

SLATT UNDERGRADUATE RESEARCH FELLOWSHIP

FINAL REPORT

SCHOLAR NAME:	Katelyn Wendt
FACULTY ADVISOR:	Brandon L. Ashfeld
PROJECT PERIOD:	June 2021-July 2021
PROJECT TITLE:	Task Specific, Thermo-responsive Ionic Liquids for Directional Solvent Extraction Water Desalination
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	<input checked="" type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear <input type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind

MAJOR GOALS AND ACCOMPLISHMENTS

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Synthesis of an IL scope aimed at enabling the energy efficient desalination of hyper salinity water.	I developed an IL scope based on previous work done in our lab consisting of phosphonium-based and imidazolium-based ILs that had promising results when tested for functionality in DSE systems.	100%
Identification of a specific IL that will improve upon the existing salt rejection rate and freshwater yield exhibited by previous work in the Ashfeld Lab.	I identified one IL specifically that showed especially promising functionality for DSE processes. I plan to perform a substrate scope to further improve functionality of this IL.	80%
Focus on IL frameworks derived from naturally occurring substances to address potential issues of environmental toxicity.	All ILs synthesized in this project were derived from naturally occurring substances.	100%

RESEARCH OUTPUT

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	
EXTERNAL AWARDS RECEIVED	
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	Hill, H. M.; Tucker, Z. D.; Rodriguez, K. X.; Wendt, K. A.; Ashfeld, B. L. "Generation of functionalized azepinone derivatives via a (4+3)-cycloaddition of vinyl ketenes and α -imino carbenes derived from N-sulfonyl-triazoles." <i>Manuscript submitted for publication.</i> Gulotty, Eva M.; Sanadhya, Sidharth; Wendt, Katelyn; Tucker, Zachary D.; Moghaddam, Saeed S.; Ashfeld, Brandon L. "A Delicate Balance of Interionic bonding in High Temperature LCST Phosphonium Ionic Liquids." <i>Manuscript in progress.</i>
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	Summer Undergraduate Research Symposium, Task Specific Thermo-Responsive Ionic Liquids for Directional Solvent Extraction Water Desalination, July 2021, University of Notre Dame
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	
INTERNAL COLLABORATIONS FOSTERED	Dr. Tengfei Luo, Department of Aerospace and Molecular Engineering, University of Notre Dame, collaborated on the development of a DSE system.
EXTERNAL COLLABORATIONS FOSTERED	Dr. Saeed Moghaddam, Department of Mechanical and Aerospace Engineering, University of Florida, collaborated on the development of high temperature LCST IL fluids
WEBSITE(S) FEATURING RESEARCH PROJECT	
OTHER PRODUCTS AND SERVICES	

RESEARCH EXPERIENCE

I really enjoyed my summer research experience. It definitely met my expectations, but in different ways than I was anticipating. I have worked in the Ashfeld lab in previous semesters, so I knew that I would be continuing with a project that other lab members had previously worked on. I didn't anticipate just how much I would be able to contribute in the few weeks that I was on campus, though. It was really enjoyable to make a significant, positive contribution to an ongoing research project. I also expected my time in the lab to be more similar to a typical 9-to-5 job, and that is not at all what I experienced. I ended up working some strange hours to utilize instrument time and learn new techniques, but this full-time, yet flexible, schedule felt true to what a career in research is actually like. It was really informative to experience a traditional academic research environment, especially as I approach my graduate school applications.

Lab personnel were especially helpful in mentoring me throughout the entire summer. They taught me new research techniques, guided me in through the scientific process of formulating and testing new hypotheses, and provided input as I developed my final poster presentation for the Summer Undergraduate Research Symposium. I especially learned about how to be a good collaborator on a research project with groups from other universities throughout this experience, which is an extremely important skill to have as I look to enter the research field myself. I attribute most of this learning experience to my PI and the lab personnel that I closely worked with.

I attended the seminars and events offered later in the summer to undergraduate researchers, but I missed out on the earlier events. These events were incredibly helpful in teaching me how to create journal quality figures and produce a formal poster presentation. I think my experience would have been improved if I had taken advantage of these opportunities and resources earlier in the summer. Otherwise, my experience was incredible, and I would highly recommend the summer undergraduate research program here at Notre Dame to my peers looking for an authentic research experience.

