendicular to the plane C1-N1-C4 in pyrrrolidinium ring b) vector \( u_{t2pp} \) is selected along the C5-C6 bond c) the vectors \( u_{tmm1} \) and \( u_{tmm2} \) are selected along the S1-C15 and S2-C16 bonds, respectively.

In order to gain insight in the rotational dynamics of [C2mpyr] [NTf₂] OIPC, the rotational autocorrelation function was analysed on selected vectors (see Figure 5.11) in both cations and anions at different temperatures and in different phases.
Figure 5-12  Rotational autocorrelation functions of vectors $u_{1pp}$ (a) and $u_{2pp}$ (b) in the cation of [C2mpyr][NTf₂] at different temperatures.
Figure 5-13 The Average of calculated of rotational autocorrelation functions of vectors $u_{imm1}$ and $u_{imm2}$ in the anion at different temperatures.

The rotational autocorrelation from MD simulations in the range of temperatures between 213 and 383K was presented in the Figures 5.12 and 5.13 above. As shown in Figures 5.12 and 5.13, in phase III at a temperature of 213K, the decay of the rotational autocorrelation is negligible within the 5ns simulation time, indicating that neither cations nor anions show any rotational motions. However, from 273 K the cations start to present rotational motions as the considerable decay can be observed for vectors $u_{c1pp}$ and $u_{c2pp}$ in Figure 5.12(a, b). However, the decay of the vector in the anion is still insignificant which indicates that, although cation starts to rotate, anions are still relatively rigid. In phase I at 333K, it is obvious that both the anion and the cation undergo rotational motions. But the cations still rotate faster than anions as the decay of vectors in Figure 5.12(a, b) is faster than that in Figure 5.13. In both cation and anion data, the fastest decay of all vectors was achieved at 383K, a temperature beyond the melting point 364K of a pure OIPC in experiment.
It has thus been observed that the NTf$_2$ anion rotates slower than the [C$_2$mpyr] cation at all temperatures investigated.
Figure 5-14  Dynamical evolution of the ionic species inspected in (top-bottom) a) pure OIPC b) inclusion of 1% vacancy and c) inclusion of 2% vacancy in pure OIPC at 333K (phase I)
As shown in Figure 5.14, the dynamical evolution of the ionic species from the trajectory of simulation for 3 ns at 333K in phase I with and without the inclusion of vacancy was investigated. In these snapshots, the rotation of the pyrrolidinium ring and the functional groups CH₃ and CH₂ in the cation, as well rotations of the SO₂ and CF₃ groups in the anion were clearly observed.

The effect of incorporation of vacancy on rotational dynamics of the OIPC was quantitatively investigated at 333K in phase I. The RAFs of the same vectors were calculated and given in Figure 5.15(a-c). As shown in Figure 5.15(a-c), in the systems with 1% and 2% vacancy, the decay of the RAF profiles become faster than in a pure OIPC system. And the difference of the effects on rotational behaviour caused by introducing 1% and 2% vacancy is not large.
Figure 5-15  Rotational autocorrelation function ut1pp (a) and ut2pp (b) of the cation and u1mm = u2mm (c) of the anion in [C2mpyr][NTf2].

For further analysis and determination of the rotational relaxation times, the time dependence of C(t) was fitted to two stretched exponentials given in equation 5.2 of the form
\[ C(t) = C_0 + A \exp(-t_1/\tau_1) + B \exp(-t_2/\tau_2) \]  

Equation 5-2

where \( C_0, A, B \) are constants or coefficients of fit parameters and \( \tau_1, \tau_2 \) are the rotational time constants defined as the slow and fast processes - the tail and head of the decay exponentials. In all cases, the relaxation behaviour was accurately fit to the two exponentials, as illustrated in Figure 5.16. Borodin et.al\cite{33, 34} reported that two well separated relaxation processes were observed in \( \text{N,N,N,N-} \text{tetramethylammonium dicyanamide [Me}_4\text{N][N(CN)}_2\text{]} \) due to the asymmetry in the \( \text{N(CN)}_2 \) which provides two dissimilar rotational behaviors. They concluded that the two-step relaxation behavior represents coupling between the fast mode and the slow mode rotation.

![Figure 5-16 The simulated (black) and fitted (red) rotational autocorrelation fitted to double exponential decay](image-url)

- 176 -
Table 5.4 summarizes the rotational relaxation times computed from equation 5.2 and the times for the slow process are presented. The relaxation time obtained from the vector perpendicular to the pyrrolidinium ring and C-C ethyl in [C2mpyr] \(^+\) shows that both the ring and C-C ethyl undergo rotation starting from phase III, as evidenced from the RDF and dihedral distribution studies. However, the relaxation time in phase III at 213K is longer than 4.5 ns, whereas this time is reduced to 0.5 ns as temperature increases to 333K in phase I. Therefore, as expected, the rotational behaviour increases as the temperature increases. Furthermore the different relaxation times between two vectors \(u_{\text{t1pp}}\) and \(u_{\text{t2pp}}\) in Table 5.3 indicate the anisotropic rotation behaviour of cations. For example, the largest discrepancies between relaxation time of two vectors are observed at 333 K, being 465.2ps for \(u_{\text{t1pp}}\) while this time increases significantly to 1390.3ps for vector \(u_{\text{t2pp}}\), indicating the rotation of vector \(u_{\text{t2pp}}\) is slower than vector \(u_{\text{t2pp}}\). This type of anisotropic rotational motion was also reported for pyrridinium based cations. Cadena et al [36, 37] studied pyrridinium based ILs with the same NTf\(_2\) anions. They found that the rotational relaxation time of the longest vector through the pyrridinium ring and long alkyl chains is much longer than the relaxation time for the other vectors in the cation, which gave strong evidence of the anisotropic rotation/tumbling motions of pyrridinium cation molecule.

Due to much larger inertia of the NTf\(_2\) anion, it is expected that the rotational relaxation time decay slower than that of cation at all the temperatures. As the S-C bonds on the either sides of the central N in the anion is symmetrical, the rotational autocorrelation functions of S1\(\rightarrow\)C15 and S2\(\rightarrow\)C16 are almost equivalent at all temperatures. The slow process observed in the lower temperature phases indicates
that the anions do not show the rotational behaviour along the two C-S bond vectors. These two vectors might be the indicator for the tumbling motions of anions because the decaying of rotational autocorrelation functions of these two vectors occurs in the higher temperature phases, where the tumbling motions are expected. However, previous IR experiments show that the CF$_3$ and SO$_2$ functional groups in the anion undergo wagging and bending motion even from a low temperature of 213K.

These findings are also consistent with the NMR experimental studies on the same OIPC [13, 25]. This prior work suggested that the cations and anion undergo anisotropic rotation. The occurrence of transformation from one anisotropic rotation to another such as ring inversion or flipping and/or additional anisotropic motions exist in the phases II and I as evidenced in the change of lattice structure. It had also been observed that the rotational relaxation times of the C-S in the anion is in the same order magnitude with the $u_{t1pp}$ and $u_{t2pp}$ values calculated for the cation at 273K, in phase III and in contrast to the value exceedingly greater than the simulation time at 213K. Furthermore, there were discrepancies observed in the rotational relaxation times between the experimental and simulation results as will be discussed in the next section in relation to the simulation times.

**Table 5-3 Relaxation time of two vectors $u_{t1pp}$ and $u_{t2pp}$ in the cation**

<table>
<thead>
<tr>
<th></th>
<th>$u_{t1pp}$</th>
<th></th>
<th>$u_{t2pp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T/K$</td>
<td>213</td>
<td>273</td>
<td>333</td>
</tr>
<tr>
<td>$\tau/\text{ps}$</td>
<td>4780</td>
<td>2461</td>
<td>465</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.995</td>
<td>0.987</td>
<td>0.949</td>
</tr>
</tbody>
</table>

- 178 -
In general, from the inspection of the rotational autocorrelation function it can be concluded that the rotation vectors cannot decay to zero whilst the cation and anion are in fixed position (ie. not fully tumbling). Furthermore, at 333K when vacancies are incorporated into the lattice, the cation and anion rotational dynamics are significantly enhanced.

