Use of Ionic Liquids in Produced Water Clean Up

NGOTP Upstream Environmental Technology Review

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David DePaoli

Joe Birdwell, Sheng Dai, Huimin Luo, Joanna McFarlane

ChevronTexaco, ConocoPhillips, Shell, Statoil

Oak Ridge National Laboratory

(depaolidw@ornl.gov)

Target Organics in Produced Water

- Strict regulatory limits on recoverable oil and grease
- Problems with current methods to remove water soluble organics
  - Effectiveness depends on the target organic
  - Buffering by oil can affect removal efficiency
  - Especially for new wells, properties and amounts of water soluble organics (WSO) not well known.
  - Polar WSO concentrations can be as high as 1000 ppm
  - Advantageous to be able to monitor process on-line
- Improved separations can be used to more efficiently remove WSO from discharge
  - Optimize chemistry of separation

Two potential uses of ionic liquids in produced water remediation are explored

- **Develop sensor for detection of organic compounds in aqueous phase**
  - **based on solubility into ionic liquid supported on quartz crystal microbalance**
- **Investigate application of ionic liquids for produced water remediation**
  - **separation of organics from brines by liquid extraction**

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Industrial use of ionic liquids is beginning

Davis & Fox, *Chem. Commun.*, 1209-1212 (2003).

FOCUS ARTICLE

ChemComm www.rsc.org/chemcomm

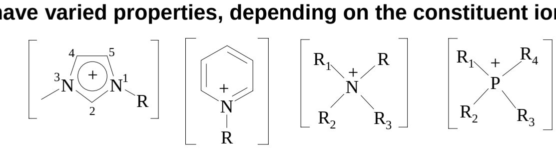
From curiosities to commodities: ionic liquids begin the transition

James H. Davis, Jr.[a,b] and Phillip A. Fox[a]

[a]Department of Chemistry, University of South Alabama, Mobile, Alabama 36688. E-mail: jdavis@jaguar1.usouthal.edu
[b]Center for Green Manufacturing, The University of Alabama, Tuscaloosa, Alabama 35487

Ionic liquids have varied properties, depending on the constituent ions

Most commonly used cations:



1-alkyl-3-methyl-imidazolium | *N*-alkyl-pyridinium | Tetraalkyl-ammonium | Tetraalkyl-phosphonium ($R_{1,2,3,4}$ = alkyl)

Some possible anions:

water-insoluble → water-soluble

water-insoluble		water-soluble
$[PF_6]^-$	$[BF_4]^-$	$[CH_3CO_2]^-$
$[(CF_3SO_2)_2N]^-$	$[CF_3SO_3]^-$	$[CF_3CO_2]^-$, $[NO_3]^-$
$[BR_1R_2R_3R_4]^-$		Br^-, Cl^-, I^-
		$[Al_2Cl_7]^-$, $[AlCl_4]^-$ (decomp.)

Most commonly used alkyl chains: ethyl, butyl, hexyl, octyl, decyl

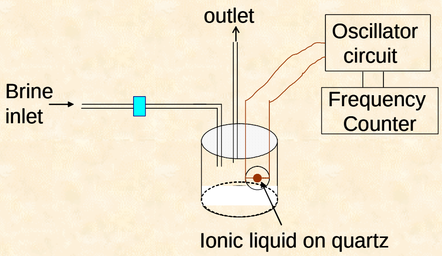
Why Ionic Liquids?
Criteria for Solvents of Water Soluble Organics

- High affinity for WSO
  - Aromatics, polar organics
  - Optimize structure/hydrophobicity/acidity for separation (high K_d possible)
  - Effective at high solute concentrations
  - Few chemical interferences
- Physical properties
  - Liquid over a wide range (~ -100°C to 300°C)
- Cost?
  - Potential to engineer low losses
    - Low vapor pressure
    - Hydrophobic
  - Thermally stable
  - Regeneration
- Possibility for low environmental impact
  - Toxicity
  - Hydrophobic

