U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Ionic Liquids for Utilization of Geothermal Energy

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Specialized Materials and Fluids and Power Plants

Overview Slide

- Timeline
  - Start date: 8/1/08 (funds received 11/08)
  - End date: 7/31/12
  - Percent completed: 30%
- Budget
  - Total: $2,472,005
  - DOE share: $1,935,500
  - Funding received in FY09: $984,000
  - Funding for FY10: $951,500
- Barriers
  - None
- Partners
  - NiSource Energy Technologies

Overview Slide

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- Project Team
  - Joan Brennecke, UND, CBE, thermodynamic measurements
  - Mark Stadtherr, UND, CBE, dynamic modeling
  - Mihir Sen, UND, AME, thermal conductivity measurements
  - Edward Maginn, UND, CBE, molecular simulation of ILs
  - Sam Paolucci, UND, AME, molecular simulation of IL/nanofluids
  - Mark McCready, UND, CBE, IL/nanoparticle mixtures
  - Mike Zdyb, Nisource Energy Technologies
  - Pete Disser, Nisource Energy Technologies

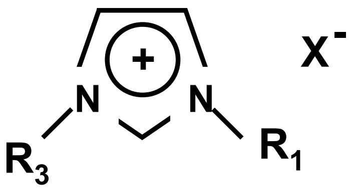
Relevance/Impact of Research

- Develop ionic liquids for two geothermal applications
- High temperature heat transfer fluids
  - Decomposition temperatures greater than common high temperature heat transfer fluids
  - Thermal conductivities as good as or better than common high temperature heat transfer fluids
- IL/water absorption refrigeration
  - COPs better than conventional system at generator T < 150 °C
- Allow efficient transfer of heat from geothermal source
- Efficiently use low temperature geothermal resources for cooling

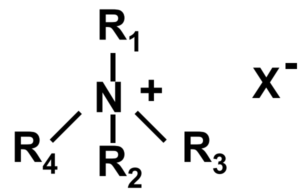
Scientific/Technical Approach

- Exploit unique properties of Ionic Liquids for geothermal applications
  - ILs are organic salts with low melting points
  - Large liquid range
  - Negligible vapor pressure/good thermal stability
  - Tunable by choice of anion, cation and substituents
- Go/no-go decisions
  - Thermal decomposition temperatures > 250 ° C
  - Thermal conductivities > silicone oil
  - COPs > LiBr/water system

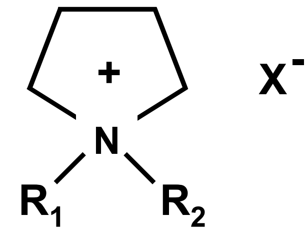
Typical Ionic Liquids



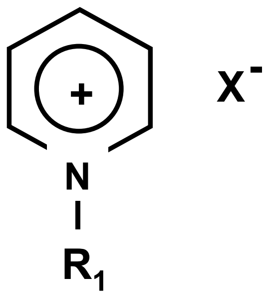
imidazolium



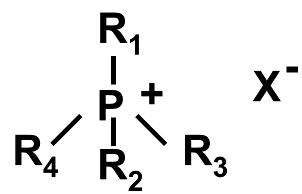
tetra alkylammonium



pyrrolidinium



pyridinium



tetra alkylphosphonium

X = Cl
NO_3
CH_3CO_2
CF_3CO_2
BF_4
CF_3SO_3
PF_6
$(CF_3SO_2)_2N$

Milestones

- ILs as heat transfer fluids
  - Measurement of thermal stability, densities, heat capacities, viscosities and thermal conductivities
  - Materials compatibility
  - Molecular simulation of IL and IL/nanoparticle mixtures
- ILs for absorption refrigeration
  - Measurement and modeling of heat capacities, vapor-liquid equilibrium, densities and heats of mixing of IL and IL/water systems
  - Calculation of COPs
  - Molecular simulation of IL/water systems
  - Dynamic process simulation

Heat Transfer Fluids

- Thermal decomposition temperatures better than silicone oils

Liquid	T_{onset} (°C)	T_{start} (°C)
[hmim][Tf_2N]	427	347
[hmDMAP][Tf_2N]	444	358
[hDMAP][Tf_2N]	443	376
Silicone Oil	~250	