5.4.4. Self–Diffusion D of the individual ionic species

The Mean square displacement (MSD) of the cation and anion are separately presented in Figure 5.17 (a, b). In the current MD simulation, the trajectory was collected under NPT for 3 ns to calculate the centre of mass MSD at temperatures of 273, 333 and 363K with and without inclusion of a vacancy defect. The slope of the MSD with time t was used to estimate the diffusion coefficient D of the anion and cation.
As it was shown earlier in the discussion of dihedral distribution and RDFs, disorder in the anion and cations due to thermal rotation occurs at 213K. Despite the beginning of onset of slow anisotropic rotation of the functional groups CF₃ and SO₂ groups in the anion, and CH₃ and CH₂ groups in the cation respectively in phase III at 213K, the MSD curve was flat. Thus it can be concluded that diffusion of anionic or cationic species does not occur between 273 and 363 K. For example, at the phase I temperature of 363K, as it can be seen from Figure 5.17, both the anion and cation MSD only showed a slight increase with time, relative to those calculated at 273 K. Ballistic motion was observed in the first 10ps followed by a nonlinear intermediate motion ‘cage escape’ with the overall MSD less than 1 Å² within a 3ns simulation time, for both the anions and cations. Such ballistic motion and non-linear intermediate motions had been previously reported in N,N,N,N-
tetramethyl-ammonium dicyanamide, diethyl(methyl)(isobutyl) phosphonium hexafluorophosphate OIPCs and different ILs, gels and glasses. Often in these materials, the experimental NMR diffusion constants cannot be replicated with the MD simulation. Molar conductivity was not calculated because the self-diffusion coefficient was underestimated in the MD simulation of the OIPC may be due to the potentials used. To obtain diffusive motions of ions requires some improvement of the force field, like including polarization effect or using scale factors on partial charges. Also it may require the longer simulation time like microseconds to achieve a fully diffusive condition of ions, which is impractical. In this OIPC, the calculated anion and cation self - diffusion coefficients are three orders of magnitude lower compared to the ILs \( \sim 10^{-10} \) m\(^2\)/s and slightly over the values \( 10^{-13} - 10^{-15} \) m\(^2\)/s in perfect crystals. As shown in Table 5.4 and Figure 5.18 a-b, the self-diffusion of both cation and anion remain roughly the same at \( \sim 3 \times 10^{-13} \) m\(^2\)/s and with slight increase to \( \sim 5 \times 10^{-13} \) m\(^2\)/s for both ionic species with the inclusion of vacancies.
Figure 5-18 Variation in centre of mass mean-squared displacement of the a) cation and b) anion in [C2mpyr][NTf2], due to vacancy inclusion at 333K

Table 5-4 Calculated self-diffusion coefficient $D$ in ($ \times 10^{-13} \text{ m}^2/\text{s} $) anion and cation

<table>
<thead>
<tr>
<th>Temp / K</th>
<th>Cation D$_+$</th>
<th>Anion D$_-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>1.50±0.03</td>
<td>1.62±0.04</td>
</tr>
<tr>
<td>333</td>
<td>3.31±0.05</td>
<td>3.49±0.06</td>
</tr>
<tr>
<td>333$_1^*$</td>
<td>5.42±0.04</td>
<td>5.14±0.04</td>
</tr>
<tr>
<td>333$_2^{**}$</td>
<td>5.99±0.05</td>
<td>7.33±0.05</td>
</tr>
</tbody>
</table>

333$_1^*$ - inclusion of 1% vacancy; 333$_2^{**}$ - inclusion of 2% vacancy at 333K
5.5. Structural Properties of [Me₄N][N(CN)₂] OIPC Doped with Na[N(CN)₂] Salt – The Radial Distribution Functions (RDF)

The radial distribution function $g(r)dr$ of Na⁺ doped tetramethylammonium dicyanamide [Me₄N][N(CN)₂] OIPC was analysed to gain understanding of the structure of a system in the temperature range of 200-500K. They were calculated based on the distances between the central nitrogens NT and ND1 (see Figure 5.1) from both the [Me₄N]⁺ cation and [N(CN)₂]⁻ anions respectively. Calculated radial distribution functions of [Me₄N]⁺-[Me₄N]⁺, [N(CN)₂]⁻-[N(CN)₂]⁻, [Me₄N]⁺-[N(CN)₂]⁻, and [Na⁺]-[Me₄N]⁺ at 200K in 5 and 15 mol% Na[N(CN)₂] mixed with [Me₄N][N(CN)₂] OIPC are presented in Figure 5.19(a,b).

As shown in Figure 5.19a, intense sharp peaks corresponding to the first coordination shell were observed with the addition of 5% Na⁺ at around 4.7Å with splits at 5.2 and 5.9 Å for [Me₄N]⁺-[N(CN)₂]⁻; 5.8Å for [Me₄N]⁺-[Me₄N]⁺ and split peaks at 4.8 and 5.1 Å for [Na⁺]-[Me₄N]⁺. For [N(CN)₂]⁻-[N(CN)₂]⁻, a broader peak was observed at 6.8 Å in a 5% Na⁺ content mixture in addition to the weaker peak (shoulder) at 4.9 Å. In the same system, the second co-ordination shell was observed in the 8-10 Å with the 8.0 Å peak for [Me₄N]⁺-[Me₄N]⁺ coincides with the weaker peak of [Na⁺]-[Me₄N]⁺. For [N(CN)₂]⁻-[N(CN)₂]⁻ and [N(CN)₂]⁻-[N(CN)₂]⁺ the RDF peaks appeared at longer distances, between 9-10 Å. Jin et al [31] have shown the RDF peaks to be concentrated within the regions 4 to 7 Å corresponding to first co-ordination shell and 8 to 12 Å to the second co-ordination shell in the Li⁺ doped [Me₄N][N(CN)₂], which are consistent with our findings.

The appearance of both short and long range orders, expressed in the presence of
sharp peaks, is due to strong confinement of atoms in their lattice positions with the inclusion of 5% \( \text{Na}^+ \) at 200K which correlates with the rigid crystal phase reported in the previous studies of the same OIPC [28-31]. It had also been suggested that the presence of the shoulder and split peak in the RDF is attributed to the two central nitrogens in the asymmetrical unit of the ionic species [28]. The broadening in the \([\text N(\text{CN})_2]^--[\text N(\text{CN})_2]^--\) might be due to different anion environment and enhanced disorder due to addition of the Na salt. As shown in Figure 5.19 b, with the addition of 15% \( \text{Na}^+ \), for some of the peaks observed in 5% \( \text{Na}^+ \), the peaks are broadened, shifted in position (as in \([\text N(\text{CN})_2]^--[\text N(\text{CN})_2]^--\)) and their height decreased at the same temperature of 200K. This indicates an expansion of the crystal structure and the loss of the short-range order. The merge of the nearest neighbour co-ordination shells is a clear indication of the loss of long-range order. In general, the system with 15% \( \text{Na}^+ \) has higher disorder compared to the 5% \( \text{Na}^+ \) doped system at this temperature.
The dependence of the RDF on the concentration of Na\(^+\) and temperature is presented in the Figures 5.20 (a-d) shown below. As shown in Figures 5.20 (a-d), the RDF at 200K is broadened and shifted upon reaching 300K indicates that the anions/cations undergo either rotational or translational disorder, or both, which will be discussed in the next sections. It is also observed that the addition of 15% Na\(^+\) exacerbated disorder and could be explained in terms of the creation of more defects at 300K in these systems. The addition of both the 5% and 15% Na\(^+\) breaks the long-range order even in the phase IV of the OIPC. It had been reported that the solid-solid transition from phase IV\(\rightarrow\)III occurs at 377K [70] while phase III\(\rightarrow\)II transition peak is observed at 390K. At temperatures above 400K, in phase II of the OIPC, broadened peaks were observed in both anion/cation species. Moreover, the \([\text{N(CN)}_2]^-\)[N(CN)]\(_2\) show amorphous or liquid like behaviour upon adding 5% or 15% Na\(^+\).
Figure 5-20 Temperature dependent radial distribution function (RDF) of the anion–cation systems a) [Me₄N]⁺-[Me₄N]⁺, b) [Me₄N]⁺-[N(CN)₂]⁻, c) [N(CN)₂]⁻-[N(CN)₂]⁻, d) [Na]⁺-[N(CN)₂]⁺ with the addition 5% Na⁺ (solid) and 15% Na⁺ into the OIPC

Seeber et al [70] generated the single crystal structure of [Me₄N][N(CN)₂] from the X-ray diffraction, which shows the alternate arranged layers of [Me₄N]⁺ cations surrounded by layers of boomerang-shaped [N(CN)₂]⁻ anion at 123K. In their ¹H NMR study [70] of the OIPC, they have shown that the Me₄N⁺ cation undergoes anisotropic rotational motions at lower temperatures before full cationic diffusion.
begins to increase dramatically at temperatures prior to the solid–solid transition from phase III - II. Previous MD study of the same OIPC [28] have confirmed the onset of rotational motions in the cation occurs at 250 K while that of the anion starts at 275 K, in phase IV. Jin et al [31] also observed some types of the motions at 300 K and the plastic crystal phase with intensive rotational motions at 400 K in Li⁺ doped [Me₄N][N(CN)₂]. It had also been reported that the layered structure of this OIPC exhibit plastic mechanical properties [70, 71] which correlates with the broadening and disappearance of RDF peaks observed in the Na⁺ doped [Me₄N][N(CN)₂]. Hence, the rotational and translational motion of constituent cations and anions in the system will be discussed further in the following sections.

5.6. Dynamical Properties of [Me₄N][N(CN)₂] OIPC Doped with Na[N(CN)₂] salt – Rotational Autocorrelation Functions

![Figure 5-21](image)

*Figure 5-21  Vectors defining the rotational autocorrelation function, C-N bond vector in [Me₄N]⁺ (u1pp); vector perpendicular to [N(CN)₂]⁻ plane (u1tmm); vector in the [N(CN)₂]⁻ plane (u2tmm) and the C-N bond vector in the [N(CN)₂]⁻ (u3tmm)*
The rotational autocorrelation function of the mixed system was scanned for over 3ns both in the cation and anion designated by $u_{1tp}$, $u_{1tm}$, $u_{2tm}$ and $u_{3tm}$ (see Figure 5.21 above) defined as the autocorrelation function of the C-N bond vector in $[\text{Me}_4\text{N}]^+$, the vector perpendicular to the N(CN)$_2$ plane, the vector in the N(CN)$_2$ plane and the C-N bond vector in N(CN)$_2$ respectively.
Figure 5-22  Rotational autocorrelation function of a) C-N bond vector in [Me₄N]+ (u1tpp); b) anion vector perpendicular to [N(CN)₂]⁻ plane (u1tmm); c) anion vector in the [N(CN)₂]⁻ plane (u2tmm) and d) C-N bond vector in the [N(CN)₂]⁻ (u3tmm) in 5% Na doped with [Me₄N][N(CN)₂] OIPC

As shown in Figures 5.22(a-d), there are variations observed in the autocorrelations of the rotation vectors in 5%Na⁺ doped [Me₄N][N(CN)₂] presented here. At temperatures above 300K in phase III, the rotational autocorrelation decays very
fast for both anion and cation vectors within less than 100ps except for the C-N bond vector \((u3tmm)\) in the \([N(CN)2]^+\). The rotational relaxation times were fitted to two stretched exponentials and the results are presented in Table 5.5. The fast decay mode rotation was observed in the rotation vectors perpendicular to \([N(CN)2]^+\) plane (Figure 5.22(b)) and in the \([N(CN)2]^+\) plane (Figure 5.22(c)) followed by the C-N bond vector in \([Me4N]^+\) (Figure 5.22(a)). The C-N bond vector in the \([N(CN)2]^+\) (Figure 5.22(d)) shows the slowest decay.

