

PRF# 57803-UR10**Synthesis and Characterization of a New Family of Solvate Ionic Liquids**

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Project Overview

The principle goal of this research project is to synthesize a new family of solvate ionic liquids (SILs) that are based on molecular solvents containing ether oxygen atoms and tertiary amines. Specific objectives include,

- Synthesizing the new molecular solvents and verifying products.
- Screening the molecular solvents in terms of their ability to produce SILs when mixed with inorganic salts in a 1:1 mole ratio.
- Characterizing the new SILs spectroscopically and thermally.
- Measuring the viscosity and conductivity of the new SILs.

The first year of this three-year grant has proven to be exceptionally productive as the PIs have made considerable progress towards our original research goals.

Accomplishments Achieved

A total of eight molecular solvents from our original proposal were examined during the first year of the project. Of these, three were commercially available and the remaining five were synthesized in-house. All of the compounds in our proposed plan of study are oligomers of ethylene oxide and/or tertiary ethylene amines. The IUPAC names for many of these compounds are rather long and cumbersome. For the sake of brevity, we will refer to the compounds according to the sequence of oxygen and nitrogen atoms present in the molecule. Therefore, OOOO represents triethylene glycol dimethyl ether, while OOOON is 1-[2-(*N,N*-dimethylamino-2-ethoxy)ethyl]-2-[2-(2-methoxyethoxy)ethyl]ether. Our initial efforts have focused on lithium-containing salts, and our overall progress is summarized in the following table.

Compound	Source	SIL Screening ^(a)		Spectroscopic Characterization		Thermal Analysis	Transport Properties
				FT-IR	FT-Raman		
OOOO	Commercial	LiTf	Forms SIL	Complete	Complete	Complete	In Progress
		LiTFSI	Forms SIL	Complete	Complete	Complete	In Progress
		LiPF ₆	Stability Issues	N/A	N/A	N/A	N/A
OONN	Synthesized	LiTf	Forms SIL	Complete	Complete	Complete	In Progress
		LiTFSI	Forms SIL	Complete	Complete	Complete	In Progress
NOON	Synthesized	LiTf	In Progress	In Progress	In Progress	In Progress	In Progress
		LiTFSI	Forms SIL	Complete	Complete	Complete	In Progress
NNNN	Commercial	LiTf	No SIL	N/A	N/A	N/A	N/A
		LiTFSI	No SIL	N/A	N/A	N/A	N/A
OOOOO	Commercial	LiTf	Forms SIL	Complete	Complete	In Progress	In Progress
		LiTFSI	Forms SIL	Complete	Complete	In Progress	In Progress
OOOON	Synthesized	LiTf	In Progress	In Progress	In Progress	In Progress	In Progress
		LiTFSI	In Progress	In Progress	In Progress	In Progress	In Progress
NOOON	Synthesized	LiTf	In Progress	In Progress	In Progress	In Progress	In Progress
		LiTFSI	In Progress	In Progress	In Progress	In Progress	In Progress
NNNNN	Synthesized	LiTf	No SIL	N/A	N/A	N/A	N/A
		LiTFSI	Forms SIL	Complete	Complete	Complete	In Progress

^(a)LiTf and LiTFSI are abbreviations for lithium trifluoromethanesulfonate and lithium bis(trifluoromethylsulfonyl)-imide, respectively.

Most of the solvents investigated are capable of forming SILs with either LiTFSI or LiTf. A notable exception is NNNN, which did not form an SIL with either salt. The ability to explore SILs with different sequences of nitrogen

and oxygen atoms provides a unique opportunity to explore how binding strength between the chelating molecule and the cation of the salt affects SIL properties. We are especially pleased that our central goal of creating these new materials is feasible. A preliminary analysis of the spectroscopic data suggests most of the SILs consist of ion paired anions, and the thermal analysis shows the materials are predominately glass formers at low temperature. Transport property measurements are currently on-going, but our general observation is that replacing oxygen atoms with nitrogen atoms in the molecular solvent is typically accompanied by an increase in SIL viscosity.

In addition to the eight compounds presented above, we elected to add four additional compounds to our list of molecular solvents: triethylene glycol, tetraethylene glycol, triethylenetetramine, and tetraethylenepentamine. These materials are the non-methylate analogues to OOOO, OOOOO, NNNN, and NNNNN. Since these solvents contain O-H and N-H moieties, any resulting SILs will be able to interact via hydrogen bonding interactions. We view this as an interesting extension to our current study. Therefore, we have chosen to examine the feasibility of synthesizing SILs with these solvents and characterizing the materials from a spectroscopic point of view. All four compounds are able to form SILs with LiTf and LiTFSI. Spectroscopic data was collected summer 2018.

Challenges and Potential Solutions

The original proposal called for the screening of our new molecular solvents with LiPF_6 ; however, we discovered this salt is particularly difficult to work with and has a propensity to undergo decomposition. Therefore, we have chosen to eliminate LiPF_6 and focus our efforts on more fruitful compounds. Furthermore, we conducted a preliminary screening of AgTf with select molecular solvents. Silver salts are notoriously difficult to work with given their photoreactive nature. However, we did not expect the Ag-containing SILs to react with the sample holders used to measure the properties of the materials. This presents a unique challenge in that we do not wish to permanently damage the sample holders for our research equipment in testing these materials. We plan to focus our immediate efforts on the Li-containing salts over the next year. This will enable us to remain on track in meeting our research goals, while providing time to identify solutions for sampling the Ag-containing materials. Finally, published procedures for the preparation of the proposed molecular solvents are multi-day experiments that produce gram-sized quantities of product. The total mass of solvent required for SIL synthesis and all of the proposed characterization using existing equipment is in the range of 15-20 g. The time required to prepare sufficient quantities of material has been problematic. We propose two solutions for this problem. First, we aim to explore microwave-assisted techniques to synthesize the molecular solvents. Microwave heating is generally more efficient than “traditional” heating methods, thereby reducing reaction time. The co-PI on this project has extensive experience with microwave-assisted synthesis. Second, we have secured funding from Northeastern State University to purchase small sample volume viscosity and conductivity meters in fall 2018. Existing equipment for measuring transport properties require the large quantities of material; smaller sample volumes afforded by the new instruments will greatly reduce the amount of molecular solvent required.

Research Outlook for the Second Year

The 2018-19 academic year will be used to complete tasks listed as “in progress” in the preceding table. We plan to pay particular attention to measuring the transport properties of the currently prepared materials as well as adapting traditional synthetic procedures for the molecular solvents to microwave-assisted procedures. Summer 2019 will see the synthesis of new molecular solvents in accordance with our original proposed plan of study.

Professional Impact on Faculty and Students

This research project has enhanced the professional careers of the faculty and students in several tangible ways. First, we have explored synthetic procedures, established protocols for characterizing the materials, and leveraged the research program to extend our professional networks. Students in particular have learned organic synthesis, spectroscopic and thermal characterization, and how to properly handle materials that are air/water sensitive. In addition, they have learned how to trouble shoot difficulties in the laboratory, how to properly analyze experimental results, and how to maintain adequate records when working in a large group. All of these skills are essential for scientific careers. Of the four undergraduate students who participated in the project, two of the students are considering graduate school. This decision is due, in part, to their experience with this ACS PRF grant.