Project Milestones

- **First year**
  - Synthesize and/or acquire ionic liquids suitable for WSO removal from produced water.
  - *DECISION: Selection of ionic liquids for hydrocarbon removal.*
  - Document successful ionic liquid separations based on simulated and actual produced water samples.
- **Second year**
  - Document the dependence of ionic-liquid based separations on organic contaminant, temperature, salinity, and pH.
  - Identify potential barriers before use in the field.
  - Demonstrate a WSO sensor using an ionic-liquid coated QCM.
  - *DECISION: Evaluate success of QCM sensor.*
- **Third year**
  - Develop ionic-liquid based sensor for field use.
  - *DECISION: Evaluate of separation technology to targeted produced water remediation.*

Several methods are undertaken to evaluate performance of ionic liquids in produced water remediation



- **Liquid-liquid extraction followed by organic analysis**
  - **Partitioning as a function of organic type and concentration, salinity, pH, temperature**
  - **Saturation/regeneration**
- **Ionic liquid/brine separation in centrifugal contactor**
- **QCM detection of organics**
  - **Sensor coated with ionic liquid**
  - ***In-situ* aqueous phase monitoring**
- **Calculation of physical properties based on molecular modeling**

Contaminant Uptake into Ionic Liquids by on Liquid-Liquid Extraction

Experimental Procedure:

Organic compounds chosen to represent contaminants in produced water (organic acids, 1-nonanol, toluene, alkanes)

Tests carried out in deionized water, seawater brine and 0.2 M NaCl

22, 37, and 75°C

pH (acidic to basic)

Liquid-liquid contacts followed by chemical analysis of the aqueous phase (by HPLC and GC)

Whitney Ridenour (Roane State/UT)
Joanna McFarlane (ORNL)
Studying gas chromatographic results

bmim$^+$, omim$^+$ + **bis[(trifluoromethyl) sulfonyl]amide (Tf_2N^-) hexafluorophosphate (PF_6^-)**

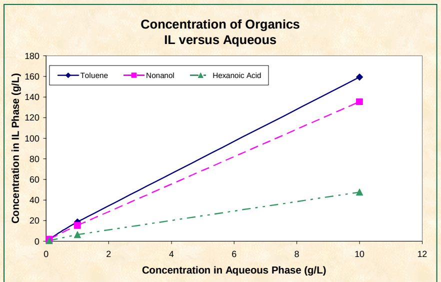
The best distribution coefficients were observed with Omim Tf_2N

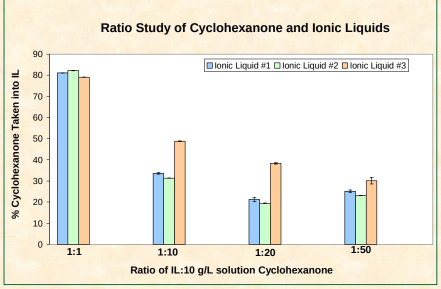
	Hexanoic acid	Succinic acid	Lactic acid	Acetic acid	1-Nonanol	Toluene
$OmimTf_2N$						
Average K_D	290 ± 30	0.5 ± 1	0.5 ± 0.8	0.6 ± 0.7	410 ± 60	500 ± 200
pH						
1.5	-	NE	0.1 ± 0.2	0.5 ± 0.7	-	-
3	-	1 ± 1	1 ± 1	0.7 ± 0.9	410 ± 60	500 ± 200
Temperature (°C)						
25	-	0.5 ± 1	0.5 ± 0.8	0.6 ± 0.7	410 ± 60	500 ± 200
Salinity ($g \cdot L^{-1}$ Cl^-)						
DI H_2O	-	NE	0.1 ± 0.2	0.5 ± 0.7	410 ± 60	500 ± 200
1.8	-	1 ± 1	1 ± 1	0.7 ± 0.9	-	-

Concentrations of organics measured in contacted and non-contacted (controls) brines.
Results were converted to distribution coefficients $K_d = [WSO]_{IL}/[WSO]_{Aq}$.
Uptake was measured as a function of pH, salinity, temperature, and concentration