The plots of rotational autocorrelation functions in 15%Na⁺ doped \([Me4N][N(CN)2]\) is also presented in Figure 5.23(a-d). As compared to the 5%Na⁺ doped \([Me4N][N(CN)2]\) similar trends were observed in 15%Na⁺ doped \([Me4N][N(CN)2]\). It can be observed that rotation vectors decay faster in the cation compared to the anion, from Figure 5.23 (a). The decay of the C-N bond vector \((u3tmm)\) in the \([N(CN)2]^+\) (Figure 5.23(d)) in the 15%Na⁺ doped \([Me4N][N(CN)2]\) is slightly slower than in 5%Na⁺ doped \([Me4N][N(CN)2]\) system, contrary to the decay in the C-N bond vector in the \([Me4N]^+\) cation (Figure 5.23(a)). The trend shows that the rotation in the \([Me4N]^+\) cation is enhanced, whereas the rotation in the anion is highly restricted with increased concentration Na⁺ cations in the OIPC. In the case of rotation vectors perpendicular to \([N(CN)2]^+\) plane (Figure 5.23(b)) and in the \([N(CN)2]^+\) plane (Figure 5.23(c)), the decay of autocorrelation function in 15% Na⁺ content is slightly slower than the 5% Na⁺ content in the OIPC.
Figure 5-23  Rotational autocorrelation function defined by a) C-N bond vector in \([\text{Me}_4\text{N}]^+\) (\(u_{1\text{tp}}\)); b) vector perpendicular to \([\text{N(CN)}_2]^−\) plane (\(u_{1\text{mm}}\)); c) vector in the \([\text{N(CN)}_2]^−\) plane (\(u_{2\text{mm}}\)) and d) C-N bond vector in the \([\text{N(CN)}_2]^−\) plane (\(u_{3\text{mm}}\)) in 15% Na⁺ doped with \([\text{Me}_4\text{N}][\text{N(CN)}_2]\) OIPC

In general, with the increase of temperature above 300K, the rotational relaxation time decreases quite rapidly for a particular Na⁺ concentration. This means that the ionic species undergo either increased anisotropic (at lower temperatures) or
isotropic rotation (at higher temperatures) in the plastic and/or liquid phase. As the anions have a fixed C-N bond to their terminal nitrogen, anisotropic rotation occurs, as previously reported [28-30]. This is consistent with our observation of a slower exponential decay in the C-N vector in the \([\text{N(CN)}_2^-]\). Hooper et al [29, 30] reported varied onset of rotational motion along the x and y axes in the \([\text{N(CN)}_2^-]\) ion and showed that the III - II phase transition display faster \([\text{N(CN)}_2^-]\) rotation than in II - I phase transition. Thus, dissimilar trends (at 300K and 350K) occur for the decay time from the rotation vectors perpendicular to and in the \([\text{N(CN)}_2^-]\) plane arising from the varying axial contribution to rotation in the boomerang shaped anion. It is not clear why the C – N rotational autocorrelation \((u_{3tmm})\) does not change significantly with increasing temperature as shown in table 5-5. The \(u_{1tmm}\) and \(u_{2tmm}\) vectors both decay rapidly at all temperatures compared to the anisotropic \(u_{3tmm}\), which is slow to relax at lower temperatures.

**Table 5-5 Rotational relaxation time calculated from the two step exponential decay in 5% Na mixed with [Me4N][ N(CN)2]OIPC**

<table>
<thead>
<tr>
<th>(u_{1tpp})</th>
<th>(u_{1tmm})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>T/K</td>
<td>300</td>
</tr>
<tr>
<td>(\tau / \text{ps})</td>
<td>51.7</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.999</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(u_{2tmm})</th>
<th>(u_{3tmm})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>T/K</td>
<td>300</td>
</tr>
<tr>
<td>(\tau / \text{ps})</td>
<td>61.7</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.999</td>
</tr>
</tbody>
</table>

As shown in Figures 5.22-a (5% Na\(^+\) content) and 5.23-a (15% Na\(^+\) content) further increase in the concentration of Na\(^+\) causes a decrease in the rotational relaxation
time in the [Me₄N]⁺ cation at all temperatures. This agrees well with the [31] study that the addition of Li⁺ into the OIPC introduce more lattice defects with increasing temperatures that lowers the energy barriers in the rigid crystal phase, and thus reduce the relaxation time. However, the trend is different in the anion rotational autocorrelation function. The rotational relaxation time in the anion increases with increasing Na⁺ concentration at all temperatures above 300K. Jin et al [31] reported similar findings with 8 and 12 mol% Li⁺ doping in the plastic crystal phase at 400 K and concluded that the motion becomes more restricted with increasing concentration of Li⁺ content due to the aggregate/cluster formation that slows down the average rotational motion of the anion. From the experimental studies on the Na N(CN)₂ salt [72-74] this confirmed the existence of two different phases and trimerization to form Na⁺ containing tricyanomelaminates ([N(CN)₂]₃)³⁻ under heat in a solid state. Thus, the formation of aggregates with the [N(CN)₂]⁻ in this system could be a possibility leading to slower rotational motion of the anion with increasing concentration of Na⁺ ions This agrees well with the finding on Li⁺ doped system in which the aggregation hinders the tumbling motion of [N(CN)₂]⁻ ion [31]. In the liquid phase at 500K, in both 5% and 15% Na⁺ content, the [Me₄N]⁺ (see Figures 5.22 (a) and 5.23(a)) undergoes isotropic rotational relaxation whilst the rotation in the [N(CN)2]⁻ is still anisotropic as evidenced by the calculation of rotational autocorrelation function (see Figures 5.22 (b-d) and 5.23(b-d)) and is in agreement with the previous studies of the OIPC and Li⁺ doped OIPC [28-31]
5.7. Dynamical Properties of $[\text{Me}_4\text{N}]^+\text{[N(CN)}_{2}]^-$ OIPC Doped with Na$^+$ Salt – Self-diffusion

The cationic ($\text{Na}^+$ and $\text{Me}_4\text{N}^+$) and anionic ($\text{[N(CN)}_{2}]^-$) mean square displacement (MSD) of the 5% and 15% Na$^+$ doped $\text{Me}_4\text{N}[\text{N(CN)}_{2}]$ OIPC as a function of temperature are presented in the Figures 5.24 (a-c) and 5.25 (a-c) respectively. The translational motion of the cations and the anion were monitored from a 3ns simulation based on the mean square displacement of central nitrogen atom (NT) in $\text{Me}_4\text{N}^+$, sodium cation $\text{Na}^+$ and the central nitrogen atom (ND) in the $\text{[N(CN)}_{2}]^-$ anion. The diffusion coefficients of respective ionic species were calculated from the slope of the MSD linear region at longer times, as shown in the Figures 5.24 (a-c) and 5.25 (a-c) and the values are presented in Table 5.6. As can be seen from Table 5.6, the self-diffusion coefficients of the $\text{Me}_4\text{N}^+$ cation and $\text{[N(CN)}_{2}]^-$ anion at 300 K are in the order of $\sim10^{-12}$ m$^2$/s in 5% and 15% Na$^+$ contents, which is an order of magnitude greater than in crystalline solids. However, this still does not mean the ionic species are fully diffusing in comparison with the $\sim10^{-10}$ m$^2$/s at 500K in a liquid state.
Figure 5-24 The means square displacement of (a)[Me₄N]⁺, (b) [N(CN)₂]⁻, and (c) Na⁺ ions in 5% Na⁺ doped [Me₄N][N(CN)₂] OIPC.