FINAL WRITTEN REPORT

Abstract:

The ability to desalinate high salinity water is critical to addressing the ongoing global water shortage¹. Undertaking this problem by minimizing energy consumption on a production level scale is necessary for rendering current polluted water to potable levels of saline content while also limiting waste. My project focuses on developing a set of *N*-heterocycle-based and phosphonium-based, task specific ionic liquids (ILs) as environmentally benign, non-toxic fluids for use in an energy efficient directional solvent extraction (DSE) process for the desalination of industrial and residential water resources². Remarkable difficulties have been encountered in the development of energy efficient large-scale water desalination processes. IL thermo-responsive fluids (TRFs) that exhibit lower critical solution temperature (LCST) and upper critical solution temperature (UCST) behavior were determined to be the most effective at pure water separation. By implementing promising ILs in DSE systems, freshwater yield has the potential to greatly increase, and energy consumption is limited¹.

Introduction:

There are 1.1 billion people worldwide who lack access to clean water³. This number is statistically high, yet there is not much that can be done to help this problem using natural freshwater resources alone, as only 1% of the earth's water is usable freshwater³. However, 97.5% of global water is made up by saltwater bodies. Desalination of these abundant natural saltwater resources is a promising means of meeting demand for freshwater and would provide for a long-lasting solution to the current global water crisis. Currently, membrane-based desalination techniques (e.g., reverse osmosis, etc.)^{4,5} are utilized to desalinate high salinity water samples on a small scale, but these methods are very energy inefficient on large scale due to the tendency of membranes to get plugged up during desalination and the higher energy sources required to unplug them.

TRFs have the potential to be incredibly useful in water desalination processes¹. They trap pure water for separation and form non-membranous DSE systems. Therefore, they require less heat and electrical energy input, lowering the monetary and environmental costs of desalination processes. Most interestingly, TRFs exhibit LCST and UCST behaviors, allowing them to undergo phase separation above (LCST) and below (UCST) specific temperatures (Fig. 1, Fig. 2). While UCST behavior is commonly observed in liquids and is well accepted, the effect of IL structure on LCST behavior is poorly understood. Throughout the course of my project, I focused on the analysis of LCST behavior of select ILs that exhibit phase separation behavior through variable temperature (VT) NMR with the goal of investigating the effect of chemical structure on LCST behavior in comparison to what is known about UCST behavior.

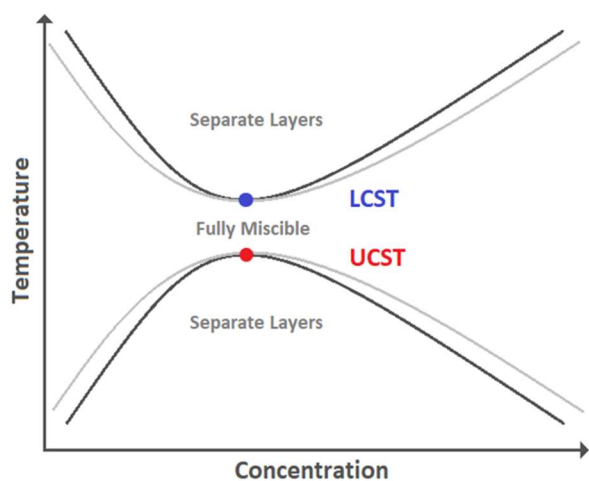


Figure 1: LCST/UCST Behavior in TRFs.¹

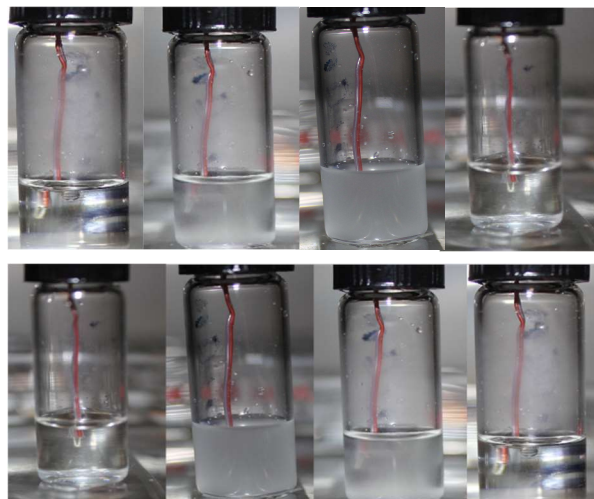


Figure 2: Images of ILs undergoing UCST (top) and LCST (bottom) phase separation.

