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Exploring the use of ionic liquid mixtures to enhance the performance of dicationic ionic liquids

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Dicationic ionic liquids (DILs) of diverse structural architectures (including symmetrical and asymmetrical ammonium, phosphonium and heterodications and the bis(trifluoromethylsulfonyl)amide (NTf₂⁻) anion) have been prepared and used as additives to *N*-methyl-*N*-ethoxyethylpyrrolidinium (P₁EOE) NTf₂, a relatively high-performing IL in terms of its transport properties (viscosity 53 mPa s). The three-ion, binary IL mixtures were characterized for their thermal and transport properties using differential scanning calorimetry, temperature dependent viscosity, conductivity and Pulsed Gradient Spin Echo (PGSE) NMR. Variable temperature ¹H, ¹⁹F and ³¹P self-diffusion coefficients were determined at 25, 60 and 75 °C. The order of the diffusion coefficients was D(P₁EOE⁺) > D(anion) > D(dication), and the composition of the dication had a strong effect on the degree to which diffusion of all three species is more or less coupled. IL mixtures containing about 30 mol % of the dicationic NTf₂ and 70 mol % of P₁EOE NTf₂ resulted in a significant decrease in glass transition temperatures and viscosities compared to the pure DIL. The mixtures extended the liquid range and potential for practical applications significantly. The data obtained here provides insight into the future design of dicationic salts tailored to exhibit lower viscosity and higher conductivities.

Introduction

Dicationic ionic liquids (DILs) have received far less attention compared to the popular monocationic ILs based on imidazolium, pyrrolidinium or tetraalkylammonium. However, there are some literature reports on the synthesis and characterization of dicationic ILs that cite their advantages over monocationic ILs. Some time ago, Lall, Engel and collaborators reported the synthesis and properties of several series of functionalized geminal ammonium-based phosphate DILs among other polycationic salts.¹⁻⁴ Ohno and co-workers also reported on imidazolium based DILs⁵ and DILs containing polyether bridges.⁶ The synthesis and properties (including thermal stability and viscosity) of symmetrical and asymmetrical DILs based on imidazolium, pyrrolidinium and ammonium ions have also been reported by Armstrong and co-workers.^{7,8} Shirota et al. recently reported a comparison between the properties of DILs and monocationic ILs including density, thermal properties, surface tension and viscosity.⁹ They reported higher densities, higher glass transition temperatures and melting points, higher thermal stabilities, larger surface tensions and higher shear viscosities for the DILs. A few other groups have also reported on the thermal properties and conductivity of DILs.^{10,11} Compared to monocationic ILs, dicationic ILs exhibit much higher thermal degradation temperatures (200-400 °C, likely related

to lower volatility),^{12,13} wider liquid ranges, and electrochemical windows in the range of 4.3 V to 4.7 V.¹² These properties make them attractive as electrolytes in high-temperature batteries¹⁴ and dye-sensitized solar cells.¹⁵ Geminal DILs have also been proposed as advantageous when used as solvents in high temperature reactions,^{16,17} as high temperature lubricants,¹⁸ and as stationary phases for gas chromatography capillary columns.¹⁹⁻²¹ Despite the particular advantages of DILs over their monocationic counterparts, they suffer from higher melting points and viscosities. Payagala et al.⁸ showed that asymmetrical DILs can have lower melting points than symmetrical DILs. In addition, the longer the length of the carbon chain linking the two cationic sites, the lower the melting point. The length of the substituents has a similar effect on the melting point. Several researchers have reported on asymmetrical DILs,^{8,22} which provide a greater degree of flexibility to tune the properties of ILs for specific applications. For example, Huang et al.²³ incorporated a diether bridge between imidazolium monocations to make DILs. They added the DILs to the monocationic IL, 1-ethyl-3-methylimidazolium NTf₂, and reported the mixture as an improved IL electrolyte for use in electric double layer capacitors. Some researchers have also added organic solvents to DILs to enhance their performance as liquid electrolytes. However, the safety hazard of flammable organic solvents still exists in such electrolyte mixtures. In this work we focus on the synthesis and characterization of IL mixtures containing symmetrical and asymmetrical DILs as additives to a high-performing, ether-functionalized monocationic IL.

Ionic Liquid Mixtures

Ionic liquid (IL) mixtures are gaining popularity as a means to access the attractive properties of individual ILs while minimizing less desirable characteristics that impede their large-scale adoption.^{6,14} In some instances an IL exhibits superior properties in one area (such as viscosity or conductivity) but falls short of requirements in another (such as electrochemical stability). For this reason, mixing two ILs together so that their favorable properties complement each other is a convenient pathway to take advantage of their desirable properties beyond what is feasible by structural modification of the individual ions of single ILs. For example, imidazolium ILs exhibit the desired low viscosities and high conductivities for battery electrolytes, but they have relatively narrow electrochemical windows due to the reduction of the cations at the cathode. Ammonium and pyrrolidinium ILs have larger electrochemical windows but higher viscosities. Hence, there exists a need for new types of ILs that exhibit the desirable set of properties in order to fully realize the potential of ILs to improve the performance of devices like batteries and supercapacitors. In particular, replacements are being sought for electrolytes based on organic solvents that are flammable. Mixtures based on ILs with different cations and a common anion,²⁴ the same cation with different lengths of alkyl chains and the same anion,²⁵ or with different anions are now being designed and characterized. Another approach is to add a lithium salt with a different anion to the IL,^{26,27} in particular lithium fluorosulfonylamide (FSA) to ILs containing bis(trifluoromethylsulfonyl)amide or NTf₂.^{28,29} There are several applications reported for IL mixtures as solvents for chemical synthesis and process chemistry,³⁰⁻³² for electrochemical applications (dye sensitized solar cells,^{33,34} batteries²⁴), in chromatography³⁵ and for the absorption of CO₂.³⁶ In most cases an enhancement in the properties are obtained from mixing the ILs together. In particular, depression of the glass transition temperature (T_g), widening of the liquid range, viscosity decreases, and conductivity increases have been reported.³⁷

Ionic Liquid Mixtures Containing Dications

Mixtures of ILs containing dications are relatively unexplored compared to IL mixtures comprised of monocations. Dicationic ILs are attractive candidates for use where increased charge density is desired. Dications also provide an additional parameter to tune IL properties by strategic manipulation of the individual monocationic sites or the bridging chain. We report herein on mixtures containing symmetrical and asymmetrical dications. The asymmetrical

dications combine imidazolium and pyrrolidinium groups tethered to trimethylammonium or triphenylphosphonium functionalities. The advantages of the imidazolium and pyrrolidinium cations in ILs are well established. Recently Davis and co-workers reported on the superior thermal stability of ILs based on arylphosphonium cations, and interest in their properties as IL cations is growing rapidly.³⁸ The major component of the mixtures we discuss in this report, *N*-ethoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide, P₁EOE NTf₂, exhibits favorable transport properties. The common anion of the mixtures is the NTf₂ anion, which is known to produce ILs exhibiting favorable transport properties and chemical stability. This work continues our exploration of the transport properties of IL mixtures containing dicationic species. Here we delve deeper into the viscosity and conductivity of the mixtures and use self-diffusion coefficients of the ions to aid our understanding of the ion dynamics.

