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Complete List of Authors:	Timmermann, George; Murray State University, Chemistry Pierce, Jordan; Murray State University, Chemistry Boyd-Becker, Taylor; Indiana University South Bend, Chemistry and Biochemistry Clear, Kasey; Indiana University South Bend, Chemistry and Biochemistry Miller, Kevin; Murray State University, Chemistry

A Non-Isocyanate Approach to Preparing Carbamate- and Thiocarbamate-Containing Ionic Liquids

George M. Timmermann,[1] Jordan C. Pierce,[1] Taylor Boyd-Becker,[2] Kasey J. Clear,[2] Kevin M. Miller[1],*

[1]Department of Chemistry, Murray State University, Murray, KY 42071

[2]Department of Chemistry and Biochemistry, Indiana University South Bend, South Bend, IN 46615

*Corresponding author (e-mail: kmiller38@murraystate.edu)

Abstract

The versatility of 1,1′-carbonyldiimidazole (CDI) as a reagent in a non-isocyanate synthesis of carbamate- and thiocarbamate-containing ionic liquids (ILs) is described herein. Through the initial reaction with various linear alcohols or thiols, followed by addition of 3-aminopropylimidazole, CDI was sequentially transformed into a series of imidazoles bearing a carbamate or thiocarbamate functional group. The imidazoles were further quaternized with various lengths of alkyl groups (C2-C12) and anion exchanges were performed, producing a small library of 20 room-temperature ILs. Fundamental temperature-dependent properties such as density, viscosity, and conductivity were determined for each material. All of the ILs were found to exhibit glass transition temperatures (T_g) below room temperature and conductivities of up to 10^{-3} S/cm at 30 °C. Changes in the counteranion ([Br], [OMs], [OTf], [NTf_2], [NFBSI]) produced the greatest breadth of physicochemical properties.

Key Words: non-isocyanate, carbamate, thiocarbamate, ionic liquid

Introduction

Carbamates and thiocarbamates are versatile compounds widely used in chemistry for various end-use applications, owing to their structural versatility and diversity. For example, carbamates are particularly useful as synthetic intermediates in forming amine and urea derivatives, and as protecting groups for amines and alcohols.[1,2] From a commercial perspective, both carbamates and thiocarbamates are found extensively in pesticides and herbicides, and in various pharmaceuticals.[3-6] In the plastics industry, the carbamate (urethane) group is utilized in polyurethanes, a broad class of polymers used in applications ranging from paints and coatings to adhesives. Due to the extensive utility of carbamates and related thiocarbamates in a wide range of applications, carbamoylation reactions continue to be an important area of research.

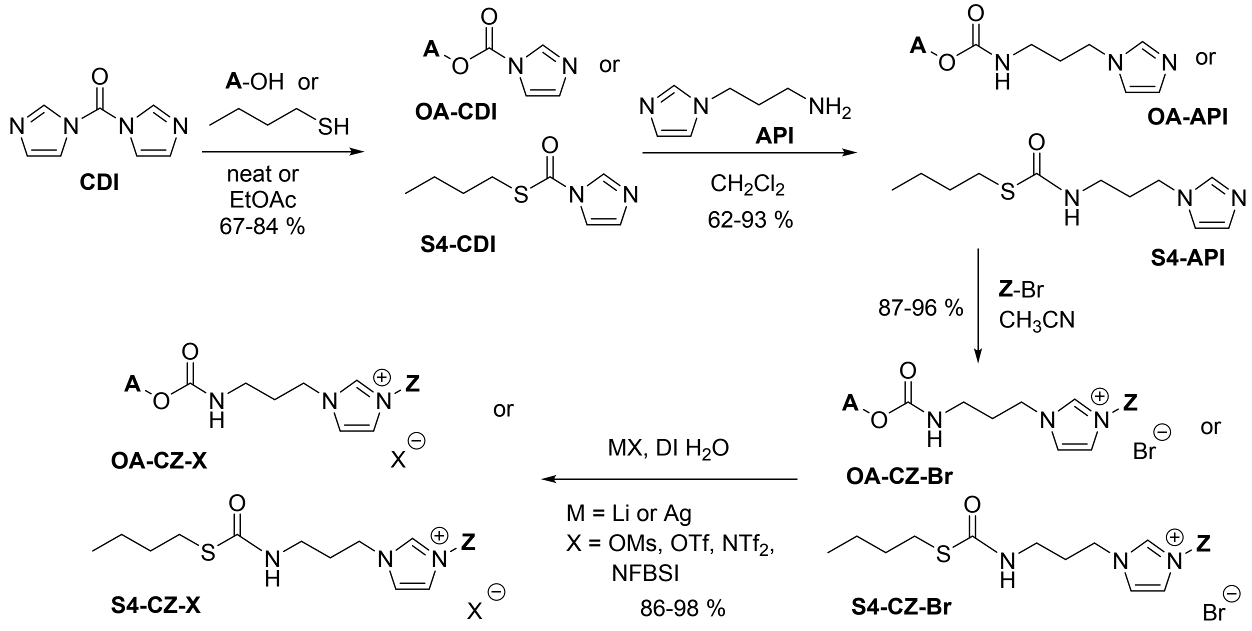
Carbamates are prepared through a number of synthetic methods, with one of the most common approaches involving the reaction of an alcohol and an isocyanate. The reaction is exothermic and does not produce any byproducts; however, isocyanates are incredibly hazardous. Not only does the synthesis of the isocyanate require the use of phosgene, a highly toxic gas, two of the most common commercial isocyanates found in the polyurethane industry, TDI (toluene diisocyanate) and MDI (methylene diphenylisocyanate), are toxic andcarcinogenic.[7,8] Furthermore, to produce carbamates with different N-substitution through an isocyanate pathway without handling phosgene, each corresponding isocyanate must be purchased individually and some may not be commercially available. Fortunately, a number of non-isocyanate or "blocked" isocyanate routes to forming carbamates have been investigated and the reader is directed towards several excellent reviews.[9-12] Of the many alternative routes described in the literature, the reaction of amines with carbonate esters is a popular non-isocyanate route for carbamate synthesis. Unlike isocyanates, carbonates are generally non-toxic and, once reacted with an amine, do not produce any byproducts.[13] Many carbonates (especially cyclic analogs), however, are prepared from phosgene, phosgene derivatives, or epihalohydrins, all of which are hazardous. Fortunately, safer preparations utilizing carbon dioxide in combination with epoxides, olefins or diols have been recently reported.[14,15]