Tests to Investigate Capacity of Ionic Liquids for Organic Uptake

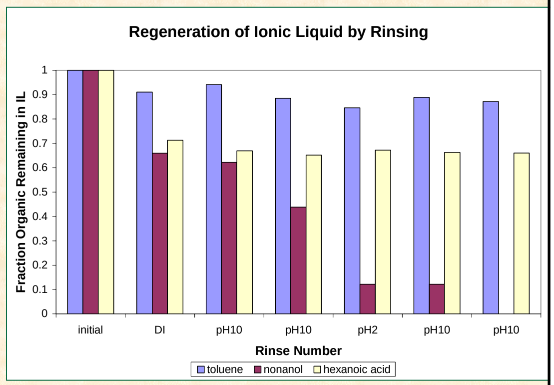
- **Solubilities of certain organics in IL were found to be high (2 orders of magnitude higher than contacted aqueous phase).**
  - **1-nonanol**
  - **Toluene**
  - **Hexanoic acid**
- **Increased concentrations of organics from 0.001 g/L to 10 g/L. Slight decrease in K_d above 1 g/L seen for toluene. No change seen for hexanoic acid.**
- **Increased ratio of ionic liquid phase to aqueous phase from 1:1 to 50:1**
  - **Slight decrease observed in K_d for cyclohexanone**





Regeneration of Ionic Liquids may be an issue

- **Aqueous rinses remove 1-nonanol**
- **Hexanoic acid somewhat removed by aqueous rinses**
  - **Residue remains in IL**
  - **When recontacted with WSO-loaded brine stock, uptake into IL reduced by amount remaining in IL after regeneration**
- **Toluene removed by heating above boiling point**
- **Bmim PF_6, used in this study, less stable than Bmim Tf_2N when heated** (Swatloski et al 2003)**.**



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Good and Bad Candidate ILs

- **Good**
  - **High K_d**
  - **Water insoluble**
  - **Regeneration possible**
  - **Low to moderate viscosity**
  - **Thermally stable**
- **Bmim TF_2N, Omim TF_2N have high Kd**
- **?**

- **Bad**
  - **Viscosity too high**
  - **Decomposition**
  - **Water solubility (* BF_4)**
  - **Toxic**
- **Bmim PF_6 decomposes when heated**
- **Sulfonate IL too viscous**

	KIL/W bmim Tf2N	Kow/10 Rodgers et al.	omim Tf2N David et al.
cyclohexane	0.5	275	10
cyclohexanone	3.5	0.65	
hexanoic acid	30	8.3	

Our measurements

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Centrifugal contactors may provide efficient means for employing ionic liquid solvents

Efficient multiphase mixing and phase separation in a single device

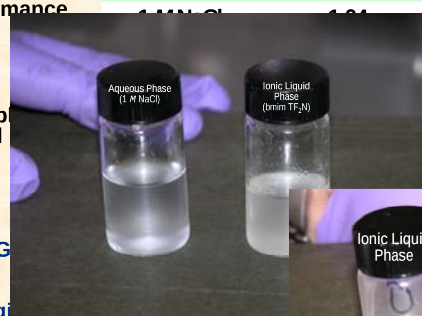
Advantages:

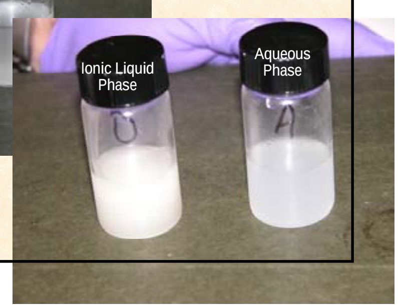
Low solvent inventory
Small footprint

Preliminary experiments show promising performance of centrifugal contactor for ionic liquid/brine combinations

- **5-cm centrifugal contactor, single stage, closed loop**
- **bmimTf$_2$N:**
  - phase-separation performance was excellent under all conditions applied
- **Terrasail™:**
  - minor amount of cross-p contamination observed both effluents
- **Additional property measurement**
  - Thermal stability DTA/TG
  - Interfacial tension
  - Uptake of Cl$^-$, H$_2$O negligi