In the range of temperatures above 350 K, the MSD increases linearly in time in both 5% and 15% Na⁺ doped systems. The calculated self-diffusion coefficients of the 5% Na⁺ content ionic species at 350K increases from 2.1 x 10⁻¹¹ m²/s to 8.4 x 10⁻¹¹ m²/s for [Me₄N]⁺; 1.1 x 10⁻¹¹ m²/s to 3.7 x 10⁻¹¹ m²/s for Na⁺ and 3.3 x 10⁻¹¹ m²/s to 10.1 x 10⁻¹¹ m²/s for [N(CN)₂]⁻ upon reaching 500K. In the 15% Na⁺ content system, calculated self-diffusion coefficients of the ionic species is lower than the 5% content in the same temperature range of 350-500K. The calculated self-diffusion coefficients varies from 1.5 x 10⁻¹¹ m²/s to 6.7 x 10⁻¹¹ m²/s for [Me₄N]⁺; 0.6 x 10⁻¹¹ m²/s to 3.1 x 10⁻¹¹ m²/s for Na⁺ and 2.0 x 10⁻¹¹ m²/s to 7.5 x 10⁻¹¹ m²/s for [N(CN)₂]⁻ in the temperature range of 350-500K. However at 300 K, increasing Na⁺ concentration from 5 to 15% actually enhances the self-diffusion coefficients of Na⁺ and [N(CN)₂]⁻ ionic species, which is contrary to the results...
above 300 K. This observation is very interesting and could suggest that, in a more ordered solid, the addition of a second component increases the defects and leads to increased ion dynamics, whereas, in a more disordered or even liquid material, the addition of more Na\(^+\) leads to more ionic association and hence lesser dynamics (both anion rotational correlation times discussed above and diffusion shown here). These results were also comparable with self-diffusion coefficients of [Me\(_4\)N]\(^+\), [N(CN)\(_2\)]\(^-\) of pure OIPC\([29]\) and the Li\(^+\) doped OIPC \([31]\). Hooper et al found self-diffusion coefficients for the [Me\(_4\)N]\(^+\) ranging from 5.4 \times 10^{-10} m\(^2\)/s to 2.1 \times 10^{-9} m\(^2\)/s and for the [N(CN)\(_2\)]\(^-\) ranged from 8.3 \times 10^{-10} m\(^2\)/s to 2.7 \times 10^{-9} m\(^2\)/s in the liquid state of the pure OIPC between 425K and 600K. The results determined here are an order of magnitude less at 425K than that the liquid state at 600K, and almost two orders of magnitude more than the reported crystalline system with a single ion pair vacancy\([29]\).

**Table 5-6 Self-diffusion of cationic and anionic species in 5% and 15% Na\(^+\) doping in [Me\(_4\)N][N(CN)\(_2\)]OIPC (x10\(^{-11}\) m\(^2\)/s)**

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>[Me(_4)N](^+)</th>
<th>[Na(^+)]</th>
<th>[N(CN)(_2)](^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5% Na(^+)</td>
<td>15% Na(^+)</td>
<td>5% Na(^+)</td>
</tr>
<tr>
<td>300</td>
<td>0.34</td>
<td>0.38</td>
<td>0.04</td>
</tr>
<tr>
<td>350</td>
<td>2.10</td>
<td>1.47</td>
<td>1.10</td>
</tr>
<tr>
<td>400</td>
<td>4.12</td>
<td>2.71</td>
<td>1.55</td>
</tr>
<tr>
<td>500</td>
<td>8.40</td>
<td>6.70</td>
<td>3.71</td>
</tr>
</tbody>
</table>
Figure 5-25  Mean square displacement of (a)[Me₄N]⁺, (b) [N(CN)₂]⁻, and (c) Na⁺ ions in 15% Na⁺ doped [Me₄N][N(CN)₂] OIPC.

It is observed that self-diffusion of the anion [N(CN)₂]⁻ is larger than the [Me₄N]⁺ in most cases, which might be attributed to the larger ionic radius of the cation. However, for the 5% Na doped system at 300 K, a slower [N(CN)₂]⁻ diffusion is observed compared to [Me₄N]⁺. In the Li⁺ doped system [31], there are two different [N(CN)₂]⁻ anions observed: the free and clustered [N(CN)₂]⁻. The slower anionic self-diffusion observed at 300K in the 5% Na⁺ content arises from the aggregation of [N(CN)₂]⁻ with Na⁺, whereas when the doped Na is increased to 15%, the aggregation interaction creates more free volume in the system that allows the non-aggregated [N(CN)₂]⁻ greater opportunity to diffuse, and thus contribute to the larger value of anionic self-diffusion. Despite the smaller ionic size of the Na⁺, it was still less mobile than both [N(CN)₂]⁻ and [Me₄N]⁺ likely due to its aggregation...
interaction with the $[\text{N(CN)}_2^-]$. However, the fact that the inclusion of the smaller cation Na$^+$ introduces more disorder in the local structure is confirmed by the shift in the RDFs and the faster decay of the rotational autocorrelation at temperatures of 350K and above discussed earlier.

5.8. Conclusions

In this chapter, the structural and dynamic properties of $[\text{C}_2\text{mpyr}][\text{NTf}_2]$ and Na$^+$ doped $[\text{Me}_4\text{N}] [\text{N(CN)}_2]$ OIPCs have been studied through MD simulation. In the former OIPC, the MD simulation was validated with previous experimental investigations. Excellent agreement was found between the simulated and experimental lattice parameters at 153K. The changes in $\beta$ from 98° to 90° while $\alpha = \gamma = 90°$ in the NST simulation at 383K clearly shows the change in shape of the simulation box. The RDF established the disorder in this OIPC while it undergoes different solid-solid transitions. From the dihedral distribution, the conformational states of both anion and cation were identified within different phases. The conformational changes in $[\text{C}_2\text{mpyr}][\text{NTf}_2]$ were discussed based on the previous Raman and the SXRD experiments [20,64,66,69]. Martinelli et al. [66] have shown that the solid crystalline phases of the anion is in $\text{trans}$ conformation and changes to the mixture of $\text{trans}$ and $\text{cis}$ occurs at the solid–liquid transition. Fujimori et al.[64] established the existence of both ax and eq-envelope in the cation while the latter is predominant in the lower temperature phases. As shown in Table 3.3, Our SXRD results have shown the changing lattice parameters as indicative of the crystal restructuring within each phase of the pure OIPC. Thus, the pure OIPC exists as
triclinic P-1 in phase III (273K) agrees well with the previous studies by Henderson [20], while the phases II (303K) and I (328K) are monoclinic CC and monoclinic C2, respectively. Our simulation agrees well with the experimental results in which the crystal restructuring in different phases of the OIPC as shown in Table 5.2. The rotational behaviour of the ionic species had also been studied and the rotational dynamics of the anion had been found to be slower than the cation at all temperatures. In the diffusion study, based on MSD analysis, it was found that neither the cation nor the anion are diffusing significantly up to a temperature of 363K in phase I of this OIPC. The calculated self-diffusion coefficient is not significant, the simulation does not show mobility which was observed in the experiment may be due to the potentials used. With the inclusion of 1% and 2% vacancy, slight increase in self diffusion coefficient were observed in the the cation and anion at 333K.

In the Na+ doped [Me4N][N(CN)2] OIPC, the structural and dynamic properties were studied in the temperature range of 200-500K. The RDF of different Na+ concentrations have shown that the anion and cation species exhibit broadened peaks at temperatures above 400K, in phase II of the OIPC and beyond and is evidence for the disorder in these materials. Moreover, the [N(CN)2]-[N(CN)2] and [Na]+-[N(CN)2]- show amorphous, liquid like behavior upon addition of both 5% and 15%Na+. The rotational autocorrelation functions undergo fast decays for the cations (within less than 100ps) for temperatures above 300K in phase III, whilst the vectors perpendicular to [N(CN)2] plane and C-N bond in the [N(CN)2]- were slower upon addition of both 5% and 15%Na+. This shows that the rotation in the [Me4N] cation is enhanced whilst the rotation in the anion is restricted with the addition of more Na+ cations in the OIPC. The self-diffusion coefficients of cations Me4N+, Na+ and the [N(CN)2]+ anion at 350K were calculated to be $2.1 \times 10^{-11}$ m$^2$/s ; $1.1 \times 10^{-11}$ m$^2$/s and $3.3 \times 10^{-11}$ m$^2$/s respectively for 5%Na+ content. At 500K, with the addition
of 15% Na, these ionic species reached diffusion values comparable to that of ILs $\sim 10^{-10}$ m$^2$/s. However, the Na$^+$ ions are less mobile than [Me$_4$N]$^+$ most likely due to former’s aggregation with the [N(CN)$_2$].

5.9. References


47. de Leeuw, S.W., J.W. Perram, and E.R. Smith, Simulation of Electrostatic Systems in Periodic Boundary Conditions. I. Lattice Sums and Dielectric


CHAPTER 6. Conclusions and Recommendations

In Chapters 3-5, the experimental studies on NaX salts where X= NTf₂, BF₄, N(CN)₂ mixed with [C₂mpyr][NTf₂], [C₃mpyr][BF₄] and [C₄mpyr][N(CN)₂] OIPCs; and the molecular dynamics studies of [C₂mpyr][NTf₂] and Na doped [Me₄N][N(CN)₂] OIPC were presented with a main focus on the investigation of structure-transport properties in these materials. An outline of the main findings of these studies and recommendations for future work are summarized as follows.

6.1. The Na [NTf₂] / [C₂mpyr][NTf₂] Binary Mixture

In this piece of work, extensive experimental studies were used to elucidate on the structure and dynamics of the mixed system. More specifically, temperature dependent structure, phase behavior, morphology, conduction mechanisms and ionic motion at different Na⁺ concentration levels within the mixed system have been thoroughly studied.

From the study on phase behaviour, two different binary phases were identified to exist: the [C₂mpyr][NTf₂] OIPC rich phase below the liquidus line and the Na⁺ rich phase of [C₂mpyr][NTf₂] / Na[NTf₂] or [C₂mpyr]₁₋ₓNaₓ[NTf₂]. A eutectic composition at 15% mol Na[NTf₂] content was found with a eutectic temperature at 63 ± 2°C. It has been demonstrated that the doping of [C₂mpyr][NTf₂] OIPC with a sodium salt Na[NTf₂] yielded up to 3 orders of magnitude of enhancement in ionic conductivities especially in phase I. The ionic conductivity in the Na⁺ doped materials was observed to drastically increase with the concentration higher than eutectic composition at 15% mol Na[NTf₂].