1,1′-Carbonyl diimidazole (CDI) is a reagent which historically has been used in the synthesis of amides and esters (from carboxylic acids) as an alternative to thionyl chloride or carbodiimides, is relatively inexpensive, produces relatively benign byproducts (imidazole and carbon dioxide depending on the use), and serves as a safer equivalent to phosgene.[6,16-19] In addition to amides and esters, CDI has also been used (albeit sparingly) in the preparation of carbonates, amides, ureas, carbamates, and thiocarbamates.[20-23] Utilizing CDI is attractive from an architectural perspective in that the targeted functional group (carbamate, thiocarbamate, urea, etc.) can be prepared in a step-wise fashion, allowing for a great deal of versatility in the structure of the final product. For example, Bansagi and coworkers demonstrated that CDI could be first reacted with an ammonium salt to produce a series of carbamoyl imidazoles, followed by reaction with an amine, alcohol, or thiol, resulting in the corresponding ureas, carbamates, or thiocarbamates.[24] Solvent-free reactions of carboxylic acids with CDI to prepare amides have been reported as well as the application of mechanochemistry to the conversion of CDI to a variety of other functional groups, including amides, carbamates, ureas, hydrazides, and hydantoins.[25-27] CDI has also been utilized in the preparation of polycarbonates and polyurethanes.[28,29] For example, Long and coworkers reported the synthesis of linear, segmented polyurethanes through the step-wise reaction of 1,4-butanediol with CDI, followed by polymerization with a series of diamines.[30] More recently our research team utilized CDI as a key reagent in the synthesis of conductive, imidazolium-containing polyurethanes.[31]

Ionic liquids (ILs), unlike traditional organic solvents, offer high thermal stability and high ionic solvation along with low volatility, and are typically composed of poorly coordinated ions. Due to their unique properties and diverse applications ILs continue to captivate the attention of researchers in fields such as electrochemical materials (batteries, fuel cells), catalysis, extractions and solvation.[32,33] Furthermore, ILs and polymers of ILs (referred to as poly(ionic liquid)s or PILs) can be fine-tuned to tailor the needs of specific applications, including CO_2 capture.[34,35] For example, ILs and PILs bearing functional groups that are capable of hydrogen bonding, such as carbamate (urethane) groups, have been shown to have a high affinity for carbon dioxide absorption.[36-40] As a result, we were interested in creating a small library of carbamate- and thiocarbamate-functionalized ILs utilizing the CDI non-isocyanate approach, with the long-term goal of evaluating carbon dioxide absorption. In this report, the synthesis and characterization of 20 different ILs is described, as well as an assessment of their physicochemical (viscosity, density), thermal and conductive properties.