Figure 1. Structures of the various NTf₂ ionic liquids used to make mixtures with *N*-ethoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (P₁EOE NTf₂)

Experimental

Materials. All chemicals used for syntheses were of reagent grade. They were obtained from Sigma-Aldrich and used as received, except for lithium bis(trifluoromethylsulfonyl)amide, which was obtained from IoLiTec Inc. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. ¹H-NMR and ¹³C-NMR spectra of all ILs except IL #3 below are provided in the Supporting Information.

Synthesis.

1. Synthesis of 1,6-bis(1-methylimidazolium)hexane chloride ((MimC₆Mim Cl₂):

1-methylimidazole (10.00 g, 121.8 mmol) was reacted with one-half equivalent of 1,6-dichlorohexane (9.44 g, 60.9 mmol) in a round bottom flask. The reaction was conducted under reflux at 60°C with 20 mL of ethyl acetate for 72 hours. The resulting white precipitate was

washed with ethyl acetate under vacuum filtration to remove any remaining starting material. The product was a white solid (14.6 g, 75.1%, 319.3 g/mol), ^1H (400 MHz; D_2O) δ 1.37-1.47 (m, 4H), 1.90-1.91 (m, 4H), 3.92 (s, 6H), 4.20-4.24 (m, 4H), 7.46 (s, 2H), 7.50 (s, 2H), 8.74 (s, 2H), ^{13}C (101 MHz; D_2O) δ 24.8, 28.9, 35.5, 49.3, 122.0, 123.4, 135.8. CAS number 349081-21-6.

2. Synthesis of 1,6-bis(1-methylimidazolium)hexane bis((trifluoromethyl)sulfonyl)amide ($\text{MimC}_6\text{Mim}(\text{NTf}_2)_2$):

$\text{MimC}_6\text{Mim Cl}_2$ (14.6 g, 61.6 mmol) dissolved in 30 mL of distilled water was reacted with two equivalents of lithium bis(trifluoromethylsulfonyl)amide (35.3 g, 123 mmol) dissolved in 50 mL of distilled water at room temperature for 24 hours. The resulting product was a liquid and was washed with distilled water, then dried through rotary evaporation and placed in a high vacuum oven at 60°C for several days. The resulting product was a yellow liquid (30.8 g, 61.7%, 808.6 g/mol, Water Content: 53 ppm, ^1H (400 MHz; $\text{DMSO}-d_6$) δ 1.28 (m, 4H), 1.77-1.80 (m, 4H), 3.85 (s, 6H), 4.13-4.16 (t, 4H), 7.68 (s, 2H), 7.73 (s, 2H), 9.08 (s, 2H), ^{13}C (101 MHz; $\text{DMSO}-d_6$) δ 24.9, 29.1, 48.7, 114.7, 117.9, 121.10, 124.4, 136.49. Water content: 55 ppm. CAS number 844468-63-9.

3. Synthesis of 1-trimethylammonium-5-(1-methylimidazolium)pentane bromide ($(\text{CH}_3)_3\text{NC}_5\text{Mim Br}_2$):*

(5-bromopentyl)trimethylammonium bromide (4.73 g, 16.4 mmol) was reacted with one equivalent of 1-methylimidazole (1.35g, 16.4 mmol) in a round bottom flask. The reaction was carried out under reflux at 60°C with 20 mL of acetonitrile. The resulting product was a viscous yellow liquid (6.08 g, 99.9%, 371.2 g/mol), ^1H (400 MHz; D_2O) δ 1.40-1.46 (m, 2H), 1.84-1.89 (m, 2H), 1.90-2.0 (m, 2H), 3.15 (s, 9H), 3.33-3.37 (m, 2H), 3.93 (s, 3H), 4.26 (t, 2H, $J = 3.6\text{Hz}$), 7.48 (s, 1H), 7.52 (s, 1H), 8.76 (s, 1H), ^{13}C (101 MHz; D_2O) δ 21.9, 22.3, 28.9, 35.7, 49.1, 52.9, 66.2, 122.2, 123.6, 135.9. CAS number 929089-60-1. *The synthesis of this compound has been previously reported by Payagala et al.⁸

4. Synthesis of 1-trimethylammonium-5-(1-methylimidazolium)pentane bis((trifluoromethyl)sulfonyl)amide ($(\text{CH}_3)_3\text{NC}_5\text{Mim}(\text{NTf}_2)_2$):

$(\text{CH}_3)_3\text{NC}_5\text{Mim Br}_2$ (6.08 g, 16.4 mmol) dissolved in 25 mL of distilled water was reacted with two equivalents of lithium bis(trifluoromethylsulfonyl)amide (9.42 g, 32.8 mmol) dissolved in 25 mL of distilled water at room temperature for 24 hours. The resulting product was a yellow liquid that was washed with distilled water, then dried through rotary evaporation and placed in a high vacuum oven at 60°C for several days (7.82 g, 61.8%, 771.6 g/mol), Water Content: 120 ppm. ^1H (400 MHz; $\text{DMSO}-d_6$) δ 1.20-1.28 (m, 2H), 1.66-1.74 (m, 2H), 1.80-1.87 (m, 2H), 3.04 (s, 9H), 3.23-3.27 (m, 2H), 3.85 (s, 3H), 4.19 (t, 2H, $J = 4\text{ Hz}$), 7.70 (s, 1H), 7.74 (s, 1H), 9.09 (s, 1H), ^{13}C (101 MHz; $\text{DMSO}-d_6$) δ 21.5, 22.3, 28.9, 35.73, 48.5, 52.2, 65.0, 114.7, 117.9, 121.1, 124.3, 136.5. Water content: 74 ppm. CAS number 929089-62-3.

5. Synthesis of 1-triphenylphosphonium-4-(1-methylimidazolium)butane bromide ($(\text{Ph})_3\text{PC}_4\text{Mim Br}_2$)

(4-bromobutyl)triphenylphosphonium bromide (5.00 g, 10.5 mmol) was reacted with one equivalent of 1-methylimidazole (.862 g, 10.5 mmol) in a round bottom flask. The reaction was carried out under reflux at 100°C with 100 mL of acetonitrile. The resulting product was initially a viscous yellow liquid that crystallized upon being dissolved in hot acetonitrile and adding cold ethyl acetate, yielding a white solid (3.84 g, 65.5%, 560.3 g/mol), ^1H (400 MHz; $\text{DMSO}-d_6$) δ 1.49-1.57 (m, 2H), 1.98-2.07 (m, 2H), 3.57-3.65 (t, 2H), 3.83 (s, 3H), 4.23-4.26 (t, 2H), 7.69-7.93 (m, 17H), 9.02 (s, 1H), ^{13}C (101 MHz; DMSO) δ 18.5, 19.5, 29.9, 35.8, 47.6, 117.8, 122.2, 123.6, 130.19, 133.6, 134.9, 136.5.