Our SEM micrographs have shown the presence of slip planes and this, together with pipe diffusion along grain boundaries, may contribute to the enhancement of ionic conductivity in phase I.

The synchrotron XRD showed that the predominantly [C₂mpyr][NTf₂] rich phase exists with varied lattice structure and the second Na⁺ rich phase was found to be consistently
monoclinic P2/1 at different temperatures. The pure [C2mpyr][NTf₂] phases were continuously restructured from triclinic P-1 at 273K and Monoclinic CC at 300K to Orthorhombic II at 328K. The crystal restructuring is attributed to the volume expansion and vacancy generation with the increase in thermal energy as the solid-solid transitions proceed to phase I. In the Raman and FTIR spectra, the presence of cis and trans conformer in the NTf₂ anions of the Na doped systems was confirmed at 295K. It was observed that weak interaction between cation and anion enhanced sodium ion mobility that brought about three orders of magnitude enhancement in conductivity with the 40% mol NaNTf₂ over the pure plastic crystal. The solid state NMR measurements confirmed the rotational disorder at low temperatures and translational mobility of both the cations (Na⁺ and [C2mpyr]⁺) and the anion [NTf₂]⁻ at temperatures as high as 333K agrees well with the SXRD analysis.

Thus, the conformational flexibility in this system is due to the rotational disorder in the anions. Furthermore, such conformational transformations or internal rotations in the anion can create a vacancy. It is known that the conductivity mechanism in the OIPCs is dominated by defects, mainly vacancies and grain boundaries. The increase in size and concentration of defect with the increased concentration of Na⁺ content resulted in an increase of ionic conductivity with increasing temperature. In conclusion, the studies of this project reveal the presence of two phases in the binary mixture and the higher conductivity of ~10⁻⁴ S/cm² at 60°C in the mixing with 40% mol NaNTf₂. These mixtures have great potential for the first possible Na⁺ ion solid-state OIPC based electrolytes to be used in in electrochemical devices such as battery, super-capacitors, sensors and fuel cells.

6.2. NaX / [Cxmpyr][X] , X=[BF₄], [N(CN)₂] Binary Mixtures

The effect of mixing Na[BF₄], Na[N(CN)₂] salts with OIPCs of similar anions [C₃mpyr][BF₄], [C₃mpyr][N(CN)₂] on thermal, structural and transport properties of the
materials was investigated using different experimental techniques: DSC, EIS, SEM, FTIR/Raman and solid state NMR spectroscopy. The SXRD was not utilized in the study of these materials due to availability of the Synchrotron.

From the DSC measurements, no change in the solid-solid transitions was observed in the temperature range of -50°C to 150°C upon mixing the \([\text{C}_2\text{mpyr}]\text{[BF}_4\text{]}\) OIPC with Na[BF\(_4\)] salt to the level of concentration of 20 mol%. There was no evidence of solid solution formation or solubility of the salt into the OIPC observed. On the other hand, the thermal behavior with the 20mol% Na[N(CN)\(_2\)] mixing in the OIPC \([\text{C}_1\text{mpyr}]\text{[N(CN)\(_2\)]}\) indicates the presence of either a possible eutectic melting which overlaps with the solid-solid transition from phase II to I to occur at ~89 °C.

The microstructures obtained from the SEM clearly showed the precipitates which occupy the inter-grain surface of the OIPC at low level of concentration of Na[BF\(_4\)] and those embedded as aggregates within the grain boundaries at high level of concentration of Na[BF\(_4\)]. Similarly, in the Na[N(CN)\(_2\)]/[\text{C}_1\text{mpyr}]\text{[N(CN)\(_2\)]} mixtures, precipitates were clearly observed as well. The precipitates in both mixtures reflect an additional Na\(^+\) rich phase.

The conductivity of the mixture of Na[BF\(_4\)] and [C\(_2\)mpyr][BF\(_4\)] did not show dramatic increase in lower temperature phases with increasing the Na\(^+\) content. However, there was slight increase in conductivity for 4 mol % Na[BF\(_4\)] in [C\(_2\)mpyr][BF\(_4\)]. With the increased level of concentration in of Na[BF\(_4\)], the precipitation of a second phase within the microstructure, especially along grain boundaries, was thought to be responsible for the blockage of the transport along the grain boundaries and thereby leads to a decrease in the conductivity. In the Na[N(CN)\(_2\)]/[\text{C}_1\text{mpyr}]\text{[N(CN)\(_2\)]} mixtures, unlike other OIPCs where the ionic conductivity usually increases upon doping or mixing with a second component of whatever Na\(^+\) concentration, the conductivity of these mixtures remains relatively the same.
and above $10^{-4}$ S.cm$^{-1}$ at ~80°C, even in the solid state.

Preliminary solid state NMR measurement at room temperature confirmed the existence of additional Na$^+$ rich phase from the observation of different Na environment in $^{23}$Na nuclei in both Na[BF$_4$]/[C$_2$mpyr][BF$_4$] (shown in appendix A.I) and Na[N(CN)$_2$]/[C$_1$mppy][N(CN)$_2$] mixtures is consistent with the appearance of precipitates. The existence of more than single Na$^+$ environment observed in the NMR agrees well with different forms of complexation or aggregation as observed in the Raman/FTIR spectra in these systems. Besides, the line narrowing in $^{23}$Na nuclei of both systems shows the mobility of Na$^+$ cation. Room temperature solid-state NMR data from $^{19}$F nuclei have shown different [BF$_4$] environments and/or the possibility of different phases (shown in appendix A.I) which is also consistent with the additional peak observed at ~ 550 cm$^{-1}$ in the FTIR spectra and ~785 cm$^{-1}$ in the Raman spectra of Na[BF$_4$]/[C$_2$mppy][BF$_4$] mixture. The nuclei $^1$H, $^{13}$C showed identical environment for the cations C$_1$mppy$^+$ and [C$_2$mppy]$^+$ apart from line narrowing observed in the mixtures, which is due to faster cationic motion in these mixtures. Despite evidences of the mobility of the cation and the anions in these materials, their direct effect on conductivity is yet to be fully elucidated. Future work will focus on phase characterisation by the SXRD and also more in depth variable temperature solid state NMR.

6.3. MD simulations in [C$_2$mppy][NTf$_2$] OIPC

Structural, thermal and dynamic properties of [C$_2$mppy][NTf$_2$] OIPC have been studied through MD simulation combined with experimental investigations. Excellent agreement of simulated lattice parameters with SXRD experimental results at different temperatures validated the accuracy of the potential function used, at least for the structural investigation. The experimental data in fact suggests that the phase III is indeed triclinic $P$-$I$, while the phase II and I are monoclinic $CC$ and Orthorhombic $I222$ respectively. The changes in $\beta$ from 98º to 90º while $\alpha = \gamma = 90º$ in the NST simulation at 383K clearly shows the change in shape of the simulation box though it is not completely cubic.

- 212 -
In the RDF, sharp peaks observed in the lower temperature phase IV at 153K is consistent with the x-ray studies indicating that both the cations and anions in the OIPC are ordered. Broadening of RDF peaks at 213K and above show that the cations and anions undergo disorder. However, at all temperatures above 273K and above, the RDF peak decreases in height and the peak position shifts while immensely broadened in all cation-cation, cation-anion and anion-anion RDFs correlates with phase changes of differing lattice structure observed from the synchrotron XRD experiment. It had been previously established from the Positron Annihilation Lifetime Spectroscopy (PALS) that the vacancy number and size increases substantially with temperature for this OIPC, which is indicative of the link between the vacancies and rotational/orientational disorder in plastic crystal phases of [C2mpyr][NTf₂] as observed from the changes in volume and RDF reported in this simulation. The difference observed at 213K and 273K, both in phase III, can be explained in terms of the increase in vacancy concentration corresponding to slight volume change and hence increase thermal disorder.. Thus defects are caused at higher temperatures have resulted in the increased plasticity and enhanced disorder in the OIPC in phases II and I and continue to expand with further increase in temperature to undermine the existence the long-range order. The addition of 1% and 2% vacancies in the OIPC at 333K (phase I), did not affect all the RDFs investigated. This could be due to the insignificant increase in the size and concentration of defects at this temperature that did not contribute in the crystal restructuring and plasticity of the OIPC. Further study is required to conclude the effect of vacancies on the RDF with increased concentration.

In the dihedral distribution function for the anion, two main peaks of the dihedral angle probability plot were identified relating to proper dihedral of 90 (trans) and 180° (cis) conformers between 213K and 333K. More peaks observed at 153K correspond to frozen conformers of the ordered structure. The trans conformer decreases as temperature increases, and dramatically so for the 333K which represents phase I, i.e. the plastic phase, for the [C2mpyr][NTf₂] crystal. The dramatic increase of cis conformers in phase I at 333K.
is consistent with the Raman observation in C_{1}mpyr NTf_{2} and with the addition of 1% and 2% vacancies to this crystal structure led to further reduction of the trans conformer and domination of cis conformer.