Results and Discussion

Carbamate- and thiocarbamate-based imidazolium ionic liquids were prepared as followed. First, carbonyldiimidazole (CDI) was reacted with various linear alcohols, 2-methoxyethanol (ROH) or 1-butanethiol, resulting in intermediates **OA-CDI** or **S4-CDI** where **A** refers to the carbon chain length (**A** = 2, 4, 8, 12 or M which refers to methoxyethyl) (**Scheme 1**).[21] In two cases (ethanol and *n*-butanol), the addition of CDI to the alcohol was completed under neat conditions. In all other cases, ethyl acetate (EtOAc) was used as the solvent. Subsequent reaction with 3-aminopropylimidazole (API) provided carbamate- or thiocarbamate-based imidazoles **OA-API** or **S4-API**. This was then followed by quaternization with an alkyl bromide, providing a series of ionic liquid bromides **OA-CZ-Br** or **S4-CZ-Br**, where **Z** refers to the length of the straight chain alkyl substituent. Anion exchange was then completed on all bromide salts with $LiNTf_2$ (lithium bis(trifluoromethylsulfonyl)imide) as this counteranion typically provides enhanced conductivity due to its plasticization ability and poor ion coordination.[41] Additionally, to investigate the influence of other counteranions on materials properties, **O4-C2-Br** was also exchanged with mesylate (OMs), triflate (OTf), and bis(nonafluorobutanesulfonyl)imide (NFBSI). All of the ILs synthesized were liquids at room temperature, regardless of side chain length or counteranion, with variable degree of viscosity and density, and confirmation of structure and purity were determined by ^1H and ^{13}C spectroscopy (**Figures S1-S70**) as well as elemental analysis. A comprehensive list of all of the ILs fully analyzed as part of this study is provided in **Table 1**.



Scheme 1. Preparation of carbamate- and thiocarbamate-containing imidazolium ionic liquids.

Table 1. Carbamate- and thiocarbamate-containing imidazolium ionic liquids: Viscosity and density data at 25 °C.

IL ID	viscosity (Pa-s)	density (g/mL)
O2-C2-NTf_2	0.336	1.43
O2-C4-NTf_2	0.419	1.37
O2-C8-NTf_2	0.471	1.30
O2-C12-NTf_2	0.550	1.23
O8-C2-NTf_2	0.329	1.30
O12-C2-NTf_2	0.547	1.22
OM-C2-NTf_2	0.270	1.43
O4-C2-Br	70.2	1.27
O4-C2-OMs	4.17	1.25
O4-C2-OTf	0.518	1.26
O4-C2-NFBSI	1.33	1.54
O4-C2-NTf_2	0.210	1.38
S4-C2-NTf_2	0.491	1.40
S4-C8-NTf_2	0.966	1.29

The viscosities and densities of the ionic liquids were examined first and the values at 25 °C are provided in **Table 1**. Graphical summaries of temperature-dependent viscosity are provided in the Supporting Information (**Figures S71-S74**). For the series of ILs in which ethanol was used as the starting alcohol (**O2-CZ-NTf$_2$**), temperature-dependent viscosity was found to increase as the carbon chain length **Z** increased with **O2-C12-NTf$_2$** observed to have the highest viscosity (0.550 Pa-s at 25 °C). Given the same imidazolium carbon chain length substituent (**OA-C2-NTf$_2$**), increasing the length of the alcohol carbon chain length initially led to a decrease in viscosity from O2 to O4 (0.336 to 0.210 Pa-s, respectively), then an increase in viscosity from O4 up to O12 (0.547 Pa-s). It is hypothesized that **O2-C4-NTf$_2$** must have the poorest degree of ion packing for this particular sub-series, leading to the lowest viscosity. Increasing the carbon chain up to O12 likely leads to increased non-covalent (van der Waals) interactions between longer alkyl chains. When investigating variations in counteranion, given the same cation structure (**O4-C2-X**), the coordinating ability (Lewis basicity) of the anion appears to be the primary factor in determining viscosity with [Br] > [OMs] > [OTf] > [NTf$_2$]. However, the overall size of the counteranion seemed to play a role, as **O4-C2-NFBSI** exhibited a higher viscosity (1.33 Pa-s) than ILs containing OTf and NTf$_2$ despite NFBSI having the weakest coordinating ability. It is presumed that the longer fluoroalkyl chains (compared with NTf$_2$) must participate in van der Waals interactions between ions, despite fluorine's low polarizability, leading to the observed increase in viscosity. Thiocarbamate **S4-C2-NTf$_2$** was found to have a viscosity more than twice that of the carbamate analog **O4-C2-NTf$_2$**. Thiocarbamates exhibit stronger dipole-dipole interactions compared to carbamates as the sulfur atom is larger and more polarizable, leading to a higher viscosity. Overall, the trends in viscosity observed here are comparable to those previously reported for other imidazolium-containing ILs.[42-45]

Densities of ionic liquids are influenced by several factors, including ionic interactions and aggregation. Stronger electrostatic interactions between ions often result in higher density due to a higher degree of ion packing.[46,47] Densities of the carbamate- and thiocarbamate-containing ILs were found to decrease with increasing temperature (**Table 1**, **Figure S75**). Increasing either the **OA** or **CZ** alkyl chain length led to a decrease in density with analog **O12-C2-NTf$_2$** exhibiting the lowest overall density (1.22 g/mL) at 25 °C. **O4-C2-NFBSI** was observed to have the highest overall density (1.54 g/mL) at 25 °C.