6. Synthesis of 1-triphenylphosphonium-4-(1-methylimidazolium)butane

bis(trifluoromethylsulfonyl)amide ((Ph)₃PC₄Mim (NTf₂)₂)

(Ph)₃PC₄Mim Br₂ (3.84, 6.85 mmol) dissolved in 15 mL of distilled water was reacted with two equivalents of lithium bis(trifluoromethylsulfonyl)amide dissolved in 15 mL of distilled water at room temperature for 24 hours. The resulting product was a white salt which was washed with distilled water, then dried through rotary evaporation and placed in a high vacuum oven at 60°C for several days. (5.32 g, 80.9%, 960.8 g/mol), ¹H (400 MHz; DMSO-*d*₆) δ 1.52-1.54 (m, 2H), 1.96-1.99 (m, 2H), 3.57-3.65 (t, 2H), 3.83 (s, 3H), 4.19-4.22 (t, 2H), 7.66-7.94 (m, 17H), 9.02 (s, 1H), ¹³C (101 MHz; DMSO-*d*₆) δ 18.6, 19.5, 30.1, 35.8, 47.7, 117.8, 118.6, 121.1, 122.2, 123.7, 130.2, 133.5, 134.9, 136.5.

7. Synthesis of 1-trimethylammonium-5-(1-methylpyrrolidinium)pentane bromide

((CH₃)₃NC₅Mpyrr Br₂)

(5-bromopentyl)trimethylammonium bromide (4.93 g, 17.1 mmol) was reacted with one equivalent of 1-methylpyrrolidine (1.45 g, 17.1 mmol) in a round bottom flask. The reaction was carried out under reflux at 60°C with 30 mL of acetonitrile. The resulting product was a viscous brown liquid that crystallized upon dissolving in hot ethanol and then adding cold ethyl acetate to yield a tan-colored salt (2.91 g, 45.6%, 374.2 g/mol), ¹H (400 MHz; D₂O) δ 1.43-1.50 (m, 2H), 1.85-1.95 (m, 4H), 2.23 (s, 4H), 3.07 (s, 3H), 3.14 (s, 9H), 3.35-3.40 (m, 4H), 3.50-3.56 (m, 4H), ¹³C (101 MHz; D₂O) δ 21.3, 22.0, 22.6, 22.8, 48.0, 52.9, 63.7, 64.4, 66.09. CAS number 109042-73-1.

8. Synthesis of 1-trimethylammonium-5-(1-methylpyrrolidinium)pentane

bis((trifluoromethyl)sulfonyl)amide ((CH₃)₃NC₅Mpyrr (NTf₂)₂)

((CH₃)₃NC₅Mpyrr Br₂) (2.91 g, 7.78 mmol) dissolved in 15 mL of distilled water was reacted with two equivalents of lithium bis(trifluoromethylsulfonyl)amide (4.47 g, 15.6 mmol) dissolved in 15 mL of distilled water at room temperature for 24 hours. The resulting product was a tan salt which was washed with distilled water, then dried through rotary evaporation and placed in a high vacuum oven at 60°C for several days (2.92 g, 48.4%, 774.8 g/mol), ¹H (400 MHz; DMSO-*d*₆) δ 1.28-1.31 (m, 2H), 1.73-1.77 (m, 4H), 2.10 (s, 4H), 2.98 (s, 3H), 3.05 (s, 9H), 3.25-3.48 (m, 8H), ¹³C (101 MHz; DMSO-*d*₆) δ 21.1, 21.6, 22.5, 22.7, 47.5, 52.2, 62.6, 63.5, 64.9, 114.6, 117.8, 121.0, 124.2.

9. Synthesis of 1-triphenylphosphonium-4-(1-methylpyrrolidinium)butane bromide

((Ph)₃PC₄Mpyrr Br₂)

(4-bromobutyl)triphenylphosphonium bromide (5.00 g, 10.5 mmol) was reacted with one equivalent of 1-methylpyrrolidine (0.894 g, 10.5 mmol) in a round bottom flask. The reaction was carried out under reflux at 60°C with 40 mL of ethanol. The resulting product was a tan-colored salt that was washed with ethyl acetate in an ultra-fine frit under vacuum filtration (5.66 g, 86.5%, 563.4 g/mol), ¹H (400 MHz; D₂O) δ 1.75-1.85 (m, 2H), 1.99-2.07 (m, 2H), 2.21 (s, 4H), 3.03 (s, 3H), 3.31-3.35 (t, 2H), 3.41-3.55 (m, 6H), 7.69-7.89 (15H) ¹³C (101 MHz; D₂O) δ 19.1, 20.1, 21.2, 24.1, 48.1, 62.9, 64.5, 118.1, 130.1, 133.5, 135.1.

10. Synthesis of 1-triphenylphosphonium-4-(1-methylpyrrolidinium)butane

bis((trifluoromethyl)sulfonyl)amide ((Ph)₃PC₄Mpyrr (NTf₂)₂)

(Ph)₃PC₄Mpyrr Br₂ (5.66 g, 10.0 mmol) dissolved in 20 mL of distilled water was reacted with two equivalents of lithium bis(trifluoromethylsulfonyl)amide (5.74, 20.0 mmol) dissolved in 20 mL of distilled water at room temperature for 24 hours. The resulting product was a tan salt which was washed with distilled water under vacuum filtration in an ultra-fine sintered glass frit, then dried through rotary evaporation and placed in a high vacuum oven at 60°C for several days

(9.50 g, 98.5%, 963.8 g/mol), ^1H (101 MHz; DMSO- d_6) δ 1.59-1.61 (m, 2H), 1.89-1.93 (m, 2H), 2.09 (s, 4H), 2.97 (s, 3H), 3.31-3.49 (t, 2H), 3.62-3.66 (m, 6H), 7.79-7.95 (m, 15H) ^{13}C (400 MHz; DMSO- d_6) δ 19.0, 20.1, 23.7, 23.8, 47.6, 61.9, 63.6, 114.6, 117.8, 121.0, 124.2, 130.2, 133.5, 135.0.

The syntheses of *N,N,N',N'*-tetradimethyl-1,6-hexanediammonium bis(trifluoromethylsulfonyl)-amide [SE6 NTf₂] (CAS number 941584-19-6) and *N*-(2-ethoxyethyl)-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide [P₁EOE NTf₂] (CAS number 663628-46-4) have been previously reported by this group.³⁹

Mixtures: The binary mixtures were prepared in a glove tent in a low moisture environment with 50:50 compositions by weight of the dicationic IL and P₁EOE NTf₂, equivalent to 31-36 mol % of the dicationic component. The water contents for the mixtures were as follows: MimC₆Mim(NTf₂)₂ / P₁EOENTf₂: 103 ppm, (CH₃)₃NC₅Mim(NTf₂)₂ / P₁EOENTf₂: 113 ppm, (Ph)₃PC₄Mim(NTf₂)₂ / P₁EOENTf₂: 68 ppm, (Ph)₃PC₄Mpyrr(NTf₂)₂ / P₁EOENTf₂: 107 ppm, (CH₃)₃PC₅Mpyrr(NTf₂)₂ / P₁EOENTf₂: 72 ppm.