Similarly, from the dihedral distribution function in a completely ordered, monoclinic phase in [C2mpyr]^{+} at 153K, it was observed that the cation exists in an eq- envelope trans conformational state. However, the variations in the dihedral distribution of [C2mpyr]^{+} at temperature above 213K arise from the disorder in the plastic crystal from the phase III. Therefore, the conformational states of ax-envelope and/or twist conformations could be triggered by the onset of rotation at 213K (in phase III) and beyond. Such combinations or the interconversion of these pseudorotations in phase III and beyond correlates with the occurrence of numerous conformational states with increasing temperature in the ILs of similar cations. However, further studies need to be done with variable temperature Raman spectroscopy for comprehensive conclusion.

From the rotational autocorrelation studies, it has been observed that the rotational relaxation times decay dramatically as temperature increase and all calculated rotational relaxation times were within the reach of the length of simulations of 5ns. The rotational relaxation time of this system in phase III at 213K is greater than 4.5 ns until it decays to the order of less than 0.5ns upon reaching phase I at 333K. Both the cation and anion exhibit slow dynamics in phase III and a slight possibility of anisotropic rotation in the functional groups is expected. The slower rotational relaxation time decay in the anion at all the temperatures is due to much larger inertia compared to the cation. The rotational autocorrelation functions of S1ÆC15 and S2ÆC16 are equivalent at all temperatures as the S-C bonds on the either sides of the central N in the anion are symmetrical. It was also observed that, the C-S bonds in the backbone of the anion do not rotate until the whole anion rotates at 383K, in the liquid phase, despite wagging and bending of some of the CF_{3} and SO_{2} functional groups starting from 213K. Thus, the slow decay we have seen in the C-S for the anion is in contrast with the vibrations observed in S=O or C-F. On the hand, the
comparison between the relaxation time obtained from the vector perpendicular to the pyrroloidinium ring and C-C ethyl in [C2mpyr]$^+$ shows that both the ring and C-C ethyl undergo rotation starting from the phase III as evidenced from the RDF and dihedral distribution studies. The occurrence of transformation from one anisotropic rotation to another such as ring inversion or flipping and/or additional anisotropic motions exist in the phases II and I as evidenced in the change of lattice structure. In general, from the inspection of the rotational autocorrelation function it can be concluded that the rotation vectors cannot decay to zero whilst the cation and anion are in fixed position (ie. not fully tumbling or diffusing). Hence at 383K, full decay of these vectors explain that the both cation and anion may undergo isotropic rotation after the melt. Furthermore, at 333K when vacancies are incorporated into the lattice, the cation and anion rotational dynamics are significantly enhanced.

Despite the onset of slow anisotropic rotation of the functional groups in the anion within the CF$_3$ and SO$_2$ and in the cation within the CH$_3$ and CH$_2$ groups respectively, starting from phase III at 213K, there was no evidence of anionic or cationic diffusion in this MD simulation at this temperature. This may be due to the shorter simulation time. The calculated anion and cation self - diffusion coefficients in this OIPC are three orders of magnitude lower than that of the ILs ($\sim 10^{-10}$ m$^2$/s) and slightly over the values $10^{-13} - 10^{-15}$ m$^2$/s in perfect crystals in phase I at 363K. The addition of vacancies did not significantly alter the self-diffusion of both cation and anion in the OIPC.

### 6.4. MD simulations in Na$^+$ Doped [Me$_4$N][N(CN)$_2$]- OIPC

Structural and dynamic properties of Na$^+$ doped [Me$_4$N][N(CN)$_2$] OIPC have been carried out using the MD simulation to gain an understanding on the mixed system in the temperature range of 200-500K.

From the RDF investigation of the mixed system, intense sharp, split peaks corresponding to the first co-ordination shell were concentrated within the regions 4 to 7 Å whilst the
second co-ordination shell was observed between 8 to 12 Å, at 200K with the addition of 5% Na⁺.

The presence of both short and long range orders and the sharp intense peaks in the RDF is due to strong confinement of atoms in their lattice positions even with the inclusion of 5% Na⁺ at 200K. The split in the \([N(CN)2^-][N(CN)2^-]\) might be attributed to different anion environment at this temperature and they eventually merge to be broadened with increasing temperature due to thermal disorder. With the addition of 15% Na⁺, some of the peaks observed in 5% Na⁺ showed either a shift in position (as in \([Me_4N]^+ [N(CN)2^-]\) or decrease in height and increase in breadth at the same temperature which indicate an expansion of the crystal structure. The disappearance in the second co-ordination shell at 300K and above is a clear indication of the loss of long-range order. In general, the mixed system of 15% Na⁺ undergoes higher disorder compared to the 5% Na⁺ system at this temperature could be explained in terms of the creation of more defects at 300K in these systems. The addition of both the 5% and 15%Na⁺ removes the long-range order even for phase IV of the OIPC. At temperatures above 400K, in phase II of the OIPC and beyond, broadened peaks were observed in both anion/cation species. Moreover, the \([N(CN)2^-][N(CN)2^-]\) shows amorphous, liquid like behavior upon addition of both 5% and 15%Na⁺.

At temperatures above 300K in phase III, the rotational autocorrelation functions undergo fast decays in both anion and cation systems (within less than 100ps) except for the C-N bond vector in the \([N(CN)2^-]\) had been observed upon addition of both 5% and 15%Na⁺ content of salt. The slightly slower decay in the C-N bond vector in the \([N(CN)2^-]\), for the 15%Na⁺ doped \([Me_4N][N(CN)2]\) compared to the 5%Na⁺ doped \([Me_4N][N(CN)2]\) system, shows that the rotation in the \([Me_4N]^+\) cation is enhanced whilst the rotation in the anion is restricted with the addition of more Na⁺ cations in the OIPC. For the rotation vectors perpendicular to \([N(CN)2^-]\) plane and in the \([N(CN)2^-]\) plane, the rotational autocorrelation
function decays slower with the increasing content of Na+, the decay in 15% Na+ content is slightly slower than for the 5% Na+ concentration.

In general, for a particular Na+ concentration, the rotational relaxation time rapidly decreases with the increase of temperature above 300K, which is explained by the possibility that, the anisotropic rotation of the ionic species at lower temperatures transforms to an isotropic rotation at higher temperatures in plastic and/or liquid phase with the introduction of more lattice defects and the lowering of the energy barriers in the otherwise rigid crystal phase. Different trends are observed in the anion rotational autocorrelation function with increasing Na+ concentration at all temperatures above 300K, due to more restricted anions as a result of aggregate/cluster formation. This observation agrees well with findings from the experimental study that confirms the existence of two different phases in a solid state. As the interaction with Na+ intensified with the increased concentrations of Na+ content, the formation of more defects is evident and the [Me₄N]⁺ cation rotates freely in the plastic phase.

In the liquid state at 500K, with both 5% and 15% Na+ content in the OIPC, the disorder facilitates the [Me₄N]⁺ cations to undergo isotropic rotational relaxation whilst the rotation in the [N(CN)₂]⁻ is still anisotropic due to steric hindrance to the anionic species as a result of aggregation/complexation.

The translational motion of the cations and anion species were monitored from a 3ns MD simulation. The self-diffusion coefficients of cations Me₄N⁺, Na⁺ and the [N(CN)₂]⁻ anion were calculated from the slope of the MSD straight lines. The calculated diffusion coefficients of the Me₄N⁺ cation and [N(CN)₂]⁻ anion at 300 K is in the order of ~10⁻¹² m²/s in 5% and 15% Na+ contents is an order of magnitude greater than in crystalline solids. In the 5% Na+ content, calculated self-diffusion coefficients at 350K increase from 2.1 x 10⁻¹¹ m²/s to 8.4 x 10⁻¹¹ m²/s in [Me₄N]⁺; 1.1 x 10⁻¹¹ m²/s to 3.7 x 10⁻¹¹ m²/s in Na⁺ and 3.3 x 10⁻¹¹ m²/s to 10.1 x 10⁻¹¹ m²/s in [N(CN)₂]⁻ respectively upon reaching 500K. However, in the
15% Na+ content OIPC system, the calculated self-diffusion coefficients of the ionic species is lower than the 5% content in the same temperature range of 350-500K varying from $1.5 \times 10^{-11}$ m$^2$/s to $6.7 \times 10^{-11}$ m$^2$/s in [Me$_4$N]$^+$; $0.6 \times 10^{-11}$ m$^2$/s to $3.1 \times 10^{-11}$ m$^2$/s in Na$^+$ and $2.0 \times 10^{-11}$ m$^2$/s to $7.5 \times 10^{-11}$ m$^2$/s in [N(CN)$_2$]. These ionic species attained full diffusion comparable to that of ILs $\sim 10^{-10}$ m$^2$/s at 500K in a liquid state is due to more free volume that facilitates the self-diffusion of all ionic species. It had been observed that the Na$^+$ had been less mobile than [Me$_4$N]$^+$ due to former’s aggregation with the [N(CN)$_2$].