Thermal transitions of the carbamate and thiocarbamate ILs were evaluated using differential scanning calorimetry (DSC), the results of which are provided in **Table 2** (graphical summaries in **Figures S76-S78**). All of the ILs were found to exhibit a glass transition temperature (T_g) and the values reported are from the second heating cycle. Two of the ILs were found to exhibit an additional melting transition (T_m): **O2-C12-NTf$_2$** (-42.9 °C) and **O12-C2-NTf$_2$** (25.6 °C). The only significant changes in T_g were observed when the alkyl chain length became very long (C12) or when the counteranion was smaller (OMs, Br), the former of which can be attributed to an increase in van der Waals interactions as a result of the chain intercalation, leading to an increase in T_g. The latter is due to the fact that small anions will be more compact, resulting in stronger ion pairing (again resulting in an increase in T_g). **O4-C2-Br** was observed to have the highest overall T_g value of -29.5 °C. The relationships observed here between side chain length and counteranion with thermal transitions of ILs are similar to data previously reported.[42-44]

Table 2. Thermal properties of carbamate- and thiocarbamate-containing imidazolium ionic liquids.

IL ID	DSC T_g (°C)	TGA $T_{d5\%}$ (°C)
O2-C2-NTf$_2$	-57.5	290
O2-C4-NTf$_2$	-56.2	289
O2-C8-NTf$_2$	-57.5	311
O2-C12-NTf$_2$	-53.0	294
O8-C2-NTf$_2$	-63.8	276
O12-C2-NTf$_2$	-41.1	271
OM-C2-NTf$_2$	-58.0	298
O4-C2-Br	-29.5	225
O4-C2-OMs	-48.8	245
O4-C2-OTf	-57.9	276
O4-C2-NFBSI	-52.2	285
O4-C2-NTf$_2$	-61.5	280
S4-C2-NTf$_2$	-56.9	242
S4-C8-NTf$_2$	-60.9	246

From a thermal stability perspective, the majority of the carbamate [NTf$_2$]-based ILs were found to exhibit $T_{d5\%}$ values in excess of 270 °C as determined from thermogravimetric analysis (TGA, **Table 2**, **Figures S79-S81**). However, the thiocarbamate [NTf$_2$] analogs were found to be less thermally stable ($T_{d5\%}$ ~ 240 °C) as the weaker C-S makes these ILs more susceptible to thermal decomposition.[48] With respect to counteranion selection, thermal stability decreased with increasing Lewis basicity (nucleophilicity) of the counteranion in the **O4-C2-X** series.[45,49] For example, **O4-C2-Br** was found to have the lowest overall $T_{d5\%}$ value of 225 °C while the weakly Lewis basic NFBSI analog was observed to have the highest $T_{d5\%}$ (285 °C) of the series.

Temperature-dependent conductivities for each of the ILs were also determined. In general, the ionic conductivity of every IL, regardless of structure, increases non-linearly with increasing temperature. Within each structural subset, changes in counteranion had the greatest effect in ionic conductivity insofar as the overall breadth of values is concerned. This is presumably due to the strong correlations that exist between ion coordinating ability and conductivity (**Figure 1**). With respect to the other structural variations, longer alkyl chains (either **OA** or **CZ**) led to slightly lower conductivities; however, all of the [NTf_2] variations exhibited conductivity on the order of 10^{-3} at 30 °C (**Figures S82** and **S83**). Any lowering of the conductivity with longer alkyl chains can be attributed to secondary structural alignment, resulting in increased van der Waals interactions and more difficulty for the ions to move from one coordination site to another. Due to their increased viscosity, the thiocarbamate ILs (**S4-OA-NTf$_2$**) exhibited lower conductivities than their carbamate counterparts (**Figure S84**). Numerical conductivity values for all of the ILs at 30 °C are listed in **Table 3**.