ILs in DSE Systems:

Directional solvent extraction systems are designed to utilize the temperature dependent separatory properties of ILs to extract pure water from a high salinity sample¹. As shown in the figure below (Fig. 3), a hyper saline solution is mixed into an

ionic liquid sample (a) at lower temperature where the two layers will remain separate. As the temperature of the solution is increased, the IL will decrease in viscosity and become fully miscible with pure water, pulling pure H₂O molecules away from highly concentrated salt ions and allowing them to precipitate out of solution (b). The precipitated salt can then be separated from the IL mixture (c) at this higher temperature as it is its own distinct layer. As you cool down the solution of IL and pure water that remains, the IL once again increases in viscosity and dissolves out of the solution (d), leaving pure water in its own layer that can be separated out from the IL (e). This system is particularly energy efficient because, unlike the current membranous systems, it doesn't require drastic increases in temperature. ILs are also extremely stable compounds, so they can be reused in DSE systems to continue purification of large hyper salinity water resources, allowing materials costs to be significantly lowered from those of current desalination processes. Based on this model, ILs have great potential for efficient and environmentally friendly success in water desalination.

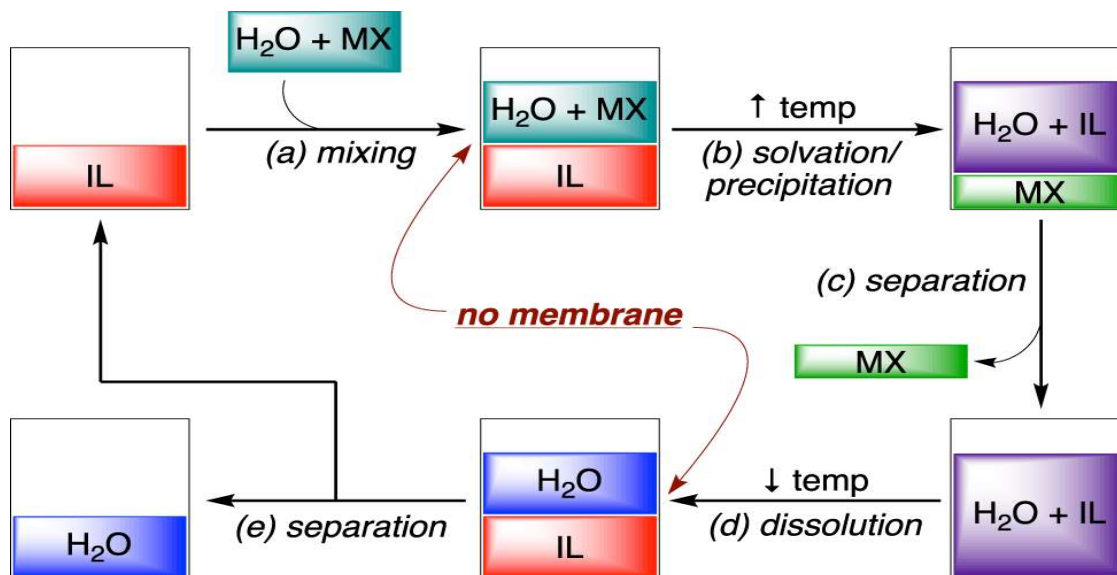


Figure 3: ILs in DSE Systems¹.

ILs vary in their efficacy of trapping pure water in contaminated samples and in their functional temperature ranges. Throughout the course of the project, I synthesized many different IL samples and analyzed their temperature ranges using VT NMR. Phosphonium-based ILs and imidazolium-based ILs proved to be the most effective for water separation and had the most viable temperature ranges based on previous work done by the Ashfeld lab, so I developed an IL scope consisting of phosphonium and imidazolium ILs that we specifically focused on for use in a DSE system (Fig. 4). Derivatives of these specific ILs were synthesized and further examined for their functionality.