Component	Density, g/mL	Viscosity, cP
Terrasail™	0.98	970
bmimTF$_2$N	1.48	52
[illegible]	[illegible]	1.10





Initial Findings

- Bmim Tf_2N has favorable chemical and physical characteristics for organic uptake.
  - Hydrocarbons of most environmental concern in produced water (alcohols and aromatics) have highest affinity for the IL.
  - Uptake of organic acids can be controlled by pH. Low pH, such as that achieved during acid springing, minimizes uptake by IL.
  - Non-polar alkanes not soluble in ionic liquids tested but have low water solubility.
- First demonstration of ionic liquid separation using a centrifugal contactor.
- Regeneration/losses and stability key to performance as solvent
  - Rinse cycles with caustic/acidic aqueous solutions effectively remove some organics
  - Aromatic organics readily removed through heating
- Thorough experimental analysis of all available ionic liquid cationic and anionic combinations would be impossible. Collaborative modeling effort to quickly identify best candidates for laboratory testing.

Technical Approach – Second Year

- Development of QCM sensor for organics in produced water
  - Enhance sensor design by employing novel ways to reduce loss of ionic liquid from quartz substrate
- Continued optimization of ionic liquid structure through modeling and laboratory testing
- Testing of physical properties of selected ionic liquids
  - In pure form (viscosity, DTA/TGA)
  - In combination with brine (contactor)
  - Organic uptake
  - Water solubility (minimization of losses)

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Determining Organic Solubility in Ionic Liquids Using a Quartz Crystal Microbalance

Coat quartz crystal with thin film of hydrophobic ionic liquid

Expose to aqueous phase

Small changes in mass from organic uptake into ionic liquid yields measurable frequency change

Previous work at ORNL (Liang et al. 2002; Baltus et al. 2004) indicates rapid mass transfer and sensor response

Modeling Will Accelerate Optimization of Separation Process

- **Molecular structure calculations to determine physical properties of untested ionic liquids**
  - **Melting point and thermal stability**
  - **Water uptake/water solubility**
  - **Partition coefficients**
  - **Effect of pH on chemical behavior**
  - **Fluidic properities (viscosity, interfacial tension)**
- **ORNL Capabilities**
  - **Spartan, NWCHEM**
- **Will optimize time spent in laboratory on ionic liquid testing**

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Industry Participation

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Project Budget ($K)

	FY 2002	FY 2003	FY 2004
ORNL	250	250	250
University	0	0	0
DOE Total	250	250	250
Industry (in kind)	50	50	50

ORNL
Dave DePaoli: PI, Separations
Joe Birdwell: Contactor
Sheng Dai: Ionic Liquids
Huimin Luo: Synthesis
Joanna McFarlane: Physical Properties

Project Impacts

- Produced water waste stream is expensive to treat
- Improved methodology for monitoring organic contamination will assist with compliance with NPDES permits
- Explore new chemical technology:
  - Ionic liquid processes may be environmentally benign
  - High separation factors possible
- Evaluate whether ionic liquids can be used for targeted produced water remediation
- Exploit existing ORNL expertise in ionic liquids and separations to solve environmental problems

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Technology Transfer

- **Presentations**
  - **W.B. Ridenour and J. McFarlane, "Room Temperature Ionic Liquids Separating Organics from Produced Water", Poster presented at the 13th Separations Science and Technology Conference, Gatlinburg, TN, October 27, 2003.**
  - **J.F. Birdwell, H. Luo, J. McFarlane, and D.W. DePaoli, "Separation of Ionic Liquid Dispersions in Centrifugal Solvent Extraction Contactors", 13th Separations Science and Technology Conference, Gatlinburg, TN, October 27, 2003.**
  - **J. McFarlane, University of Tennessee Chemical Engineering Department, Knoxville, TN, September 23, 2003.**
  - **W.B. Ridenour, "Room Temperature Ionic Liquids Separating Organics from Produced Water", Poster presented at the Oak Ridge National Laboratory student fair, August 6, 2003.**