Accomplishments, Expected Outcomes and Progress

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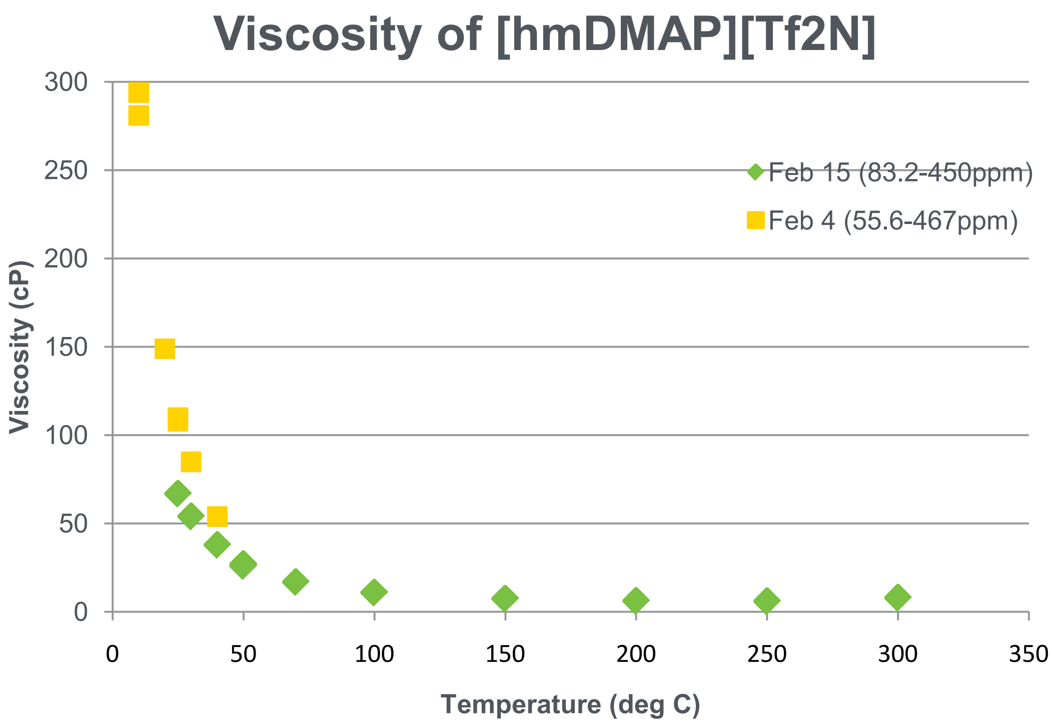
Heat Transfer Fluids

- Thermal conductivities better than common heat transfer fluids

Ionic Liquid	K (W/mK)	Standard Fluids	K (W/mK)
[hmim][Tf_2N]	0.128	Alcohol	0.170
[hmDMAP][Tf_2N]	0.132	Freon 12	0.073
[hDMAP][Tf_2N]	0.138	Glycerol	0.280
[bDMAP][Tf_2N]	0.136	Engine Oil	0.150
		Silicone Oil	0.100
		Water	0.606