Physical measurements: Water contents of the ionic liquid samples were determined using a Mettler Toledo DL39 coulometric Karl Fischer titrator connected to an analytical balance. The water contents of the samples used for the physical property measurements ranged from 68-155 ppm.

Viscosities were measured with a Cambridge Applied Systems ViscoLab 4100 electromagnetic reciprocating piston viscometer that was temperature regulated by a Lauda RM-6 circulating bath a 70/30 v/v propylene glycol/water mixture. The viscometer was calibrated with S600S viscosity reference standard from Koehler Instrument Company (Bohemia, NY). Viscosities for the ILs were recorded at intervals between -6 and 96 °C in ascending and descending order within their liquid ranges.

Thermal profiles: A TA Instruments Q100 Differential Scanning Calorimeter (DSC) was used to determine melting points and glass transition onset temperatures (T_g). Scan rates were 5 °C/min over temperature ranges of -170 to 70 °C for room-temperature liquids and -170 to 120 °C for solid samples. The data were analyzed using TA Universal Analysis 2000 software.

Variable temperature ionic conductivities were determined using a Yellow Springs Instruments YSI 3200 conductivity meter using a YSI 3253 probe that was temperature regulated by a Lauda RM-6 recirculating water bath and housed in a moisture controlled dry box. The conductivity meter was calibrated using Hanna conductivity standards (NIST standardized KCl and AgNO₃ solutions, 1413 $\mu\text{S}/\text{cm}$, Sigma-Aldrich USA).

Densities were determined gravimetrically using a 1 mL volumetric flask.

Self-diffusion coefficients of ^1H , ^{19}F , and ^{31}P nuclei were measured with a Varian 300 WB Direct Drive spectrometer equipped with a DOTY z-gradient probe operating at 301.4, 283.6 and 122.0 MHz, respectively. Experiments were done at 25, 60 and 75 °C. All diffusion measurements were done using a stimulated echo sequence,⁴⁰ except the experiments performed at 60 and 75 °C for the samples (CH₃)₃NC₅Mim(NTf₂)₂, (CH₃)₃NC₅Mpyrr(NTf₂)₂, and MimC₆Mim(NTf₂)₂. In these latter cases a double-stimulated echo sequence was used to suppress convection artifacts.⁴¹ Recovery delays d_1 of 5-12 s, gradient pulses durations δ of 2-3 ms, and diffusion delay Δ of 50-300 ms were used. The gradient strength g was linearly increased from 2 up to 900 G cm⁻¹ as needed. ^{31}P and ^{19}F experiments consisted of arrays of 16 g values, whereas 32 g values were

used for ^1H experiments. Water at 25°C was used as the gradient calibration reference for the self-diffusion coefficient measurements. The value of $2.3 \times 10^{-9} \text{ m}^2/\text{s}$ was used and the estimated error in the self-diffusion coefficients was at most 5%.

Results and Discussion

The physicochemical properties of seven pure bis(trifluoromethylsulfonyl)amide (NTf_2) ionic liquids and 50 weight % binary mixtures of them with *N*-ethoxyethyl-*N*-methylpyrrolidinium NTf_2 ($\text{P}_1\text{EOE NTf}_2$) were determined. In all cases the cation was dicationic (containing two quaternary ammonium or imidazolium sites, or one phosphonium site with one ammonium or imidazolium site). The common anion for all of the ILs was NTf_2 , giving rise to binary IL mixtures⁶ or three-ion Double Salt Ionic Liquids (DSILs).⁴²

Thermal Properties. The phase transitions of the pure ionic liquids as well as their binary mixtures were determined from their DSC thermograms and are shown in Table I. In all cases the glass transition temperatures of the mixtures lie in between those of the pure ILs. In all but three cases, the pure ILs and their mixtures did not crystallize and melting points were not observed. The exceptions are the pure dicationic NTf_2 salts bearing triphenylphosphonium, $((\text{Ph})_3\text{PC}_4\text{Mpyrr} (\text{NTf}_2)_2$ melts at 109°C and $(\text{Ph})_3\text{PC}_4\text{Mim} (\text{NTf}_2)_2$ melts at 71°C), and trimethylpentylammonium methylpyrrolidinium, $((\text{CH}_3)_3\text{NC}_5\text{Mpyrr} (\text{NTf}_2)_2$ which melts at 53°C . However, the 50 weight % mixtures of these solids with $\text{P}_1\text{EOE NTf}_2$ did not crystallize. This behavior underscores the utility of IL mixtures as a means of extending their useful properties. In this case the liquid range has been extended as far as the glass transition temperature, making these IL mixtures suitable for use in low-temperature applications. MacFarlane's group made a similar observation when analyzing IL mixtures.³⁷ The pure heterodications containing triphenylphosphonium sites exhibited the highest T_g values and the highest melting points. $(\text{Ph})_3\text{PC}_4\text{Mim} (\text{NTf}_2)_2$ has a T_g of -20°C and a melting point of 71°C while $(\text{Ph})_3\text{PC}_4\text{Mpyrr}(\text{NTf}_2)_2$ has a T_g of -17°C and a melting point of 109°C . Since T_g represents the onset of translational mobility, the elevated T_g values indicate restricted mobility of the heterodications most likely due to the bulky phenyl groups on the phosphonium cation.

TABLE I. Thermal properties and densities of the pure NTf₂ salts and binary IL mixtures.

Cation(s)	Glass Transition Point, T_g ^[a] °C	Melting Point, T_m ^[a] °C	Density, g/cm³ 25 °C
[P ₁ EOE] ⁺	-91	^[b]	1.41
[SE6] ²⁺ ³⁹	-61	^[b]	1.44
[SE6] ²⁺ + [P ₁ EOE] ⁺ (25/75%)	-87	^[b]	1.41
[SE6] ²⁺ + [P ₁ EOE] ⁺ (50/50%)	-78	^[b]	1.43
[MimC ₆ Mim] ²⁺	-65	^[b]	1.50
[P ₁ EOE] ⁺ + [MimC ₆ Mim] ²⁺	-76	^[b]	1.46
[(CH ₃) ₃ NC ₅ Mim] ²⁺	-56	^[b]	1.53
[P ₁ EOE] ⁺ + [(CH ₃) ₃ NC ₅ Mim] ²⁺	-76	^[b]	1.46
[(Ph) ₃ PC ₄ Mim] ²⁺	-20	71	^[c]
[P ₁ EOE] ⁺ + [(Ph) ₃ PC ₄ Mim] ²⁺	-66	^[b]	1.41
[(CH ₃) ₃ NC ₅ Mpyrr] ²⁺	-35	53	^[c]
[P ₁ EOE] ⁺ + [(CH ₃) ₃ NC ₅ Mpyrr] ²⁺	-76	^[b]	1.46
[(Ph) ₃ PC ₄ Mpyrr] ²⁺	-17	109	^[c]
[P ₁ EOE] ⁺ + [(Ph) ₃ PC ₄ Mpyrr] ²⁺	-66	^[b]	1.45

^[a] All values are onset temperatures, ± 1 °C. ^[b] Not observed. ^[c] Solid at room temperature.