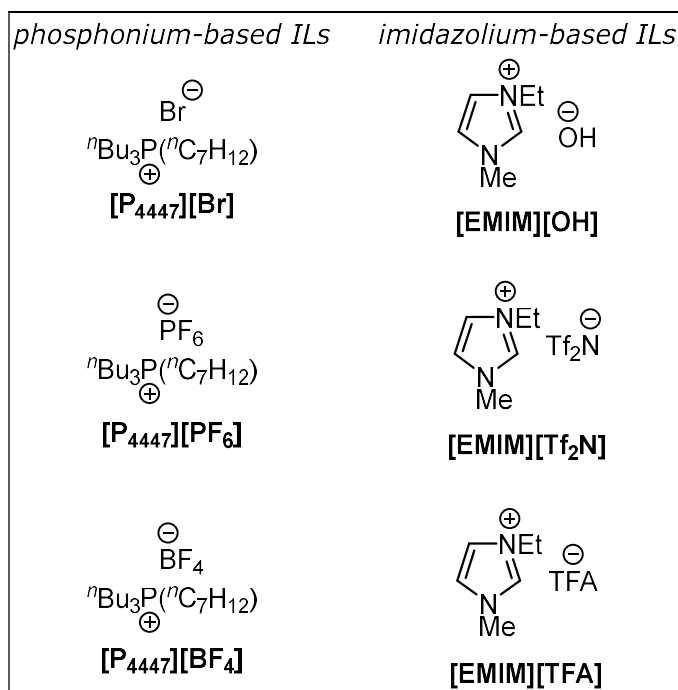


Figure 4: IL Scope.

TRF DSE Desalination Performance:

In previous work completed by the Ashfeld lab, with our collaborators in the Luo lab¹, a different set of phosphonium and imidazolium ILs were tested for their ion rejection rate (%), solubility in H₂O (ppm), and pure H₂O yield (%/°C) following desalination. After testing these parameters, the imidazolium-based ILs proved to yield the most promising results, with [EMIM][Tf₂N] showing the greatest promise¹. Table 1 compares these parameters across the imidazolium ILs [BMIM][Tf₂N] and [EMIM][Tf₂N], as well as for decanoic acid, which was the standard IL used for desalination processes prior to the work done by our lab (Table 1).

IL	Ion Rejection	Solubility in H ₂ O (ppm)	H ₂ O Yield (%/°C)
[BMIM][Tf ₂ N]	70.5 ± 2.9%	<90	<0.082
[EMIM][Tf ₂ N]	97.5 ± 0.8%	130–150	0.304 ± 0.023
Decanoic acid	96.9–98.0%	36–1506,29	0.025 ± 0.0026

Table 1: Performance of TRFs in Desalination Processes.

After [EMIM][Tf₂N] was identified as the most efficient IL for water desalination, a temperature study was conducted to compare the freshwater yield (wt%) of both [EMIM][Tf₂N] and the decanoic acid standard across a viable temperature range (Fig. 5). [EMIM][Tf₂N] showed significantly greater separation (an over tenfold increase) than decanoic acid across the entire temperature range¹. The functionality of [EMIM][Tf₂N] in desalination processes was further examined by testing its ability to produce high freshwater yields from water samples of varying levels of salinity. Even at highly concentrated saltwater samples, [EMIM][Tf₂N] was able to recover significant amounts of pure water within a reasonable temperature range (Fig.5).

