Final Technical Report

Federal Agency and Organization: DOE EERE – Geothermal Technologies Program

Recipient Organization: University of Notre Dame
DUNS Number: 824910376
Recipient Address: 180 Fitzpatrick Hall, Notre Dame, IN 46556

Award Number: DE-FG-3608-GO88020-AO
Project Title: Notre Dame Geothermal Ionic Liquids Research: Ionic Liquids for Utilization of Geothermal Energy
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DOE Project Team: DOE Contracting Officer – Genevieve Wozniak
DOE Project Officer – William Vandermeer
Project Monitor – Pete Simon

STATUS / ACCOMPLISHMENTS

Project Summary: The goal of this project was to develop ionic liquids for two geothermal energy related applications. The first goal was to design ionic liquids as high temperature heat transfer fluids. We identified appropriate compounds based on both experiments and molecular simulations. We synthesized the new ILs, and measured their thermal stability, measured storage density, viscosity, and thermal conductivity. We found that the most promising compounds for this application are aminopyridinium bis(trifluoromethylsulfonyl)imide based ILs. We also performed some measurements of thermal stability of IL mixtures and used molecular simulations to better understand the thermal conductivity of nanofluids (i.e., mixtures of ILs and nanoparticles). We found that the mixtures do not follow ideal mixture theories and that the addition of nanoparticles to ILs may well have a beneficial influence on the thermal and transport properties of IL-based heat transfer fluids. The second goal was to use ionic liquids in geothermally driven absorption refrigeration systems. We performed copious thermodynamic measurements and modeling of ionic liquid/water systems, including modeling of the absorption refrigeration systems and the resulting coefficients of performance. We explored some IL/organic solvent mixtures as candidates for this application, both with experimentation and molecular simulations. We found that the COPs of all of the IL/water systems were higher than the conventional system – LiBr/H_2O. Thus, IL/water systems appear very attractive for absorption refrigeration applications.

Task 1.0 Heat transfer fluids

The purpose of this task was to design, develop and test ionic liquids as heat transfer fluids for geothermal applications.

1. **Planned Activities**: This Task included eight Subtasks that are listed below.
   Subtask 1.1 Selection, Design, Synthesis and Purification of ILs
   Subtask 1.2 Thermal Stability
   Subtask 1.3 Storage Density: Heat Capacity and Density
   Subtask 1.4 Viscosity
   Subtask 1.5 Thermal Conductivity
   Subtask 1.6 Materials Compatibility
   Subtask 1.7 Molecular Simulation of IL Properties
   Subtask 1.8 Molecular Simulation of Properties of IL/nanoparticle Mixtures
   All of the subtasks were completed as planned.

2. **Actual Accomplishments**

The ILs that we designed, synthesized and tested as potential heat transfer fluids were 1-hexyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide ([hmim][Tf_2N]), 1-hexyldimethylaminopyridinium bis(trifluoromethylsulfonyl)imide ([hDMAP][Tf_2N]), 1-butyl-dimethylaminopyridinium bis(trifluoromethyl-sulfonyl)imide ([bDMAP][Tf_2N]), and 1-hexyl-3-methyldimethyl- aminopyridinium bis(trifluoromethyl-sulfonyl)imide ([hmDMAP][Tf_2N]).. In

order to evaluate their potential as heat transfer fluids, we measured densities, viscosities, heat capacities and thermal conductivities of these compounds. The thermal decomposition temperatures are higher than silicone oil, the thermal conductivities are higher than silicone oil and the viscosities are attractive.

In addition, at high temperature, the ILs do not decompose. Rather, they evaporate slowly due to extremely low vapor pressures. The vapor pressures and enthalpies of vaporization that we measured for two of the ILs are shown in Table 1.

Table 1. Vapor pressures and enthalpies of vaporization of ionic liquids

IL	Vapor pressure (Pascals)					Enthalpy of vaporization (kJ/mol)
	240°C	260°C	280°C	300°C	320°C	
[bDMApy][Tf_2N]	0.16	0.43	1.05	2.86	5.79	112.4 ± 1.2
[hmim][Tf_2N]	0.44	1.40	3.01	10.85	20.48	121.2 ± 4.2

The thermodynamic and transport properties of IL might be even further improved by the addition of nanoparticles. There are various conflicting reports of very small concentrations of nanoparticles having a large impact on the properties of conventional liquids, including concerns about the experimental measurements. Therefore, we have investigating this phenomenon with molecular simulations. Wehave simulated the thermodynamic and transport properties of aqueous based nanofluids containing between 1 and 15 volume % gold particles. The primary finding is that these properties do not follow ideal mixture theories. Based on these results, the addition of nanoparticles to ILs may well have a beneficial influence on the thermal and transport properties of IL-based heat transfer fluids.