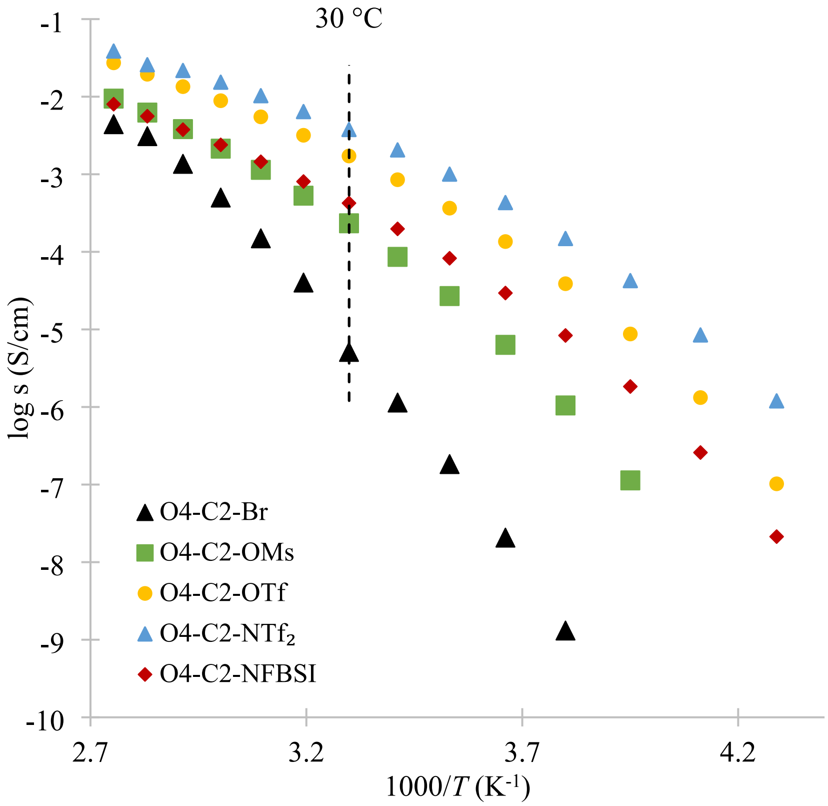


Figure 1. Overlay of temperature-dependent ionic conductivity curves for **O4-C2-X**.

The ionicity of an IL, which describes the degree of ion coordination, is highly dependent on viscosity, and can be measured using the Walden rule:

$$\log \Lambda_m = \log C + \alpha \log \eta^{-1}$$

where Λ_m is the molar conductivity, η is the viscosity, and C (intercept) is a constant that represents the deviation from the ideal line (dilute KCl solution). The degree of deviation from the ideal line has been used to classify ILs as "good", "poor" or "superionic".[50] **Figure 2** shows the Walden plot for all the ILs in this study with the dashed line representing the "ideal" KCl line. The fitting parameters for each set of IL data are provided in **Table 3**. Generally speaking, these ILs deviated from the ideal KCl line more so than [bmim][NTf_2] ($\alpha = 0.936$, $\log C = -0.205$) which serves as a standard IL.[50-52] In all of the ILs studied here, the insertion of a carbamate or thiocarbamate results in functional groups that can exhibit some extent of hydrogen bonding, generally resulting in an increase in viscosity and lower ionic conductivity. Within the **O4-C2-X** series of ILs, use of poorly coordinating counteranions (OTf, NTf_2) led to ionicities close to the ideal line and could be classified as "good" ILs. Increasing coordination with smaller, more highly coordinating anions such as Br, OMs led to poorer performance and larger deviations from the ideal line. As observed with the ionic conductivity and viscosity data sets, longer alkyl chains in the **OA-C2-NTf$_2$** and **O2-CZ-NTf$_2$** series lead to increased van der Waal interactions between cations, lower ionic conductivity, and higher viscosity. This further results in slightly larger deviations from the ideal line within their respective series. For example, the log C value for **O2-C2-NTf$_2$** is -0.411 S-cm^2-mol^{-1} but -0.669 for **O2-C12-NTf$_2$**. Thiocarbamates deviated farther from the ideal line than carbamate ILs, again due to an increase in dipole-dipole interactions.

Table 3. Conductivity values and linear fit parameters from the Walden plot.

IL ID	σ at 30 °C (S/cm)	α	log C (S-cm^2-mol^{-1})
O2-C2-NTf$_2$	5.08 x 10^{-3}	1.032	-0.411
O2-C4-NTf$_2$	3.39 x 10^{-3}	0.981	-0.410
O2-C8-NTf$_2$	2.23 x 10^{-3}	1.170	-0.595
O2-C12-NTf$_2$	1.02 x 10^{-3}	0.958	-0.669
O8-C2-NTf$_2$	2.36 x 10^{-3}	0.961	-0.501
O12-C2-NTf$_2$	1.15 x 10^{-3}	0.912	-0.588
OM-C2-NTf$_2$	4.56 x 10^{-3}	0.930	-0.483
O4-C2-Br	3.91 x 10^{-5}	1.107	-0.710
O4-C2-OMs	2.23 x 10^{-4}	1.013	-0.782
O4-C2-OTf	1.23 x 10^{-3}	0.990	-0.661
O4-C2-NFBSI	4.25 x 10^{-4}	0.950	-0.701
O4-C2-NTf$_2$	3.78 x 10^{-3}	0.880	-0.484
S4-C2-NTf$_2$	2.59 x 10^{-3}	0.877	-0.420
S4-C8-NTf$_2$	7.55 x 10^{-4}	0.956	-0.607