Densities. The densities of the pure ILs that are liquids at room temperature and the IL mixtures are shown in Table I. The densities of the mixtures lie in between those of the pure ILs.

Viscosities. The viscosity profiles of the pure dicationic ILs and their 50 weight percent binary mixtures with P₁EOE NTf₂ are shown in Table II. Three of the dicationic salts, including the two heterodicationic NTf₂ salts, melt above room temperature. The NTf₂ salt of the dication containing triphenylphosphonium bridged to *N*-methylpyrrolidinium by a butyl chain [(Ph)₃PC₄Mpyrr]²⁺ melts at 109 °C making it difficult to obtain transport properties of the pure compound. The pure dicationic NTf₂ ILs exhibit viscosities that are one to two orders of magnitude higher than the P₁EOE NTf₂ “solvent.” The viscosities of the pure dicationic NTf₂ ILs at 25 °C range from 1582 mPa s for the linear symmetrical SE6 NTf₂ to 679 mPa s for the symmetrical MimC₆Mim (NTf₂)₂. Mixing the highly viscous or solid dicationic ILs with P₁EOE NTf₂ (viscosity 53 mPa s at 25 °C) in a 31-36 mol % ratio (50 weight %) results in a reduction in viscosity up to 80 % compared to the pure dicationic liquid or solid. Therefore, it is advantageous to use IL mixtures as a means to lower IL viscosity for practical applications where it is desirable to have the constituent ions of the solid or high viscosity liquid present.

TABLE II. Viscosity profiles of the pure ILs and binary IL mixtures and VTF fit parameters for the viscosities.

Cation(s)	Viscosity mPa s, 25 °C ^[a]	$\ln(\eta_0/\text{mPa s})$	D	T_0 , K	T_g/T_0
[P ₁ EOE] ⁺	53	-2.09	5.59	155.1	1.17
[SE6] ²⁺ ³⁹	1582	-2.78	7.34	173.5	1.22
[SE6] ²⁺ + [P ₁ EOE] ⁺ (25/75%)	106	-2.32	6.39	155.7	1.20
[SE6] ²⁺ + [P ₁ EOE] ⁺ (50/50%)	247	-2.49	6.80	161.1	1.21
[MimC ₆ Mim] ²⁺	679	-2.07	5.99	175.7	1.18
[P ₁ EOE] ⁺ + [MimC ₆ Mim] ²⁺	186	-1.83	5.44	168.3	1.17
[(CH ₃) ₃ NC ₅ Mim] ²⁺	1019	-1.43	5.03	187.1	1.17
[P ₁ EOE] ⁺ + [(CH ₃) ₃ NC ₅ Mim] ²⁺	225	-2.14	6.01	166.0	1.19
[(Ph) ₃ PC ₄ Mim] ²⁺	^[b]	-	-	-	-
[P ₁ EOE] ⁺ + [(Ph) ₃ PC ₄ Mim] ²⁺ ^[c]	535	-2.16	5.97	174.7	1.19
[(CH ₃) ₃ NC ₅ Mpyrr] ²⁺	^[b]	-	-	-	-
[P ₁ EOE] ⁺ + [(CH ₃) ₃ NC ₅ Mpyrr] ²⁺	221	-1.77	5.57	167.7	1.17
[(Ph) ₃ PC ₄ Mpyrr] ²⁺	^[b]	-	-	-	-
[P ₁ EOE] ⁺ + [(Ph) ₃ PC ₄ Mpyrr] ²⁺ ^[d]	651	-2.05	6.08	174.4	1.19

^[a] Calculated from the VTF parameters. ^[b] Solid at room temperature. ^[c] Mixture phase separates and becomes heterogeneous below 50 °C. ^[d] Mixture phase separates and becomes heterogeneous below 60 °C

Figure 2 shows a plot of the temperature-dependent viscosities of the pure ILs and their mixtures with P₁EOE NTf₂, which naturally decrease in viscosity with increasing temperature. The monocationic P₁EOE NTf₂ is the least viscous. The effect of ether side chains in lowering viscosity of ILs has been reported by many groups. More recently MD simulations and X-ray diffraction data have shown that this decrease in viscosity can be attributed to the attraction between the polar ether chain and the cation resulting in the ether chain curling inwards.^{43,44} This in turn disrupts and suppresses the nanosegregation typically observed in ILs with alkyl side chains, resulting in heterogeneity and disorder. The anions adjoin both the positive site of the cation as well as the polar ether chains and there is no polar-apolar segregation. The result is an increase in ion mobility and consequently a reduction in viscosity. The 25% SE6 NTf₂ mixture has the lowest viscosity of the mixtures studied. This is the only mixture we studied at different concentrations. At 25% the properties of the mixture lie closer to the solvent P₁EOE NTf₂. The 50% mixtures all exhibit a dramatic drop in viscosity compared to those of the pure DILs. The DILs containing triphenylphosphonium sites are not room temperature liquids and we do not report viscosities for those pure DILs. The 50% mixtures of those DILs exhibit higher viscosities compared to the other 50% mixtures. This is most likely due to the large size of the aryl groups and the possibility that they may segregate to enhance aryl-aryl interactions, thus increasing structural order in the IL mixture and impeding the movement of the ions.

Figure 2: Viscosities versus temperature for the pure ILs and their mixtures (25 or 50 wt. %) with P₁EOE NTf₂

The temperature-dependent viscosity behaviors for the pure ILs and mixtures are described by the Vogel-Tamman-Fulcher (VTF) fitting parameters listed in Table II. The data were fit to the logarithmic form of the VTF relation for viscosity (Eqn. 1), where T is the temperature, η_0 is the limiting viscosity at high temperature, D is the fragility parameter, and T_0 is the singularity temperature at which the viscosity diverges.

$$\ln(\eta(T)) = \ln(\eta_0) + DT_0/(T-T_0) \quad (1)$$

In the cases where data was obtained for both pure ILs as well as a mixture, the VTF parameters lie in between those of the pure ILs. The fragility parameter D , is related to the rate of the drop in viscosity as the temperature increases from T_g . The smaller the D values the more fragile the liquids are and the more they deviate from Arrhenius behavior. Thus it can be seen from Table II that generally the mixtures are more fragile than the pure dicationic ILs they are made from, with the curious exception of (Me)₃NC₅mim (NTf₂)₂. Fragile liquids are desirable for many applications because the viscosity drops faster with increasing temperatures than in Arrhenius liquids, and the conductivity proportionally increases.