Task 2.0 Absorption refrigeration

The goal of this part of the project was to investigate the development of IL/water absorption refrigeration systems that are capable of exploiting even relatively *low* temperature heat sources, characteristic of shallow geothermal energy sources.

1. **Planned Activities**: This Task included three Subtasks that are listed below.
   Subtask 2.1 Ionic Liquids Studied
   Subtask 2.2 Molecular Simulation
   Subtask 2.3 Dynamic Simulation
   All the subtasks were completed as planned.

2. **Actual Accomplishments**

While using low temperature geothermal resources for heating is attractive, using that same energy to provide cooling would be even more valuable, especially in summer and in southern climates. In this project we evaluated the use of IL/water systems for absorption refrigeration, especially considering regenerator temperatures less than 150 °C.

The heat capacities, densities, vapor-liquid equilibrium and excess enthalpies for all of the IL/water mixtures under consideration of absorption refrigeration systems were measured and modeled. Using measured and re-examined modeled thermodynamic data, we confirmed that the coefficients of performance (COPs) of all of the IL/water systems are higher than the conventional system – LiBr/H_2O. Thus, IL/water systems appear very attractive for absorption refrigeration applications. The systems with the highest COPs actually have positive enthalpies of mixing. The water concentration in the ILs is relatively low, both in the absorber and the generator. Therefore, flowrates in the absorption side of the refrigeration system will have to be significantly higher than in the condenser/evaporator portion of the system. A process model showed that equipment sizes for a 1 ton IL/water refrigeration system are quite reasonable. We also developed a full dynamic model of the absorption refrigeration process. Using the thermodynamic data for [emim][OTf], we have found that operation of the IL/water absorption refrigeration system is extremely robust. Both startup and shutdown proceed smoothly and the dynamics are relatively insensitive to system upsets. Overall, the dynamic process modeling has confirmed the viability of IL/water absorption refrigeration, using low temperature geothermal heat sources.

PRODUCTS / DELIVERABLES

Training and Professional Development:

The following co-workers were trained as a part of this grant:

Lindsey Ficke, Ph.D. student
Marjorie Massel, Ph.D. student
Yong Huang, Ph.D. student
Gianluca Puliti, Ph.D. student
D. Andrei Maces, Ph.D. student
Dr. Amir Vahid, post-doctoral research associate
Dr. Craig Tenney, post-doctoral research associate

Publications, Conference Papers, and Presentations:

This is the full list to date of publication, presentations and Ph.D. theses resulting from this project.

Publications

- G. Puliti, S. Paolucci and M. Sen, "Transport Properties of Nanofluids," *Proceedings of the 2008 ASME International Mechanical Engineering Congress and Exposition*, Paper No. IMECE2008-68819, Boston, MA, October 31-November 6, 2008.
- G. Puliti, S. Paolucci, M. Sen, and D. Gezelter, "The Study of Solvation Effects on Thermodynamic Properties of Nanofluids Using Molecular Dynamics," *Bulletin of the American Physical Society*, Vol. 53, p. 308, (2008).
- G. Puliti, S. Paolucci and M. Sen, "Properties of Nanofluids," *Bulletin of the American Physical Society*, Vol. 54, p. 235, (2009).
- G. Puliti, S. Paolucci and M. Sen, "Properties of Nanofluids," *Proceedings of the 2009 ASME International Mechanical Engineering Congress and Exposition*, Paper No. IMECE2009-10398, Lake Buena Vista, FL, November 13-19, 2009.
- J. A. Enszer and M. A. Stadtherr, "Rigorous Propagation of Imprecise Probabilities in Process Models," in *Design for Energy and the Environment*. Proceedings of the 7th International Conference on the Foundations of Computer-Aided Process Design (eds. M. M. El-Halwagi and A. A. Linninger), Taylor & Francis (2009).
- L. D. Simoni, J. F. Brennecke and M. A. Stadtherr, "Asymmetric Framework for Predicting Liquid-Liquid Equilibrium of Ionic Liquid-Mixed Solvent Systems. 1. Theory, Phase Stability Analysis, and Parameter Estimation," *Ind. Eng. Chem. Res.*, 48, 7246–7256 (2009).
- L. D. Simoni, A. Chapeaux, J. F. Brennecke and M. A. Stadtherr, "Asymmetric Framework for Predicting Liquid-Liquid Equilibrium of Ionic Liquid-Mixed Solvent Systems. 2. Prediction of Ternary Systems, *Ind. Eng. Chem. Res.*, 48, 7257–7265 (2009).
- C. M. Tenney and E. J. Maginn, "Limitations and recommendations for the calculation of shear viscosity using reverse nonequilibrium molecular dynamics," *J. Chem. Phys*., 132, (2009).
- G. Puliti, S. Paolucci and M. Sen, "A Molecular Dynamic Study of Properties of Nanofluids," *Proceedings of the ASME-ATI-UIT Conference on Thermal and Environmental Issues in Energy Systems*, pp. 1113-1118, Sorrento, Italy, May 16-19, 2010.
- G. Puliti, S. Paolucci and M. Sen, "Thermodynamic Properties of Nanofluids," *Proceedings of the 2010 ASME International Mechanical Engineering Congress and Exposition*, Paper No. IMECE2010-39006, Vancouver, BC, November 12-18, 2010.
- J. A. Enszer, Y. Lin, S. Ferson, G. F. Corliss and M. A. Stadtherr, "Probability Bounds Analysis for Nonlinear Dynamic Process Models," *AIChE J*., 57, 404-422 (2010).
- L. D. Simoni, L. E. Ficke, C. A. Lambert, M. A. Stadtherr, and J. F. Brennecke, "Measurement and Prediction of Vapor-Liquid Equilibrium of Aqueous 1-Ethyl-3-methylimidazolium-Based Ionic Liquid Systems," *Ind. Eng. Chem. Res.*, 49(8), 3893-3901 (2010).
- L. E. Ficke and J. F. Brennecke, "Interactions of Ionic Liquids with Water," *J. Phys. Chem. B*, 114(32), 10496-10501 (2010).

