Syntheses of Novel Solvent Molecules for use in Solvate Ionic Liquids

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Abstract

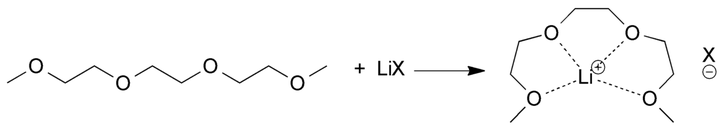
Solvate ionic liquids (SILs) are a subset of ionic liquids where an organic solvent molecule, containing atoms capable of donating one or more pairs of electrons, wraps around a solute cation. SILs have practical applications in lithium batteries, in pharmaceuticals, in the food industry, as dispersing agents, and as lubricants. SILs have high thermal stability meaning they have low flammability, are highly conductive, are not volatile, and have melting points below 100°C. As part of a larger project, novel solvent molecules containing nitrogen moieties were synthesized to be used in the study of the formation and properties of new SILs. Four different solvents were targeted initially to be synthesized: 1,2-bis[2-(N,N-diethylamino)ethoxy]ethane (NOON), 1,2-bis-[2-(N,N-dimethylamino-2-ethoxy)ethyl]ether (NOOON), 1-[2-(N,N-diethylamino)ethoxy]-2-(2-methoxyethoxy)ethane (OOON), and 1-[2-(N,N-dimethylamino-2-ethoxy)ethyl]-2-[2-(2-methoxyethoxy)ethyl]ether (OOOON). The syntheses of NOON and NOOON were successful as evidenced by the IR and NMR spectra of the compounds. The OOON appears to have been synthesized from analyses of the IR spectra, but the integration values from the ^{1}H NMR are not what was expected so further work in the preparation of OOON and OOOON is needed.

Objective

To prepare a family of novel solvent molecules containing tertiary amines that will be used to study how cation-solvent interaction affect SIL properties.

Introduction

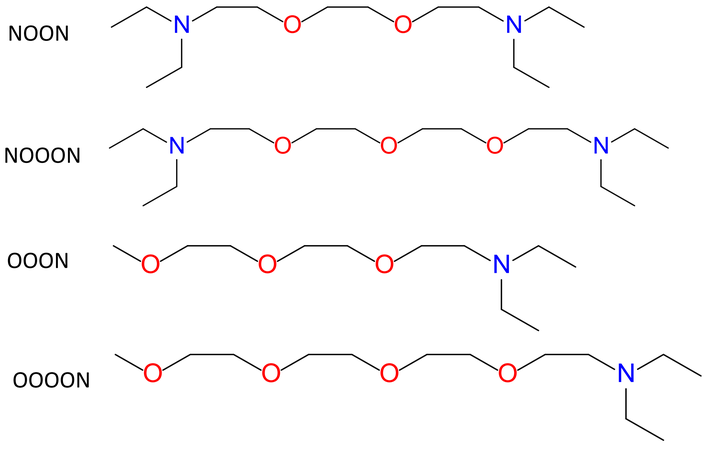
When methyl-capped ethylene glycols (glymes) are mixed in equimolar ratios with inorganic salts, the ether oxygen atoms of the solvent coordinates the cation to form a complex cation. In the case of linear glymes, the solvent molecule wraps around the cation to from the crown-ether like structure. In an ideal SIL, the cations are coordinated primarily by the solvent molecule with few cation-anion interactions, leaving the anions to exist as solvent separated species.[1,2]



Generic reaction between a triglyme molecule and LiX to form a SIL.

Target Molecules

The following molecules are the solvent molecules that were targeted to be synthesized for this part of the project.



Experimental Methods

A 3-step synthesis based on a literature procedure[3] was used to prepare each of the target molecules.

Step 1 – Bromination R-OH + PBr_3 → R-Br

Step 2 – Amination R-Br + $(CH_3CH_2)_2NH$ → R-N$(CH_2CH_3)_2$

Step 3 – Isolation of the Target Solvent

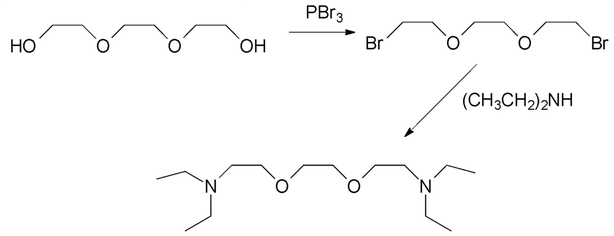
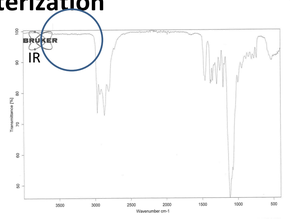
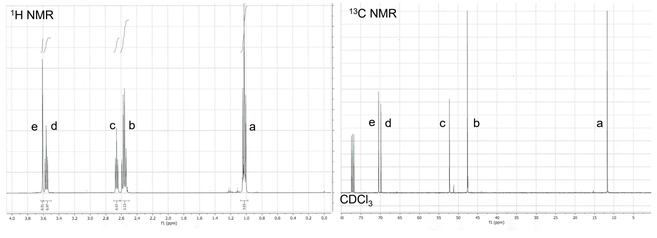


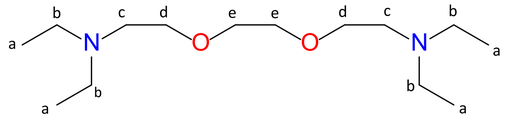
Illustration of the steps in the 3-day synthesis of the target molecules, specifically 1,2-bis[2-(N,N-diethylamino)ethoxy]ethane, referred to in this project as NOON.