6.5. Recommendations and Future Work

In this work the structure, phase behaviour and dynamics of organic ionic plastic crystals mixed with sodium salts of different anions was investigated through advanced experimental characterizations and molecular dynamics simulation. The work is believed to have a positive scientific contribution towards the realization of sodium ion solid state electrolytes in sodium ion energy storage and sources. As this area of research is at its infancy, there are much to work ahead for the proper utilization of these electrolytes in devices. Further studies on the structure and dynamical properties of Na$_x$[C$_2$mpyr]$_{1-x}$[BF$_4$] and Na$_x$[C$_1$mpyr]$_{1-x}$[N(CN)$_2$] binary mixtures using SXRD and solid state NMR are required. In the simulation work related to [C$_2$mpyr][NTf$_2$] OIPC, due to lower self-diffusion coefficient the calculated conductivity turns to be lower than experiment. Thus, in the area of molecular dynamics simulation there is a need for improved potential functions to calculate conductivity from self-diffusion coefficients. There was no test carried out in the devices and also no stability data was collected in this work. Therefore, important work ahead should be the testing and optimizing for use in the sodium ion batteries.
APPENDICES

A.I. Solid State NMR of Na Salt Mixed with N-ethyl-N-methylpyrrolidinium Tetrafluoroborate OIPC

Room temperature solid-state NMR was used to study the structural and dynamic behavior in the pure OIPC and Na salt mixed samples. The OIPC and samples of Na\(^+\) ion content were probed through NMR active nuclei of \(^1\)H, \(^{13}\)C to study the \([C_2mpyr]\) cation; \(^{11}\)B and \(^{19}\)F for the \([BF_4]\) anion and \(^{23}\)Na for the added Na\(^+\) ions. Furthermore, the \(^{13}\)C CPMAS spectra were used to study the local environment of OIPC cation.

Figure A-1 \(^1\)H RT-MAS solid-state NMR spectra for the mixtures Na\(_{0.04}[C_2mpyr]_{0.96}[BF_4]\) and Na\(_{0.15}[C_2mpyr]_{0.85}[BF_4]\).
Figure A-2 $^{19}$F RT-MAS solid-state NMR spectra for the mixtures Na$_{0.04}$[C$_2$mpyr]$_{0.96}$[BF$_4$] and Na$_{0.15}$[C$_2$mpyr]$_{0.85}$[BF$_4$].

Figure A-3 $^{13}$C RT-CPMAS solid-state NMR spectra for the mixtures Na$_{0.04}$[C$_2$mpyr]$_{0.96}$[BF$_4$] and Na$_{0.15}$[C$_2$mpyr]$_{0.85}$[BF$_4$].
Figure A- 4 $^{11}$B RT-MAS solid-state NMR spectra for the mixtures Na$_{0.04}$[C$_2$mpyr]$_{0.96}$[BF$_4$] and Na$_{0.15}$[C$_2$mpyr]$_{0.85}$[BF$_4$].

Figure A- 5 $^{23}$Na RT-MAS solid-state NMR spectra for the mixtures Na$_{0.04}$[C$_2$mpyr]$_{0.96}$[BF$_4$] and Na$_{0.15}$[C$_2$mpyr]$_{0.85}$[BF$_4$].
As it can be seen from Figure A-1, the proton NMR spectra of the samples of Na_{0.04}[C_{2}mpyr]_{0.96}[BF_{4}] and Na_{0.15}[C_{2}mpyr]_{0.85}[BF_{4}] did not show significant difference. Similarly, in the $^{13}$C CPMAS spectra (Figure A-3), very narrow signals were observed as in the proton NMR. However, the spectra were unaffected by Na$^{+}$ addition when compared with the spectra of pure OIPC [1,2]. The narrow lines in these spectra are attributed to high mobility and/or fast rotation of cation and the result correlates with the vibrations of predominant functional groups (CH$_{3}$, CH$_{2}$ as well the pyrrolidinium ring bending and stretching) of the cation discussed in relation to FTIR/Raman spectroscopy. Thus, the narrow lines in the proton and carbon signals indicate the high rotational disorder of the molecule averages out the dipolar interactions present in solids and thus decreases the line width in the solid-state spectra. On the other hand, it was not possible to distinguish between different phases in carbon spectra due to bad S/N.

The $^{11}$B spectra (see Figure A-4) are identical in the mixed samples and suggest that the average boron environment is unchanged. The narrow Boron signal indicates the occurrence of highly isotropic environment and fast motion of the anion. However, the $^{19}$F spectra (see Figure A-2) show several signals, one increasing with increasing Na$^{+}$ content indicating different [BF$_{4}$] environments and/or the possibility of different phases. One of the chemical shifts in 19F also corresponds to [BF$_{3}$·2Et$_{2}$O] is consistent with the previous report [3] that a molecular anion of tetrafluoroborate anion is Lewis acid/base complex involving BF$_{3}$ (Lewis acid) and the fluoride ion (Lewis base) and a Na[BF$_{4}$] forms a cluster ion of (Na[BF$_{4}$])$_{n}$Na$^{+}$ or (NaF)$_{n}$Na$^{+}$. In $^{23}$Na spectra (see Figure A-5) significant changes were observed with the content of Na$^{+}$ addition in the OIPC could be due to the variation in the
aggregation which traps mobile ions in the \([\text{C}_2\text{mpyr}]_x[\text{Na}]_{1-x}[\text{BF}_4]\) system. At this stage due low S/N, the deconvolution of \(^{23}\text{Na}\) spectra is not feasible.

References


A.II. Force field parameters for \([\text{C}_2\text{mpyr}][\text{NTf}_2]\) OIPC

### CHARMM parameter file for conversion to DL_POLY's FIELD file.
# To be used in conjunction with DL_FIELD.
# C W Yong November, STFC, Daresbury Laboratory.
# Revision 2.1 - 26 July 2011

#### POTENTIAL CHARMM

# \( V(b) = k(b - b0)^2 \)
# \( k = \) force constant with unit kcal/mole/A^2
# DL_FIELD will scale this as \( 2 \times k \) in FIELD file, because DL_POLY will rescale
# this as \( k/2 \).
# \( b0 = \) equilibrium length in A (angstrom)

<table>
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<th>( b0 )</th>
<th>remark</th>
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<tr>
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<td>1.0930</td>
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<tr>
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END BOND

# \( V(\theta) = K(\theta - \theta0)^2 \)
# \( K = \) force constant in unit kcal/mole/rad^2
# theta0 = equilibrium angle in degrees

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<th>Remark</th>
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### END ANGLE

# V(ub) = Kub(S - S0)^2
# ub = Urey-Bradley
# Kub = force constant in unit kcal/mole/A^2
# S0 = Equilibrium distance between atom 1-3 in unit angstrom
# DL_FIELD will scale force constants as 2*k in FIELD file, because DLPOLY
# will rescale this as k/2.

# V(Lennard-Jones) = \[E_{ij}(R_{min,ij}/r_{ij})^{12} - 2(R_{min,ij}/r_{ij})^{6}\]
# Eps in unit kcal/mole, Eps_{ij} = \sqrt(Eps_i * Eps_j)
# Rmin in unit angstrom, R_{min,ij} = R_{min,i} + R_{min,j}
# To convert to A/r^{12}-B/r^{6} form as in DL_POLY, use the following relationship
# A = 4*Eps*sigma^{12} and B = 4*Eps*sigma^{6} where sigma = R_{min,ij}/(2^{0.1666667})

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</table>

### END VDW

# V(dihedral) = Kchi(1 + cos(n(chi) - delta))
# Kchi: kcal/mole
# n = multiplicity
# delta = degrees
# Note: X-i-i-X must be listed towards the end of the DIHEDRAL

### DIHEDRAL

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-224-
NRP  CR   CR   HCMM  0.139  3     0.00
NRP  CR   CR   CR   -0.324  1     0.00
NRP  CR   CR   CR   0.275  2   180.00
NRP  CR   CR   CR   0.295  3     0.00
CR    NRP  CR   CR   0.125  3     0.00
CR    NRP  CR   HCMM  0.123  3     0.00
CR    CR   CR   HCMM  0.320  1     0.00
CR    CR   CR   CR   -0.315  2   180.00
CR    CR   CR   CR   0.132  3     0.00
CR    CR   CR   CR   0.051  1     0.00
CR    CR   CR   CR   0.341  2   180.00
CR    CR   CR   CR   0.166  3     0.00
HCMM CR   CR   HCMM  0.142  1     0.00
HCMM CR   CR   HCMM -0.693  2   180.00
HCMM CR   CR   HCMM  0.157  3     0.00
NSO2 SO2  CR1  F    0.050  3     0.00
SO2  NSO2 SO2  O2CM 0.175  3     0.00
SO2  NSO2 SO2  CR1 0.175  3     0.00
O2CM SO2  CR1  F    0.050  3     0.00

END DIHEDRAL

END POTENTIAL
TERMINATE

# CHARMM Structure file EMP_TFS for conversion to DLPOLY's FIELD file
# To be used in conjunction with DL_FIELD program
# Tarekegn Chimdi
# April 03 2012
# The ATOM_TYPE command is where the index of all types were being defined.
# Same elements in different molecules can have different chemical behaviour
# and hence different potential parameters.
# The key is the unique identity of the different types and is used to
# define the corresponding parameters.
ATOM_TYPE      key  element  mass     remark
N_EMP          NRP  N       14.0067  EMP_N
C_EMP          CR   C       12.011   EMP_C
H_EMP          HCMM H       1.00797 EMP_H
N_TFS          NSO2 N       14.0067  TFS_N
S_TFS          SO2  S       32.066   TFS_S
O_TFS          O2CM O       15.9994  TFS_O
C_TFS          CR1  C       12.011   TFS_C
F_TFS          F    F       18.9984  TFS_F

END ATOM_TYPE

# The MOLECULE_TYPE command is the index of all molecule types are
# defined. The corresponding key type is used in the configuration (.pdb)
# file to identify the particular molecular residue.