- L. E. Ficke, R. R. Novak and J. F. Brennecke, "Thermodynamic and Thermophysical Properties of Ionic Liquid + Water Systems," *J. Chem. Eng. Data*, 55(11), 4946-4950 (2010).
- G. Puliti, S. Paolucci and M. Sen, "Thermodynamics Properties of Gold-Water Nanolayer Mixtures Using Molecular Dynamics," *Journal of Nanoparticle Research*, 13(9), 4277-4293 (2011).
- W. Cai, M. Sen and S. Paolucci, "Dynamic Simulation of an Ammonia-Water Absorption Refrigeration System," *Industrial & Engineering Chemistry Research*, 51, 2070-2076 (2012).
- G. Puliti, S. Paolucci and M. Sen, "Understanding Nanofluids," Nanofluids and their properties. *Appl. Mech. Rev*. 65(2): 021001 (2012).
- Puliti, G., Paolucci, S., Sen, M., "Thermodynamics properties of gold-water nanofluids using molecular dynamics," *Journal of Nanoparticle Research*, 14(12), 1296 (2012).
- Craig M. Tenney, Marjorie Massel, Jason M. Mayes, Mihir Sen, Joan F. Brennecke and Edward J. Maginn, "A Computational and Experimental Study of the Heat Transfer Properties of Nine Different Ionic Liquids," J. Chem. Eng. Data, 2014, 59(2), 391-399.
- Marjorie Massel, Anne-Laure Revelli, Ethan Paharik, Maribeth Rauh, Lesli O. Mark and Joan F. Brennecke, "Phase Equilibrium, Excess Enthalpies and Densities of Binary Mixtures of Trimethylbutylammonium Bis(trifluoromethylsulfonyl)imide with Ethanol, 1-Propanol and Dimethylformamide," J. Chem. Eng. Data, 2015, 60(1), 65-73.

Presentations

- W. Cai, J.K. K. Ibrahim, J. Mayes, G. Puliti, S. Paolucci and M. Sen, "Steady-Flow Modeling of an Absorption Refrigeration System Using Ionic Liquids," *2nd Annual Notre Dame Energy Week*, Notre Dame, IN Sept. 17-23, 2008.
- J. F. Brennecke, "Ionic Liquids for Absorption Refrigeration," Department of Chemical and Biological Engineering, University of Colorado, Boulder, October 7, 2008.
- G. Puliti, S. Paolucci and M. Sen, "Transport Properties of Nanofluids," *2008 ASME International Mechanical Engineering Congress and Exposition*, Boston, MA, October 31-November 6, 2008.
- J. A. Enszer and M. A. Stadtherr, "Rigorous Propagation of Imprecise Probabilities in Process Models," Plenary Talk, 7th International Conference on Foundations of Computer-Aided Process Design (FOCAPD 2009), Breckenridge, CO, June 7-12, 2009.
- G. Puliti, S. Paolucci and M. Sen, "Properties of Nanofluids," *47th AIAA Aerospace Sciences Meeting*, Orlando, FL, January 5-8, 2009.
- G. Puliti, S. Paolucci and M. Sen, "A Molecular Dynamic Study of Properties of Nanofluids," *10th US National Congress on Computational Mechanics*, Columbus, OH, July 16-19, 2009.
- G. Puliti, S. Paolucci and M. Sen, "Properties of Nanofluids," *2009 ASME International Mechanical Engineering Congress and Exposition*, Lake Buena Vista, FL, November 13-19, 2009.