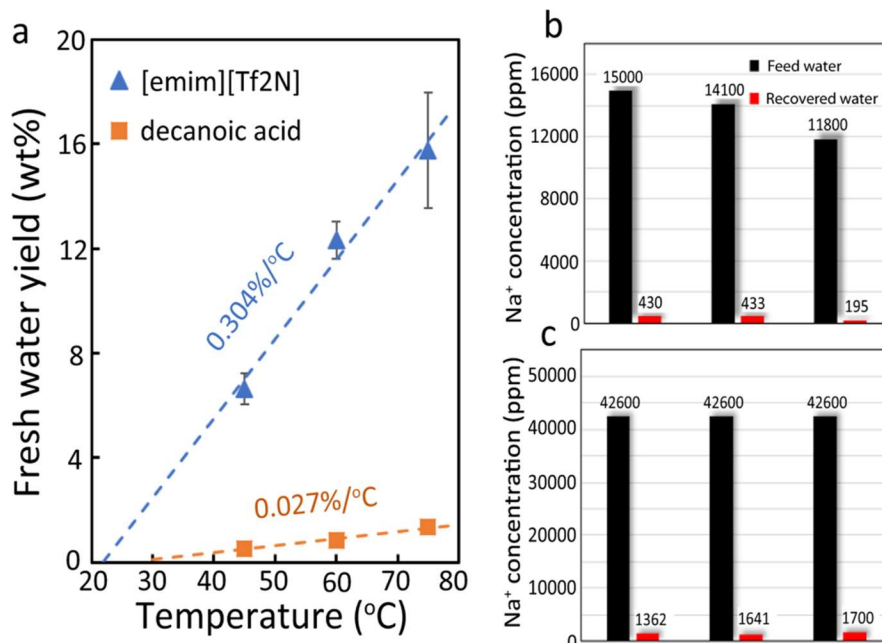


Figure 5¹: (a) Water yield and temperature relationship of [EMIM][Tf₂N] and decanoic acid. (b) Desalination of moderate salt content water (3.7–5.0 wt%). (c) Desalination of high salt content water (10.8 wt%).

From this data, I determined that the best direction to take the project would be to optimize [EMIM][Tf₂N] functionality as well as the longer chain phosphonium ILs (Fig. 4), which also efficiently yielded pure water over a reasonable temperature range. While previous work showed that [EMIM] was the most optimal imidazolium cation for DSE processes, I synthesized other [EMIM] derivatives by varying the anion present. Both [EMIM][OH] and [EMIM][TFA] proved to be too volatile for DSE processes, so [EMIM][Tf₂N] remained the optimized structure. However, I found that mixtures of [EMIM][Tf₂N] and these [EMIM] additives, [EMIM][OH] or [EMIM][TFA], in varying ratios produced more promising results in desalination processes than [EMIM][Tf₂N] alone. Not much is understood about why these mixtures seem more efficient and effective in DSE systems than [EMIM][Tf₂N] alone, but we plan on continuing to examine this finding by testing other [EMIM] additives in mixtures with [EMIM][Tf₂N].

Future Directions:

Our lab has reported [EMIM][Tf₂N] as the most promising IL for DSE processes, as it enables a tenfold increase in freshwater yield over current techniques. Specifically, mixtures of [EMIM][Tf₂N] with other [EMIM] additives showed great promise for efficient water desalination using a DSE system. We will improve and expand upon these results by synthesizing

derivatives of this specific IL to further improve its functionality and testing them in mixtures of varying ratios with [EMIM][Tf₂N]. The utilization of ILs exhibiting LCST behavior has the potential to substantially improve the energy efficiency of DSE processes and would enable DSE systems for water treatment on a global scale, so we are continuing to work towards optimization of [EMIM][Tf₂N] for DSE processes.

References:

- (1) Guo, J.; Tucker, Z. D.; Wang, Y.; Ashfeld, B. L.; Luo, T. "Ionic liquid enables highly efficient low temperature desalination by directional solvent extraction." *Nat. Commun.* **12**, 437 (2021)
- (2) Hill, H. M.; Tucker, Z. D.; Rodriguez, K. X.; Wendt, K. A.; Ashfeld, B. L. "Generation of functionalized azepinone derivatives via a (4+3)-cycloaddition of vinyl ketenes and α -imino carbenes derived from N-sulfonyl-triazoles." *Manuscript submitted for publication.*
- (3) Chakraborti, R. K.; Kaur, J.; Kaur, H. Water Shortage Challenges and a Way Forward in India. *Journal: American Water Works Association* **111**, (2019).
- (4) Elimelech, M. & Phillip, W. A. The future of seawater desalination: energy, technology, and the environment. *Science* **333**, 712–717 (2011).
- (5) Y. Zhong, X. Feng, W. Chen, X. Wang, K.-W. Huang, Y. Gnanou and Z. Lai, *Environmental Science & Technology* **50**, 1039-1045 (2016).