-225-
# Note: Hyphens mean it is a residue that is used to link to other molecules.
# To find out what is available: First work out the molecular weight using
# the values shown below then look for molecules correspond to this weight.
# H=1.00797  O=15.99940   S=32.066  N=14.0067   C=12.0110
# F=18.9984

MOLECULE_TYPE    key      mw        remark
EMP              EMP      114.21074 cation
TFS              TFS      280.1487   anion
END MOLECULE_TYPE

# List of molecules fitted according to the CHARMM formalism.
# Format:
# MOLECULE molecule_name total_atoms total_charge
# Atom_label  Atom_type  Charge
# Note: Every Atom_label must be unique in each MOLECULE
#       The CONNECT statement sequence must follow that of atom
#       definitions.# CHARMM Structure file EMP_TFS for conversion to DLPOLY’s FIELD file
# To be used in conjunction with DL_FIELD program
# Tarekegn Chimdi
# April 03 2012

MOLECULE EMP 24 1.0
N1   N_EMP -1.0120
C1   C_EMP  0.5030
H1A  H_EMP  0.0000
H1B  H_EMP  0.0000
C2   C_EMP  0.0000
H2A  H_EMP  0.0000
H2B  H_EMP  0.0000
C3   C_EMP  0.0000
H3A  H_EMP  0.0000
H3B  H_EMP  0.0000
C4   C_EMP  0.5030
H4A  H_EMP  0.0000
H4B  H_EMP  0.0000
C5   C_EMP  0.5030
H5A  H_EMP  0.0000
H5B  H_EMP  0.0000
C6   C_EMP  0.0000
H6A  H_EMP  0.0000
H6B  H_EMP  0.0000
H6C  H_EMP  0.0000
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H7A  H_EMP  0.0000
H7B  H_EMP  0.0000
H7C  H_EMP  0.0000
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CONNECT C1 > N1 C2 H1A H2A

- 226 -
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CONNECT H1B > C1
CONNECT C2 > C1 C3 H2A H2B
CONNECT H2A > C2
CONNECT H2B > C2
CONNECT C3 > C2 C4 H3A H3B
CONNECT H3A > C3
CONNECT H3B > C3
CONNECT C4 > N1 C3 H4A H4B
CONNECT H4A > C4
CONNECT H4B > C4
CONNECT C5 > N1 H5A H5B C6
CONNECT H5A > C5
CONNECT H5B > C5
CONNECT C6 > C5 H6A H6B H6C
CONNECT H6A > C6
CONNECT H6B > C6
CONNECT H6C > C6
CONNECT C7 > N1 H7A H7B H7C
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CONNECT H7C > C7
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O5 O_TFS -0.53
O6 O_TFS -0.53
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F7 F_TFS -0.16
F8 F_TFS -0.16
F9 F_TFS -0.16
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CONNECT F9 > C17
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CONNECT O7 > S4
CONNECT O8 > S4
CONNECT C18 > S4 F10 F11 F12
CONNECT F10 > C18
CONNECT F11 > C18
CONNECT F12 > C18
A.III. Force field parameters for Na⁺ Doped [Me₄N][N(CN)₂]-OIPC

# CHARMM parameter file for conversion to DL_POLY's FIELD file.
# To be used in conjunction with DL_FIELD.
# C W Yong November, STFC, Daresbury Laboratory.
# Revision 2.1 - 26 July 2011

# Parameter from c32b1 directory

POTENTIAL CHARMM

# V(b) = k(b - b0)^2
# k = force constant with unit kcal/mole/A^2
# DL_FIELD will scale this as 2*k in FIELD file, because DL_POLY will rescale
# this as k/2.
# b0 = equilibrium length in Å (angstrom)

BOND k b0 remark
CT HT 771 0.9931 average all methyl C-H bonds
CT NT 719 1.4987 average all TMA C-N bonds
CD ND1 1278 1.3120 average both DCA N-C bonds
CD ND2 2075 1.1539 average both DCA C---N bonds

END BOND

# V(theta) = K(theta - theta0)^2
# K = force constant in unit kcal/mole/rad^2
# theta0 = equilibrium angle in degrees
#
# V(ub) = Kub(S - S0)^2
# ub = Urey-Bradley
# Kub = force constant in unit kcal/mole/A^2
# S0 = Equilibrium distance between atom 1-3 in unit angstrom
# DL_FIELD will scale force constants as 2*k in FIELD file, because DL_POLY
# will rescale this as k/2.

ANGLE K theta0 Kub S0 Remark
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NT CT HT 111 107.21 0.0 0.0 TMA N-C-H
HT CT HT 73 111.74 0.0 0.0 TMA H-C-H
CD ND1 CD 70 120.71 0.0 0.0 DCA C-N-C
ND1 CD ND2 93 173.25 0.0 0.0 DCA N---C-N

END ANGLE
# V(Lennard-Jones) = Eps_ij[(Rmin_ij/r_ij)**12 - 2(Rmin_ij/r_ij)**6]
# Eps in unit kcal/mole, Eps_ij = sqrt(Eps_i*Eps_j)
# Rmin in unit angstrom, Rmin_ij = Rmin_i+Rmin_j
# To convert to A/r^12-B/r^6 form as in DL_POLY, use the following relationship
# A = 4*Eps*sigma^12 and B = 4*Eps*sigma^6 where sigma = Rmin_ij/(2^0.1666667)

VDW   Eps    Rmin/2   Eps_1-4  Rmin/2,1-4  Remark
CT    0.02   2.1720   0.0      0.0
HT    0.0055 1.3919   0.0      0.0
NT    0.05   1.9531   0.0      0.0
ND1   0.05   1.9531   0.0      0.0
CD    0.0225 1.9026   0.0      0.0
ND2   0.05   1.9531   0.0      0.0
Na    0.0469 2.7275 0.0      0.0
END VDW

# V(dihedral) = Kchi(1 + cos(n(chi) - delta))
# Kchi: kcal/mole
# n = multiplicity
# delta = degrees
# Note: X-i-i-X must be listed towards the end of the DIHEDRAL

DIHEDRAL         Kchi   n   delta  Remark
HT  CT  NT  CT     0    0     0
CT  NT  CT  HT     0    0     0
CD  ND1 CD  ND2    0 0     0
ND2 CD  ND1 CD     0    0     0
END DIHEDRAL

END POTENTIAL
TERMINATE

# CHARMM Structure file TMA_DCA for conversion to DLPOLY's FIELD file
# To be used in conjunction with DL_FIELD program
# Tarekegn Chimdi
# June 25 2012

# The ATOM_TYPE command is where the index of all atom types were being defined.
# Same elements in different molecules can have different chemical behaviour
# and hence different potential parameters.
# The key is the unique identity of the different atom types
# and is used to define the corresponding parameters.

ATOM_TYPE      key  element mass     remark
C_TMA          CT   C       12.011   TMA_C
C_DCA          CD   C       12.011   DCA_C
H_TMA          HT   H       1.00797 TMA_H
N_TMA          NT   N       14.0067 TMA_N
N_DCA1         ND1  N       14.0067 DCA_N1
N_DCA2         ND2  N       14.0067 DCA_N2
Na_ion         Na   Na      22.990   Na_ions
The MOLECULE_TYPE command is the index of all molecule types as defined. The corresponding key type is used in the configuration (.pdb) file to identify the particular molecular residue. Note: Hyphens mean it is a residue that is used to link to other molecules.

To find out what is available: First work out the molecular weight using the values shown below then look for molecules corresponding to this weight.

\[
\begin{align*}
\text{H} &= 1.00797 \\
\text{O} &= 15.99940 \\
\text{S} &= 32.065 \\
\text{N} &= 14.0067 \\
\text{C} &= 12.0110 \\
\text{ZN} &= 65.37 \\
\text{Cl} &= 35.453
\end{align*}
\]

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<td>cation</td>
</tr>
</tbody>
</table>

List of molecules fitted according to the CHARMM formalism.

Format:

MOLECULE molecule_name total_atoms total_charge

Atom label Atom_type Charge

Note: Every Atom_label must be unique in each MOLECULE. The CONNECT statement sequence must follow that of atom definitions.

MOLECULE TMA 17 1.0

C1  C_TMA -0.277
H11 H_TMA 0.16
H12 H_TMA 0.16
H13 H_TMA 0.16
C2  C_TMA -0.277
H21 H_TMA 0.16
H22 H_TMA 0.16
H23 H_TMA 0.16
C3  C_TMA -0.277
H31 H_TMA 0.16
H32 H_TMA 0.16
H33 H_TMA 0.16
C4  C_TMA -0.277
H41 H_TMA 0.16
H42 H_TMA 0.16
H43 H_TMA 0.16
N  N_TMA 0.188

CONNECT C1 > H11 H12 H13 N
CONNECT H11 > C1
CONNECT H12 > C1
CONNECT H13 > C1
CONNECT C2 > H21 H22 H23 N
CONNECT H21 > C2
CONNECT H22 > C2
CONNECT H23 > C2
CONNECT C3 > H31 H32 H33 N
CONNECT H31 > C3
CONNECT H32 > C3
CONNECT H33 > C3
CONNECT C4 > H41 H42 H43 N
CONNECT H41 > C4
CONNECT H42 > C4
CONNECT H43 > C4
CONNECT N > C1 C2 C3 C4
END MOLECULE

MOLECULE DCA 5 -1.0
N1     N_DCA1  -0.7018
C1     C_DCA    0.5797
C2     C_DCA    0.5797
N21    N_DCA2  -0.7288
N22    N_DCA2  -0.7288
CONNECT N1 > C1 C2
CONNECT C1 > N1 N21
CONNECT C2 > N1 N22
CONNECT N21 > C1
CONNECT N22 > C2

MOLECULE Na 1 1.0
Na     Na_ion 1.0

END MOLECULE

TERMINATE