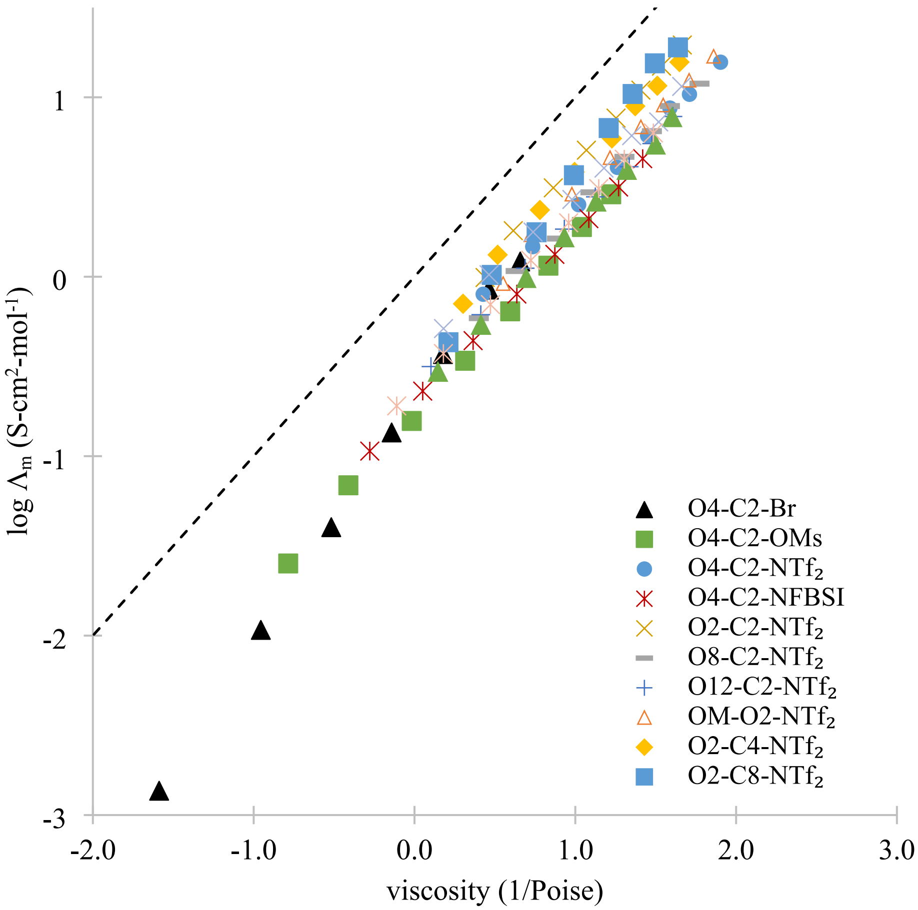


Figure 2. Walden plot comparison of temperature-dependent molar ionic conductivity as a function of inverse viscosity for carbamate- and thiocarbamate-ILs.

Conclusion

Carbamates and thiocarbamates are functional groups which are utilized in a variety of diverse applications ranging from pesticides and herbicides to plastics. Traditionally, these functional groups have bene prepared using toxic isocyanate chemistry; however, recent studies have suggested that alternative "non-isocyanate" routes can substitute as a safer, more versatile synthetic routes. A small library of 20 carbamate- and thiocarbamate-containing ionic liquids were prepared using a non-isocyanate approach whereby CDI was reacted sequentially with various alcohols (or 1-butanethiol) then 3-aminopropylamine (API). After quaternization and anion exchange, the resulting ILs were evaluated for various physicochemical properties and relationships between properties and architectural changes were made. Within the series reported here, changes in counteranion led to the largest breadth in properties such as viscosity, T_g and conductivity. Evaluation of molar ionic conductivity using a Walden plot indicated that many of the ILs prepared here would be considered “good” but not “superionic”. Going forward, there is interest in evaluating these ILs for their carbon dioxide absorption properties wither as neat materials or as gels when combined with commercial polymers or PILs.

Experimental Section

General. All materials were purchased from Sigma-Aldrich or Fisher Scientific (Reagent Grade ACS) and were used as received unless otherwise noted. Ultrapure deionized (DI) water was purified using an ELGA Purelab Ultra filtration device with a resistivity of 18 MΩ-cm. ^1H and ^{13}C NMR spectroscopy (JEOL-ECS 400 MHz spectrometer) were used to verify the purity and composition of the compounds synthesized, and chemical shift values are reported in reference to residual solvent signals (DMSO-d_6: ^1H 2.50 ppm; ^{13}C 39.52 ppm and $CDCl_3$: ^1H 7.24 ppm; ^{13}C 77.0 ppm). Elemental analyses were performed on a PerkinElmer 2400 CHNS/O Series II Elemental Analyzer. Residual bromide content of the anion exchanged ionic liquids was determined by ion chromatography (Dionex ICS-1100) using a 4.5 mM CO_3^{2-}/1.4 mM HCO_3^- eluent at a flow rate of 1.3 mL/min with a 31 mA suppressor current. Calibration was completed using a serial dilution of a 1000 ppm [Br] stock solution, prepared from sodium bromide (Aldrich, > 99.9%). A small amount (5-10 mg) of material was dissolved in 1 mL of acetonitrile/water (50:50) and injected. Residual bromide across all samples was found to be less than 0.8% w/w.