Figure 3 shows a plot of the viscosities of the pure dication ILs and their mixtures versus the inverse temperature normalized to each IL or mixture's T_g . The use of a T_g -scaled temperature coordinate is another way to judge the relative fragilities of the different mixtures, as employed by Angell and co-workers.¹⁴ Fragile ILs have trendlines closer to the lower right corner of the plot while “strong” ILs have trendlines closer to the upper left. Consistent with the fragility parameters D in Table II, pure (Me)₃NC₅mim (NTf₂)₂ and the 50% MimC₆Mim (NTf₂)₂ mixture are among the relatively more fragile ILs, while the 50% mixture of SE6 (NTf₂)₂ and the pure SE6 (NTf₂)₂ are among the relatively less fragile (stronger) ILs. Among the pure ILs it is interesting to note the progression in fragility from SE6 (NTf₂)₂ (two ammonium centers, $D = 7.34$) to MimC₆Mim (NTf₂)₂ (two imidazolium centers, $D = 5.99$) to (Me)₃NC₅mim (NTf₂)₂ (one ammonium and one imidazolium center, $D = 5.03$), which is also evident by inspection of Figure

3. If one could discern why the fragility is greatest for the heterodication IL it might be possible to use that principle to design lower-viscosity ILs.

Figure 3: Plot of viscosities versus inverse temperature scaled to the respective glass transition temperatures for the pure ILs and their mixtures with P₁EOE NTf₂.

Conductivities. The conductivities and Walden products of the pure ILs and their binary mixtures are shown in Table III. The Walden product is the product of the viscosity and molar conductivity. Walden products are useful for determining the deviations of IL behavior from ideality. A Walden product of one is considered ideal for a 1:1 electrolyte, although it is difficult to conclude what is “ideal” in terms of ionic conductivity.⁴² The Walden products for the pure diactionic ILs SE6 (NTf₂)₂ and MimC₆Mim (NTf₂)₂ are close to 1. The conductivity of 1.5 mS/cm for (CH₃)₃NC₅Mim (NTf₂)₂ appears to be anomalous and will be repeated. When comparing the conductivities of the pure dicationic ILs to those of the mixtures, an increase in conductivity is observed relative to the pure dicationic IL but not relative to P₁EOE NTf₂.

TABLE III. Conductivity properties and molarities of the pure ILs and binary IL mixtures.

Cation(s)	$\chi_{\text{solute}}^{\text{[a]}}$ %	Conductivity mS/cm, 25 °C	Conductivity mS/cm, 60 °C	Conductivity mS/cm, 75 °C	Ion Molarity ^[b] M	Walden Product P S cm ² /mol
[P ₁ EOE] ⁺ ³⁹		3.4	11.6	17.4	3.22	0.56
[SE6] ²⁺ ³⁹		0.19	1.3	2.3	3.29	0.95
[SE6] ²⁺ + [P ₁ EOE] ⁺ (25/75%)	14.3	1.4	3.1	3.9	3.21	0.46
[SE6] ²⁺ + [P ₁ EOE] ⁺ (50/50%)	33.3	0.70	2.0	2.7	3.25	0.53
[MimC ₆ Mim] ²⁺		0.63	2.3	3.4	3.71	1.09
[P ₁ EOE] ⁺ + [MimC ₆ Mim] ²⁺	35.2	0.77	2.7	3.4	3.47	0.41
[(CH ₃) ₃ NC ₅ Mim] ²⁺		1.5	3.1	3.8	3.97	4.37
[P ₁ EOE] ⁺ + [(CH ₃) ₃ NC ₅ Mim] ²⁺	36.2	0.74	2.5	3.3	3.56	0.47
[(Ph) ₃ PC ₄ Mim] ²⁺		^[c]	0.11	0.24		
[P ₁ EOE] ⁺ + [(Ph) ₃ PC ₄ Mim] ²⁺	31.3	0.38	1.5	1.8	2.34	0.87
[(CH ₃) ₃ NC ₅ Mpyrr] ²⁺		^[c]				
[P ₁ EOE] ⁺ + [(CH ₃) ₃ NC ₅ Mpyrr] ²⁺	36.2	0.96	2.4	3.1	2.61	0.81
[(Ph) ₃ PC ₄ Mpyrr] ²⁺		^[c]				
[P ₁ EOE] ⁺ + [(Ph) ₃ PC ₄ Mpyrr] ²⁺	31.2	0.32	1.2	1.7	3.30	0.63

^[a]Mole fraction of dicationic IL in mixture. ^[b]Total concentration of cations (dications count double). ^[c]Melting point too high.

Diffusion measurements. Variable temperature ^1H , ^{19}F and ^{31}P self-diffusion coefficients (D) were determined at 25, 60, and 75 °C for mixtures of the dication ILs (MimC₆Mim (NTf₂)₂, (CH₃)₃NC₅Mim (NTf₂)₂, (CH₃)₃NC₅Mpyrr (NTf₂)₂, (Ph)₃PC₄Mim (NTf₂)₂, and (Ph)₃PC₄Mpyrr (NTf₂)₂) with the common solvent P₁EOE NTf₂. The results are given in Table IV. ^1H spin echoes showed multiple peaks, while both ^{19}F and ^{31}P echoes showed a single peak. The assignments of the solvent and dication proton peaks were based on their respective chemical shifts. The general trend observed for all diffusion coefficients was an increase with increasing temperature. The order of the diffusion coefficients for all five mixtures was $D(\text{solvent, P}_1\text{EOE}^+) > D(\text{anion, NTf}_2^-) > D(\text{dication}) \sim D(\text{phosphorus})$. The close agreement between the $D(\text{phosphorus})$ and $D(\text{dication})$ in phosphorus-containing mixtures validated the peak assignments for the dication species. Diffusion coefficients of all of the components of the two mixtures containing triphenylphosphonium dications were smaller than those for the other mixtures.

Table IV. Self-diffusion coefficients for IL mixtures at three temperatures (m²/s, x 10⁻¹²).