Results – Characterization

Example IR spectrum is shown to the right. (NOON). IR spectroscopy was used to confirm the replacement of the –OH groups and that there was no excess diethyl amine present by examining the region of the IR where O-H and N-H bands would appear.







Example ^{1}H and ^{13}C NMR spectra for one of the solvent molecules prepared (NOON) are shown above. NMR spectroscopy was used to confirm the identify of the formed products. Integration values from ^{1}H NMR spectroscopy were particularly useful in assaying the purity of the formed products.

Acknowledgments

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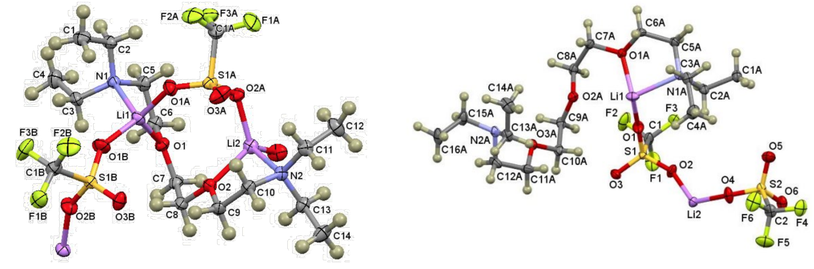
Results – Analyses of Formed SILs

Molecule	Conductivity @25°C, µS/cm	Conductivity, @35°C, µS/cm	Conductivity, @45°C, µS/cm	Conductivity, @55°C, µS/cm	Viscometry, mPa * s	T_m or T_g, °C
OOOO LiTf	274	368	466	576	348.6 @ 23.83°C	34.7
OOOO LiTFSI	1982	2390	2780	3200	50.46 @ 21.83°C	-58.14
NOON LiTf	37.7	51.5	69.1	89.0	OUT OF RANGE	>250
NOON LiTFSI	92.6	167.2	277	424	2186 @ 22.98°C	
OOOOO LiTf	346	442	545	653	77.16 @ 25.16°C	-59.9
OOOOO LiTFSI	2230	2710	3160	3640	37.71 @ 22.24°C	-48.36
NOOON LiTFSI	85.1	152.9	253	389	1261 @ 26.64°C	-68.15
OOOON LiTFSI	26.5	51.6	92.0	150.6	4038 @ 26.89°C	

Above is a table that denotes all of the data obtained by running conductivity, viscosity, and DSC tests on the solvate ionic liquids made from mixing the aforementioned target molecules and salts. The OOOO solvent molecule was commercially available. SILs formed with LiTf had lower conductivities than those formed with LiTFSI in all cases.



Single crystals of NOON$(LiTf)_2$ (left) and NOOON$(LiTf)_2$ (right) were isolated. Each anion coordinates two Li^+. The Li^+ ions are four-fold coordinated in each compound. The cations preferentially interact with the N atoms of the solvent molecules. SILs created from LiTFSI did not form crystals at room temperature.

Conclusions

In conclusion, two of the four target molecules were synthesized accurately as confirmed by IR and NMR analyses. Our ability to tune SIL properties through the placement of tertiary amines along the backbone of the solvent provides crucial information on how solvent structure affect SIL properties. Furthermore, the salt anion plays an important role in the transport properties of our compounds, with LiTFSI-based SILs out-performing LiTf-based SILs.

Future Research

Further investigation as to why the integration values were off in the ^{1}H NMR spectra of OOON is needed. When a successful synthetic procedure is developed, the same procedure will be used to prepare the OOOON solvent molecule. Then the next two novel solvent molecules that will be targeted to prepare will be 1,2-bis[(2-methoxy-N-ethyl)-N-methyl]ethylenediamine (ONNO) and N,N-bis[2-(2-methoxyethoxy)ethyl]-N-methylamine (OONOO). The remaining target novel solvent molecules of interest are *N,N*-bis[2-(*N,N*-dimethylamino-2-ethoxy)ethyl]-*N*-methylamine (NONON) and 1,2-bis[2-((2-methoxy-*N*-ethyl)-*N*-methyl)aminoethyl]ether (ONONO).

References

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3) Davidson, R.; Goodin, J. The Polymerization of acrylates using a combination of a carbonyl compound and an amine as a photo-initiator system. *European Polymer Journal* 1982, 18, 597–606.