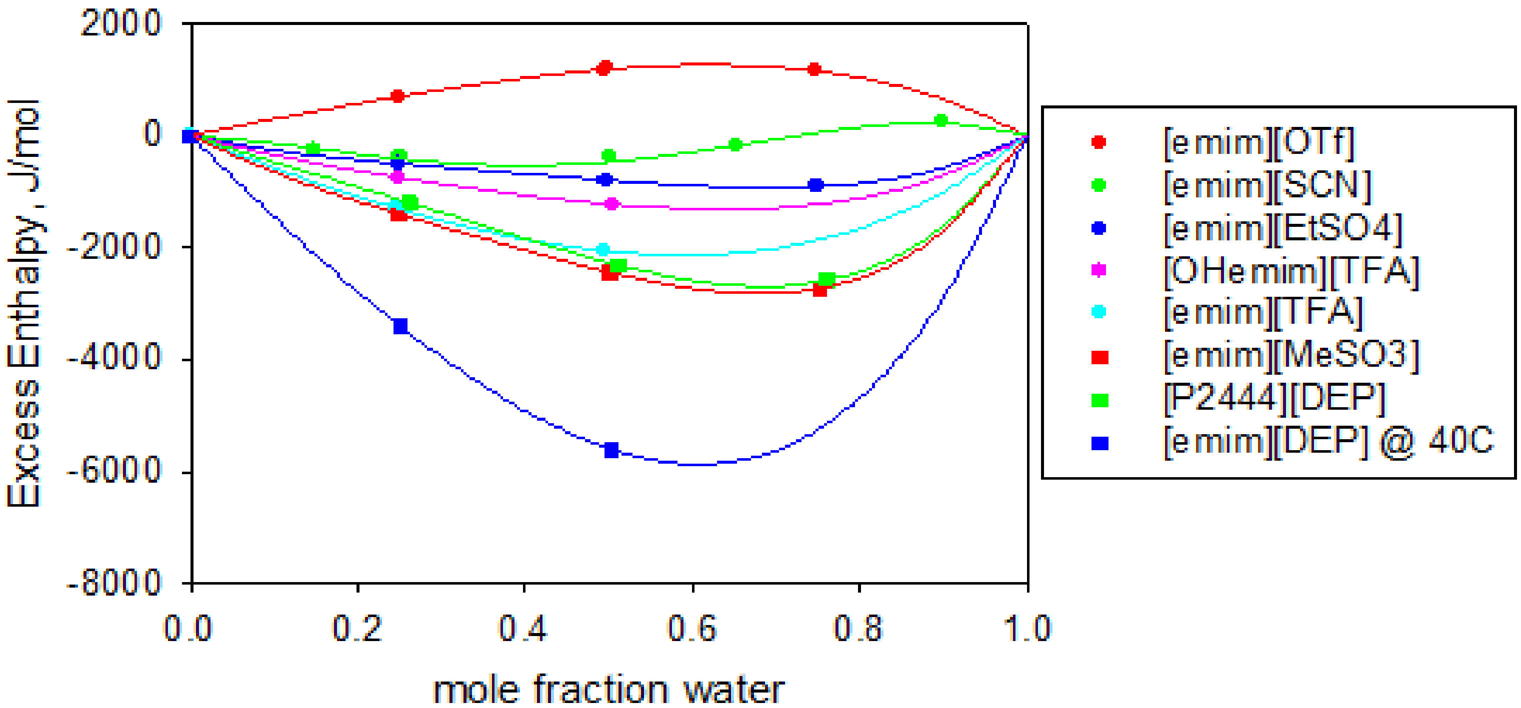
Heat Transfer Fluids

- Reasonable viscosities



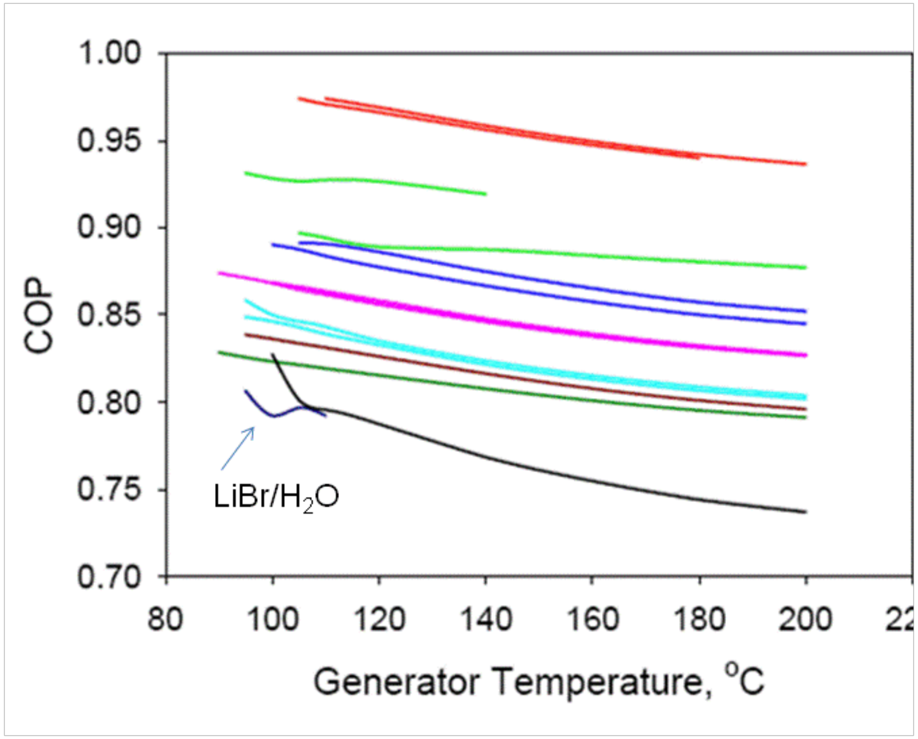
Absorption Refrigeration

- Small heats of mixing
- Other key data: vapor-liquid equilibrium, heat capacities



Absorption Refrigeration

- Excellent coefficients of performance, especially for generation temperatures < 150 ° C



T_{evap} = 5 ºC
T_{cond} = 50 ºC
T_{abs} = 40 ºC

Accomplishments, Expected Outcomes and Progress

- New capabilities
  - Measurement of thermal conductivity
  - Measurement of viscosities at temperatures >70° C
  - Gas Chromatography/Mass Spectrometry system to analyze decomposition products
  - New 'automated' forcefield development system
  - Molecular simulation method for liquid/nanoparticle systems

Accomplishments, Expected Outcomes and Progress

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- PI (Joan Brennecke) received the 2009 E. O. Lawrence Award in Environmental Science and Technology from the Department of Energy.

- Co-PI (Edward Maginn) received the 2009 inaugural American Institute of Chemical Engineers CoMSEF (Computational Molecular Science and Engineering Forum) Early Career Award for outstanding research.
- Researcher (Gianluca Puliti) received a graduate award by the American Institute of Aeronautics and Astronautics (AIAA) during the 47th AIAA Aerospace Sciences Meeting in Orlando, Florida on January 6, 2009.

Project Management/Coordination

- Group meetings every 2-3 weeks with all PIs, researchers, NiSource representative
- Meeting of PIs and researchers with NiSource management 5/3/10
- Careful budget tracking by PI
- All 2009 funds spent by 7/31/10 except corrosion testing
- Continuation of project with 2010 funds starting 8/1/10

Future Directions

- Decomposition mechanisms from GC-MS
- Design of even more thermally stable ILs, guided by molecular simulations
- Testing of IL/nanofluids systems, guided by molecular simulations
- Exploration of IL/CO_2 systems for absorption refrigeration