Cation Mixture	^{19}F	^{31}P	^1H Dication	^1H Solvent
(Ph)₃PC₄Mpyrr²⁺/P₁EOE⁺				
25 °C	2.11	0.906	0.990	2.91
60 °C	17.6	8.27	8.63	24.0
75 °C	32.2	15.8	16.4	43.1
(Ph)₃PC₄Mim²⁺/P₁EOE⁺				
25 °C	2.45	1.10	1.24	3.43
60 °C	20.7	9.87	10.2	26.3
75 °C	41.3	30.0	30.0	53.5
MimC₆Mim²⁺/P₁EOE⁺				
25 °C	5.55		4.30	6.79
60 °C	34.4		26.0	44.1
75 °C	56.8		54.0	69.9
(CH₃)₃NC₅Mim²⁺/P₁EOE⁺				
25 °C	4.52		3.57	6.20
60 °C	31.4		2.48	38.4
75 °C	52.3		3.86	64.3
(CH₃)₃NC₅Mpyrr²⁺/P₁EOE⁺				
25 °C	5.48		5.45	6.20
60 °C	34.4		31.2	36.3
75 °C	55.3		49.9	58.1

Cation diffusion: ^1H and ^{31}P results. The ^1H diffusion coefficients for the P₁EOE⁺ solvent and the several dication species are shown in Figures 4 and 5 respectively. (The ^{31}P diffusion coefficients for the phosphonium dications are in excellent agreement with the proton results, thus there is no need for another figure.) $D(\text{solvent})$ values for the mixtures with the different cations are in the order MimC₆Mim²⁺ > (CH₃)₃NC₅Mim²⁺ ~ (CH₃)₃NC₅Mpyrr²⁺ > (Ph)₃PC₄Mim²⁺ > (Ph)₃PC₄Mpyrr²⁺. The values for the dications follow nearly the same order, with (CH₃)₃NC₅Mpyrr²⁺ > MimC₆Mim²⁺ > (CH₃)₃NC₅Mim²⁺ > (Ph)₃PC₄Mim²⁺ > (Ph)₃PC₄Mpyrr²⁺. The differences between the cation self-diffusion coefficients for the mixtures without triphenylphosphonium ((Ph)₃P) groups are relatively small, while those with (Ph)₃P groups are clearly slower. The order could be an indication of the available free volume in the mixtures, as greater free volume is often correlated with greater translational and rotational mobilities. As such, the MimC₆Mim²⁺ and (Ph)₃PC₄Mpyrr²⁺ dication mixtures would have the most and least available free volumes respectively. The trend observed among the $D(\text{solvent})$

values is consistent with the conductivity measurements reported in Table III and across the whole range of viscosity measurements shown in Figure 2.

Figure 4. Variable-temperature ^1H self-diffusion coefficients for the solvent P_1EOE^+ cation in the dicationic IL mixtures.

Figure 5. Variable-temperature ^1H self-diffusion coefficients for the dicationic species in dicationic IL mixtures.

For the IL mixtures containing $(\text{CH}_3)_3\text{NC}_5$ and $(\text{Ph})_3\text{PC}_4$ groups, the imidazolium (Mim) versions have higher $D(\text{solvent})$ values compared to the Mpyrr-containing dications. In addition, ^1H and ^{31}P diffusion coefficients for the $(\text{Ph})_3\text{PC}_4\text{Mim}^{2+}$ dication in its mixture are larger compared to the $(\text{Ph})_3\text{PC}_4\text{Mpyrr}^{2+}$ case. Several factors could contribute to this difference. First, the Mim group is planar while the Mpyrr group is not, and this may affect diffusivity. Second, the absence of the double bonds on the Pyrr ring structure means the electron density is more localized, leaving the net positive charge localized on the nitrogen atom. The result of this would be a stronger interaction site for neighboring anions. The localization of the partial positive charge on the lone nitrogen atom would also create less positive charge on the ring terminated methyl group and greater electron density on the ring carbons. A similar phenomenon was observed by Hunt et al., who showed through molecular dynamics simulations⁴⁵ that a strongly localized positive charge at the phosphonium atom in tetraalkylphosphonium compounds resulted in a smaller positive charge on the methyl group in the tetraalkylphosphonium compound compared to the tetraalkylammonium one. The anion could experience increase Coulombic attraction and repulsion as a result, and the motions of both the cations and anion would be affected.

NTf₂⁻ anion diffusion: ¹⁹F results. Figure 6 depicts the dependence of anion diffusion on temperature. The order for the ¹⁹F diffusion coefficients at higher temperatures is MimC₆Mim²⁺ ~ (CH₃)₃NC₅Mpyrr²⁺ > (CH₃)₃NC₅Mim²⁺ > (Ph)₃PC₄Mim²⁺ > (Ph)₃PC₄Mpyrr²⁺. A comparison between the *D*(anion) values at 75 °C gave 2.7%, 8.2%, 32% and 55% differences relative to the value for the MimC₆Mim²⁺ dication. The MimC₆Mim²⁺ sample has the possibility of multiple conformations due to its symmetric nature and its alkyl chain. It should also have the greatest propensity for hydrogen bond donation by virtue of the imidazolium ring protons, which are relatively acidic compared to alkyl and phenyl groups. By comparison, the conductivities at 75 °C given in Table III show a similar pattern to the *D*(anion) values, with similar values for MimC₆Mim²⁺ (3.4 mS/cm), (CH₃)₃NC₅Mim²⁺ (3.3 mS/cm) and (CH₃)₃NC₅Mpyrr²⁺ (3.1 mS/cm) dications, while values of 1.8 and 1.7 mS/cm were obtained for (Ph)₃PC₄Mim²⁺ and (Ph)₃PC₄Mpyrr²⁺ respectively.

Figure 6. Variable-temperature ¹⁹F self-diffusion coefficients for NTf₂⁻ anion in the dicationic IL mixtures.

The activation energies calculated from the self-diffusion coefficients given in Table V for the three phosphorus-free dication mixtures show essentially no dependence on the species. Values ranged from 39 to 43 kJ/mol. In contrast, all the self-diffusion coefficients for the phosphonium dication mixtures had activation energies from 47 to 56 kJ/mol, with the largest value being obtained for the phosphorus nuclei. It is notable that although the steric bulk of the triphenylphosphonium group would be expected to increase the activation energy for diffusion of the dication, it also increases the activation energies for diffusion of P₁EOE⁺ and NTf₂⁻ by significant, albeit lesser, amounts. The higher activation energies for P₁EOE⁺ and NTf₂⁻ in the phosphonium cases are related to the higher viscosities of these mixtures, as will be shown in the following section.

Table V. Activation energies for self-diffusion of the NTf₂⁻ anion, dications and the P₁EOE⁺ solvent cation.

Dication in Mixture	Activation Energy (kJ/mol)			
	¹⁹ F Anion	³¹ P Dication	¹ H Dication	¹ H Solvent
(Ph) ₃ PC ₄ Mpyrr ²⁺	48 ± 2	50 ± 2	49 ± 2	47 ± 3
(Ph) ₃ PC ₄ Mim ²⁺	49 ± 1	56 ± 4	54 ± 4	48 ± 1
(CH ₃) ₃ NC ₅ Mim ²⁺	43 ± 3	NA	42 ± 4	41 ± 2
(CH ₃) ₃ NC ₅ Mpyrr ²⁺	41 ± 3	NA	39 ± 2	39 ± 2
MimC ₆ Mim ²⁺	41 ± 2	NA	41 ± 2	41 ± 3

Stokes-Einstein treatment of the diffusion results. The Stokes-Einstein relation (Eqn. 2) is often used to predict diffusion coefficients, assuming a particular hydrodynamic radius r_H .

$$D_{SE} = k_B T / 6\pi\eta r_H \quad (2)$$

In practice, and particularly in ionic liquids,⁴⁶ the effective hydrodynamic radius of a diffusing species can vary significantly from its actual molecular size, as represented by a van der Waals radius, for example. The Stokes-Einstein relation can be used empirically to obtain effective hydrodynamic radii from measured diffusion coefficients and viscosities, which can be used to infer the relative diffusive coupling of the solution components in relation to the bulk viscosity. Eqn. 2 can be rearranged and expressed as Eqn. 3; and experimental D/T values can be plotted against the fluidity ($1/\eta$) as shown in Figure 7 for the self-diffusion of the P₁EOE⁺ cation.

$$\ln(D/T) = \ln(k_B/6\pi r_H) + \ln(1/\eta) \quad (3)$$

Figure 7. Stokes-Einstein plot of the ¹H self-diffusion coefficients for the solvent P₁EOE⁺ cation in the dicationic IL mixtures. The dotted grey lines represent the Stokes-Einstein predictions for hydrodynamic radii of 1, 2, 3, and 4 Å from top to bottom.