Ionic Liquid Analysis. Prior to any of the analyses described below, the IL of interest was dried in a vacuum oven (60 °C, < 0.1 mm Hg) for 72 hr. Isothermal thermogravimetric analysis (TGA) of the IL was then conducted (120 °C, 2 hr) in which water loss was found to be < 0.02 wt-%.

Thermal Analysis. Differential scanning calorimetry (DSC) was utilized to determine any thermal transitions of the polymers at a heating rate of 2 °C/min on 3-8 mg samples. Glass transition temperatures (T_g) were determined by the inflection point of the curve observed from the second heating cycle. All DSC T_g experiments were performed in duplicate with an error of $\pm$ 2.0 °C. A TA instruments Q550 TGA (thermogravimetric analyzer) was used to evaluate $T_{d5\%}$ values (the temperature at which 5% of the material had decomposed) by heating the material under a constant dry nitrogen flow at a heating rate of 10 °C/min.

Viscosity and Density Measurements. Viscosity were measured using a TA Instruments DHR-2 discovery hybrid rheometer equipped with a temperature-controlled Peltier plate and a 40 mm, 2° cone. Each IL was placed on the Peltier plate, set at 25 °C and the cone was lowered to achieve a gap of 500 μm. The sample was soaked at 25 °C for 15 min, then viscosity was monitored at a rate of 0.5 °C/min at a shear rate of 1.0 s^{-1}. Temperature-dependent densities were measured using an Anton-Parr DMA 4100M instrument, calibrated with air and deionized water according to the manufacturer's instructions. Densities were recorded at 5 C intervals over a range from 20 C to 90 C. Density measurements were found to be reproducible within ± 0.001 g/mL.

Conductivity. Anhydrous ionic conductivities were measured using a TA Instruments DHR-2 discovery hybrid rheometer equipped with a dielectric accessory and a Keysight Technologies E4980AL/120 LCR meter was utilized. Each IL sample was placed between two 25 mm stainless steel parallel plate electrodes and the gap set to 500 μm. Any excess material (squeeze out) was carefully removed with a PFTE razor blade. The environmental chamber was closed and kept under an atmosphere of dry nitrogen. Temperature was controlled using the environmental chamber in combination with liquid nitrogen. Dielectric permittivity and conductivity were measured isothermally over a frequency range of $20.0{-}10^6$ Hz in 10 °C steps with an ac amplitude of ±0.01 V from 90 to -40 °C. Samples were soaked at each temperature for 45 min prior to obtaining measurements. The DC conductivity (σ_{DC}) was determined from the plateau value observed in the spectral dependence of the conductivity function ($\sigma' = \omega\varepsilon''\varepsilon_o$, where ω is the frequency, ε'' is the dielectric loss, and ε_o is the vacuum permittivity).

Synthesis. As a representative example, then synthetic details for the preparation of **O2-C4-NTf$_2$** are provided here. Synthetic details for the other IL analogs can found in the Supporting Information section.

Synthesis of ***ethyl-1-imidazolecarboxylate*** (**O2-CDI**).[51] In a 25-mL round-bottomed flask with magnetic stirring was added absolute ethanol (14.21 g, 0.308 mol). Carbonyl diimidazole (CDI, 5.00 g, 0.0308 mol) was added in portions over a 5 min period, and the resulting solution was stirred for 2 hr. The excess ethanol was removed under reduced pressure and the residue was purified by column chromatography on silica gel with an eluent of 50:50 hexanes:ethyl acetate. Purification resulted in 2.61 g (67 %) of a clear, colorless oil. ^{1}H NMR ($CDCl_3$): δ 8.08 (s, 1 H), 7.37 (s, 1 H), 7.00 (s, 1 H), 4.42 (q, 2 H, *J* = 7.1 Hz), 1.38 (t, 3 H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ148.53, 136.94, 130.40, 116.96, 64.33, 14.02. Anal. Calcd. For $C_6H_8N_2O_2$: C 51.42, H 5.75, N 19.99. Found: C 51.15, H 5.86, N 19.88.

