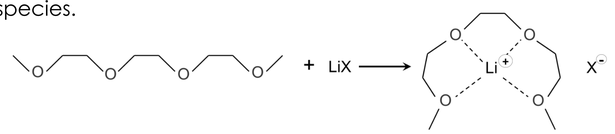
Synthesis of Novel Solvent Molecules for use in Solvate Ionic Liquids

Amanda Liske, Jacob Allred, Spence Pilcher, Christopher M. Burba

Department of Natural Sciences, College of Science and Health Professions
Northeastern State University, Tahlequah, OK 74464

Background

Solvate ionic liquids (SILs) are a subgroup of ionic liquids in which an organic solvent, which contains atoms capable of donating one or more electron pairs, wraps around a solute cation molecule. Methyl capped ethylene glycols, or "glymes", and crown ethers are commonly used for the molecular solvent portion of SILs. In the case of linear glymes, the solvent molecule wraps around the cation to form a 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 separated species.



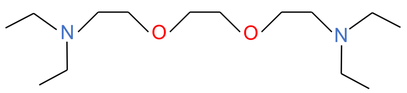
Generic reaction between a triglyme and LiX to form a SIL.

A possible way to expand the array of properties allowed by SILs is to replace glymes with different molecular solvents which are capable of coordinating with cations.

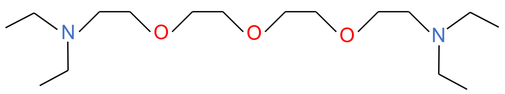
Objective

In order to study the formation and properties of new SILs and as a part of a larger project, this research focused on synthesizing novel solvent molecules by systematically replacing all or part of the oxygen atoms in glymes with tertiary amines. Six different solvents were targeted 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**), 1-[2-(*N*,*N*-dimethylamino-2-ethoxy)ethyl]-2-[2-(2-methoxyethoxy)ethyl] ether (**OOOON**), 1,2-bis[(2-methoxy-*N*-ethyl)-*N*-methyl]ethylenediamine (**ONNO**), and 1-(*N*-methyl-*N*',*N*'-diethylethylene diamine)-2-(2-methoxyethoxy)ethane (**NNOO**).

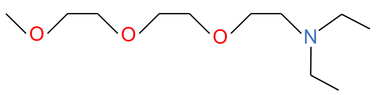
NOON



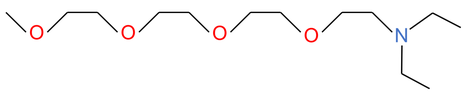
NOOON



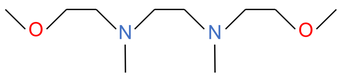
OOON



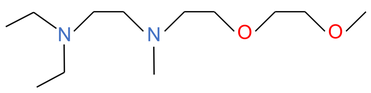
OOOON



ONNO



NNOO



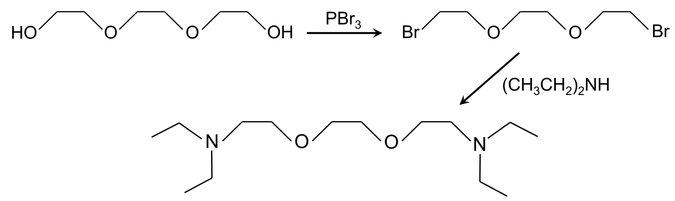
Methods

NOON and NOOON Synthesis Reaction:

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

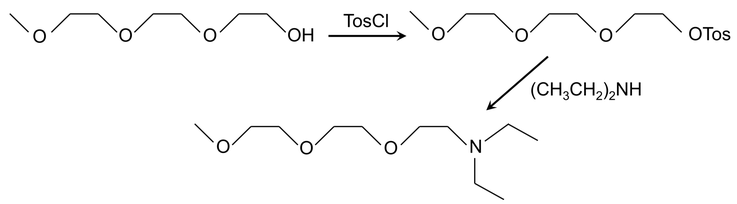


OOON and OOOON Synthesis Reaction:

Step 1 – Tosylation R-OH + TosCl → R-OTos

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

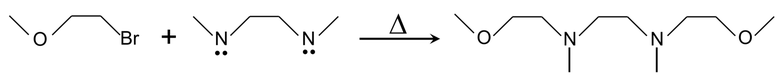
Step 3 – Isolation of the Target Solvent



ONNO Synthesis Reaction:

Step 1 – Substitution R_1-Br + N-R_2-N → R_1-N-R_2-N-R_1

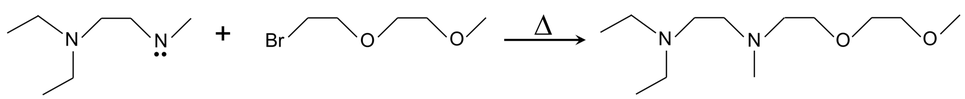
Step 2 – Isolation of the Target Solvent



NNOO Synthesis Reaction:

Step 1 – Substitution R_1-N + Br-R_2 → R_1-N-R_2

Step 2 – Isolation of the Target Solvent



Acknowledgements

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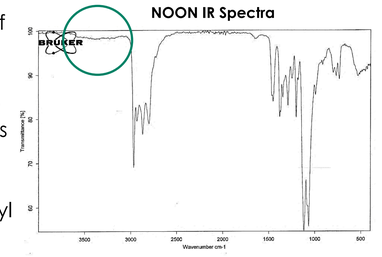
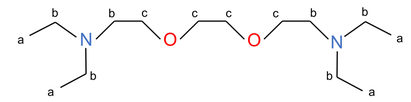
Data & Analysis

Infrared (IR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy were used to confirm the structures and purity of all intermediate molecules and products . Example characterization using these methods for NOON is as follows:

By examining the region of the IR where O-H and N-H bands would appear, IR spectroscopy was used to confirm (1) the –OH groups on the starting molecule were replaced and (2) there was no excess diethyl amine present.



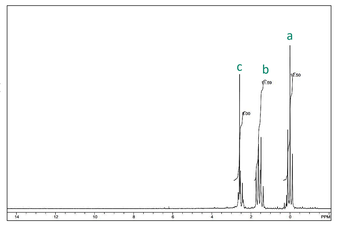
Expected peaks and integration values were predicted by analyzing the structure of the molecule. Observed values in the ^{1}H NMR spectra were used to confirm these predictions.



NOON ^{1}H NMR Spectra

<u>Expected Integration Values (ppm)</u>:
12.00 (a), 12.00 (b), 8.00 (c)

<u>Observed Integration Values (ppm)</u>:
12.50 (a), 11.59 (b), 8.00 (c)



Discussion & Future Research

The six novel solvent molecules synthesized in this project can be combined with various salts to create new SILs. The array of properties offered by these SILs may be studied by measuring their conductibility, viscosity, and testing them in batteries. These measurements and tests are being conducted as a separate portion of this larger project with SILs. The next novel solvent molecules to be targeted are *N*,*N*-bis[2-(2-methoxyethoxy)ethyl]-*N*-methylamine (OONOO), *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).

Relevance of Study

Solvate ionic liquids possess high thermal stability- meaning they are highly conductive, non-volatile, and have melting points below 100˚C. They have practical applications in lithium batteries, pharmaceuticals, and food industry. In the context of petroleum research, SILs created from lithium salts may function as replacements for existing solvents in applications as diverse as heat transfer fluids, lubricants, or electrolyte solutions. In synthesizing the solvents used in SILs, the array of properties offered may be expanded.