- Continued discussions with commercial absorption refrigeration manufacturer (Dometic)

Mandatory Summary Slide

- Dimethylaminopyridinium-based ionic liquids have excellent thermal stability and good thermal conductivity; excellent candidates for high temperature heat transfer fluids
- Numerous IL/water systems tested have higher Coefficients of Performance (COP) than conventional LiBr/water systems at low generator temperatures
- IL/water absorption refrigeration ideally suited for obtaining COOLING from low temperature geothermal resources

Supplemental Slides

Publications

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

- 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, and S. Paolucci “Properties of Nanofluids,” Bulletin of the American Physical Society, Vol. 54, p. 235, (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).
- Craig M. Tenney and Edward J. Maginn, “Limitations and recommendations for the calculation of shear viscosity using reverse nonequilibrium molecular dynamics,” The Journal of Chemical Physics, 132, (2009).
- J. A. Enszer, Y. Lin, S. Ferson, G. F. Corliss and M. A. Stadtherr, “Probability Bounds Analysis for Nonlinear Dynamic Process Models,” *AIChE J.*, in press (2010).

Presentations

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

- W. Cai, J.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.
- 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.
- 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, "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," Proceedings of the 2009 ASME International Mechanical Engineering Congress and Exposition, Paper No. IMECE2009-10398, Lake Buena Vista, FL, November 13-19, 2009.
- Craig Tenney, "Defining Limits of Application of the Reverse Nonequilibrium Molecular Dynamics Method for Shear Viscosity Calculation," AIChE Annual Meeting, November 2009.
- Craig Tenney, "Using LAMMPS for Reverse Nonequilibrium MD Simulations," LAMMPS Users' Workshop, Sandia National Laboratories, February 2010.