*Synthesis of **O2-API***. In a 50-mL round-bottomed flask with magnetic stirring was dissolved ethyl-1-imidazolecarboxylate (2.49 g, 0.0197 mol) in CH_2Cl_2 (25 mL). Aminopropylimidazole (API, 2.47 g, 0.0197 mol) was added and the resulting solution was stirred at rt overnight. The reaction was then diluted with CH_2Cl_2 (100 mL), transferred to a separatory funnel and washed sequentially with DI water (2 x 75 mL) and brine (75 mL). The organic phase was then dried over Na_2SO_4/$MgSO_4$, filtered, and solvent removed under reduced pressure to afford 2.85 g (79 %) of a viscous yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.42 (s, 1 H), 6.97 (s, 1 H), 6.87 (s, 1 H), 5.53 (br.s, 1H), 4.03 (q, 2 H, *J* = 6.9 Hz), 3.93 (t, 2 H, *J* = 6.8 Hz), 3.09 (m, 2 H), 1.91 (quintet, 2 H, *J* = 6.8 Hz), 1.16 (t, 3 H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ 156.85, 136.98, 129.28, 118.71, 60.68, 44.12, 37.68, 31.35, 14.48. Anal. Calcd. For $C_9H_{15}N_3O_2$: C 54.81, H 7.67, N 21.30. Found: C 54.93, H 7.89, N 20.99.

*Synthesis of **O2-C4-Br***. **O2-API** (2.60 g, 0.0142 mol) was dissolved in acetonitrile (35 mL) in a 100-mL round-bottomed flask with magnetic stirring. 1-Bromobutane (3.81 g, 0.0284 mol) was added and the resulting solution was heated to 50 °C where it was held stirring for 24 hr. The volatiles were then removed under reduced pressure, and the residue was washed vigorously with anhydrous THF (3 x 35 mL), then dried under reduced pressure (0.1 mm Hg at 60 °C) for 48 hr, resulting in a brown oil (4.13 g, 87 %). ^{1}H NMR (DMSO-d_6): δ 9.32 (s, 1 H), 7.84 (s, 1 H), 7.83 (s, 1 H), 7.23 (t, 1 H, *J* = 5.6 Hz), 4.14-4.21 (m, 4 H), 3.95 (q, 2 H, *J* = 6.9 Hz), 2.96 (q, 2 H, *J* = 6.3 Hz), 1.92 (quintet, 2 H, *J* = 6.6 Hz), 1.75 (quintet, 2 H, *J* = 7.5 Hz), 1.23 (quintet, 2 H, *J* = 7.5 Hz), 1.13 (t, 3 H, *J* = 7.2 Hz), 0.88 (t, 3 H, *J* = 7.2 Hz). ^{13}C NMR (DMSO-d_6): δ 156.33, 136.19, 122.43, 59.67, 48.55, 46.54, 36.79, 31.26, 29.78, 18.76, 14.63, 13.29. Anal. Calcd. For $C_{13}H_{24}BrN_3O_2$: C 46.71, H 7.24, N 12.57. Found: C 44.66, H 7.03, N 11.96.

*Synthesis of **O2-C4-NTf$_2$***. **O2-C4-Br** (3.75 g, 0.0112 mol) was dissolved in DI water (35 mL) in a 250-mL round-bottomed flask with magnetic stirring. A solution of $LiNTf_2$ (3.38 g, 0.0118 mol) in DI water (15 mL) was added and the resulting mixture was stirred at RT overnight. Dichloromethane (75 mL) was then added and stirring continued for one hour. The organic layer was separated, washed with DI water (3 x 40 mL), and solvent removed under reduced pressure, resulting in 5.57 g (93 %) of a light, yellow oil. ^{1}H NMR (DMSO-d_6): δ 9.13 (s, 1 H), 7.74 (s, 1 H), 7.73 (s, 1 H), 7.17 (t, 1 H, J = 5.6 Hz), 4.10-4.16 (m, 4 H), 3.94 (q, 2 H, J = 7.2 Hz), 2.94 (q, 2 H, J = 6.3 Hz), 1.90 (quintet, 2 H, J = 6.6 Hz), 1.73 (quintet, 2 H, J = 7.5 Hz), 1.23 (quintet, 2 H, J = 7.4 Hz), 1.12 (t, 3 H, J = 7.2 Hz), 0.86 (t, 3 H, J = 7.4 Hz). ^{13}C NMR (DMSO-d_6): δ 156.41, 136.19, 122.48, 122.47, 119.51 (q, J = 320 Hz, -CF_3), 59.71, 48.64, 46.61, 36.82, 31.27, 29.83, 18.80, 14.59, 13.21. Anal. Calcd. For $C_{15}H_{24}F_6N_4O_6S_2$: C 33.71, H 4.53, N 10.48, S 12.00. Found: C 32.88, H 4.44, N 10.01, S 12.25.

Data Availability Statement. The data supporting this article have been included as part of the ESI. This includes additional experimental procedures, ^{1}H and ^{13}C NMR spectra for all ILs and intermediates, temperature-dependent viscosity, density, and conductivity data, as well as DSC and TGA thermograms.

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The data supporting this article have been included as part of the Supplementary Information.