- C. Tenney, "Defining Limits of Application of the Reverse Nonequilibrium Molecular Dynamics Method for Shear Viscosity Calculation," AIChE Annual Meeting, November 2009.
- L. E. Ficke and J. F. Brennecke, "Experimental Measurements of Ionic Liquid and Water Systems for Absorption Refrigeration," AIChE Annual Meeting, Nashville, TN, Nov. 8-13, 2009.
- G. Puliti, S. Paolucci and M. Sen, "A Molecular Dynamic Study of Properties of Nanofluids," *ASME-ATI-UIT 2010 Conference on Thermal and Environmental Issues in Energy Systems International*, Sorrento, Italy, May 16-19, 2010.
- G. Puliti, S. Paolucci and M. Sen, "Molecular Dynamic Study of Nanofluids," *2010 Midwest Thermodynamics and Statistical Mechanics Conference*, Notre Dame, Indiana, June 2-3, 2010.
- G. Puliti, S. Paolucci and M. Sen, "Thermodynamic Properties of Nanofluids," *2010 ASME International Mechanical Engineering Congress and Exposition*, Vancouver, BC, November 12-18, 2010.
- C. Tenney, "Using LAMMPS for Reverse Nonequilibrium MD Simulations," LAMMPS Users' Workshop, Sandia National Laboratories, February 2010.
- Joan F. Brennecke, "Energy applications of ionic liquids: Is it green chemistry?" ACS National Meeting, San Francisco, CA, March 21-25, 2010.
- Puliti, G., Paolucci, S., Sen, M. Properties of Water/Gold Nanofluids. 64th Annual Meeting of the APS Division of Fluid Dynamics, November 20-22, 2011, Baltimore, MD
- Puliti, G., Paolucci, S., Sen, M. Study of Thermodynamic and Transport Properties of Water/Gold Nanofluids using Equilibrium Molecular Dynamics. 2012 ASME 3rd Micro/Nanoscale Heat and Mass Transfer International Conference, March 3-6, 2012, Atlanta, GA
- Puliti, G., Paolucci, S., Sen, M. Study of Thermodynamic and Transport Properties of Water/Gold Nanofluids using Molecular Dynamics. 2012 ASME International Mechanical Engineering Congress and Exposition, November 9-15, 2012, Houston, TX
- D. Andrei Măceș and Mark A. Stadtherr, Dynamic Modeling for Ionic Liquid-Based Absorption Refrigeration Systems," AIChE Annual Meeting, Minneapolis, MN, October 16-21, 2011.

Ph.D. Theses

- Ficke, L. E., Thermodynamic Properties of Imidazolium and Phosphonium Based Ionic Liquid Mixtures with Water or Carbon Dioxide, University of Notre Dame, Notre Dame, IN, 2010.
- Cuellar, A. G. A Heat Conduction Study at Non-continuum Scales, University of Notre Dame, Notre Dame, IN, 2011.
- Puliti, G. Properties of Au–H_2O Nanofluids using Molecular Dynamics, University of Notre Dame, Notre Dame, IN, 2012.
- Massel, M., Thermodynamic and Thermophysical Properties of Ionic Liquids Mixtures, University of Notre Dame, Notre Dame, IN, 2014
- Huang, Y., Thermal Stability and Phase Transitions of Ionic Liquids, University of Notre

Dame, Notre Dame, IN, 2013

- Măceş, D. A., Uncertainty Propagation in Models for Dynamic Nonlinear Systems: Methods and Applications, University of Notre Dame, Notre Dame, IN, 2013

Patents and IP: Nothing to report.

Other Products / Deliverables: We formed a start-up company, Ionic Research Technology (IRT), based in part on the results of this grant. IRT obtained a subcontract from Oak Ridge National Laboratory for the evaluation of IL/water systems for heat pump applications. This was a direct result of this grant. We are no longer associated with the company so do not know if they are continuing work in this area.