Figure 7 shows that the P₁EOE⁺ cation has a smaller effective r_H in the mixtures with triphenylphosphonium dications than in the mixtures containing only quaternary ammonium and imidazolium dications, meaning that P₁EOE⁺ diffusion is less coupled to the bulk viscosity of the mixtures with the sterically bulkier triphenylphosphonium dications than with the other dications.

Figure 8 shows that the triphenylphosphonium dications have the largest effective hydrodynamic radii, as expected. Interestingly, the mixture containing $(\text{CH}_3)_3\text{NC}_5\text{Mpyrr}^{2+}$ stands out among the five mixtures studied. This asymmetric dication with quaternary ammonium groups on both ends has a smaller effective r_H in comparison to the other dications, even including $(\text{CH}_3)_3\text{NC}_5\text{Mim}^{2+}$ and $\text{MimC}_6\text{Mim}^{2+}$. Indeed, the self-diffusion coefficients of the $(\text{CH}_3)_3\text{NC}_5\text{Mpyrr}^{2+}$ dication are not much slower than those for P_1EOE^+ (Figure 7) and NTf_2^- (Figure 9) in the same mixture, suggesting that the dynamics of all three components are strongly coupled, in contrast to the triphenylphosphonium mixtures. This is possibly due to the structural similarity of both ends of the $(\text{CH}_3)_3\text{NC}_5\text{Mpyrr}^{2+}$ dication to the P_1EOE^+ “solvent” cation, which could lead to more or less uniform mixing of the mono- and dicationic components. On the other hand, there would appear to be significant degree of structural segregation in the two phosphonium mixtures. The $(\text{CH}_3)_3\text{NC}_5\text{Mim}^{2+}$ and $\text{MimC}_6\text{Mim}^{2+}$ mixtures are intermediate between the two extremes.

Figure 8. Stokes-Einstein plot of the ^1H self-diffusion coefficients for the dications in the dicationic IL mixtures. The dotted grey lines represent the Stokes-Einstein predictions for hydrodynamic radii of 1, 2, 3, and 4 Å from top to bottom.

Figure 9. Stokes-Einstein plot of the ^{19}F self-diffusion coefficients for the NTf_2^- anion in the dicationic IL mixtures. The dotted grey lines represent the Stokes-Einstein predictions for hydrodynamic radii of 1, 2, 3, and 4 Å from top to bottom.

Figure 9 shows that self-diffusion of the NTf_2^- anion in the tetraphenylphosphonium mixtures is less strongly coupled to the bulk viscosity than in the other cases, as was found for the P_1EOE^+ cation. The anion self-diffusion results reinforce the suggestion of different degrees of structural segregation in the different classes of dication mixtures inferred from the transport

dynamics. Similar effects were reported by Wang et al. in mixtures of 1-ethyl-3-methylimidazolium⁴⁷ and 1-butyl-3-methylimidazolium⁴⁸ cations with the very aliphatic trihexyl(tetradecyl)phosphonium cation, and NTf₂⁻ as the common anion. In both cases, NMR spectroscopy as function of cation mole ratio indicated a preferential interaction between the NTf₂⁻ anion and the imidazolium cations.

Conclusion

The strategy of combining ionic liquids together adds a great deal of tunability to the already remarkable range of IL properties. In this work we explored the effect of using mixtures to tune the properties of ionic liquids containing dications. IL mixtures containing about one-third mole fraction of dications and about two-thirds mole fraction of P₁EOE⁺ cation with the common NTf₂⁻ anion result in significant reductions in viscosity compared to the pure dicationic ILs. The conductivity of the mixtures shows a general increase relative to the pure dicationic ILs, however the trend is less consistent. The pure heterodicationic ILs containing triphenylphosphonium and methylimidazolium or methylpyrrolidinium exhibited the highest glass transition temperatures and melting points, making them less useful for practical applications at ambient temperatures. However, when the heterodicationic ILs were mixed with about 70 mol % of a low-viscosity room temperature IL there was a 46 to 49 degree drop in the T_g and the mixtures did not crystallize, extending the liquid range and the potential for practical applications significantly.

Measurements of variable temperature, species-specific (solvent, dication and anion) self-diffusion coefficients on five IL mixtures show significant trends that suggest major differences in structural segregation between the different families of dications. Stokes-Einstein plots of P₁EOE⁺ cation and NTf₂⁻ anion self-diffusion in the various mixtures indicate that the translational dynamics of the cation and anion are most decoupled from that of the dication for the triphenylphosphonium mixtures ((Ph)₃PC₄Mim²⁺ and (Ph)₃PC₄Mpyrr²⁺) and well coupled to that of the (CH₃)₃NC₅Mpyrr²⁺ dication in that mixture. The imidazolium-containing cations (CH₃)₃NC₅Mim²⁺ and MimC₆Mim²⁺ are an intermediate case. The aryl groups of the phosphonium cations differ in polarizability from the P₁EOE⁺ solvent cation, whereas both ends of the (CH₃)₃NC₅Mpyrr²⁺ dication are structurally similar to it, implying that differences in the nanoscale organization of the IL mixtures may be responsible for the observed differences in self-diffusion and other transport properties.

The perspectives gained from the Stokes-Einstein plots suggest that it would be very interesting to perform X-ray scattering experiments and molecular dynamics simulations on these mixtures to quantify the degrees of structural segregation as functions of dication structure that are implied by the self-diffusion results. Such techniques have been applied to mixtures of ILs with molecular solvents, neutral solutes and inorganic salts⁴⁹ as well as mixtures of ILs⁵⁰ with different cation chain lengths⁵¹ and anions,^{52,53} however we are not aware of any similar studies on IL mixtures of the complexity of those studied here.

The results reported here show that the choice of functional groups can have a profound impact on the transport properties of individual ions in IL mixtures. This concept should be further developed and applied to the design of tailored IL mixtures with desirable performance characteristics.

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Supporting Information

NMR spectra are provided for all compounds for which NMR data is reported.

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