Use of Ionic Liquids in Produced Water Clean Up

ORNL, ChevronTexaco, ConocoPhillips, and Shell

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Water-Soluble Organics in Produced Water

- **Strict regulatory limits on recoverable oil and grease**
- **Acid springing technology currently used to remove WSO**
  - **Buffering by oil can affect removal efficiency**
  - **Especially for new wells, properties and amounts of 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**

Can ionic liquids be used in produced water analysis and remediation?

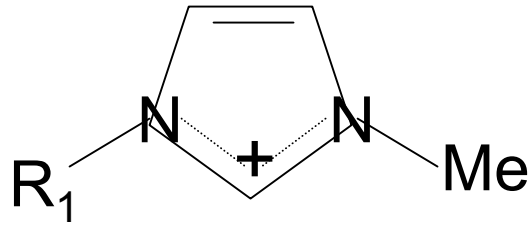
- **Objective:** ***Develop sensor for detection of organic compounds in aqueous phase, based on solubility into ionic liquid supported on quartz crystal microbalance***

- **Ultimate Goal:** ***To investigate application of ionic liquid technology to produced water remediation including separation of organics from brines***

Room Temperature Ionic Liquids

- ***Ionic salts that are liquid over a wide range (~ -100°C to 300°C)***
- ***No measurable vapor pressure***
- ***Nonflammable, thermally stable***
- ***Solvent for a broad spectrum of chemical species***
- ***Can optimize structure/hydrophobicity/acidity for separation (high Kd possible)***
- ***Effective at high solute concentrations***
- ***Potential for "green" synthesis and separations***

Imidazolium Based Cations:



Anions:

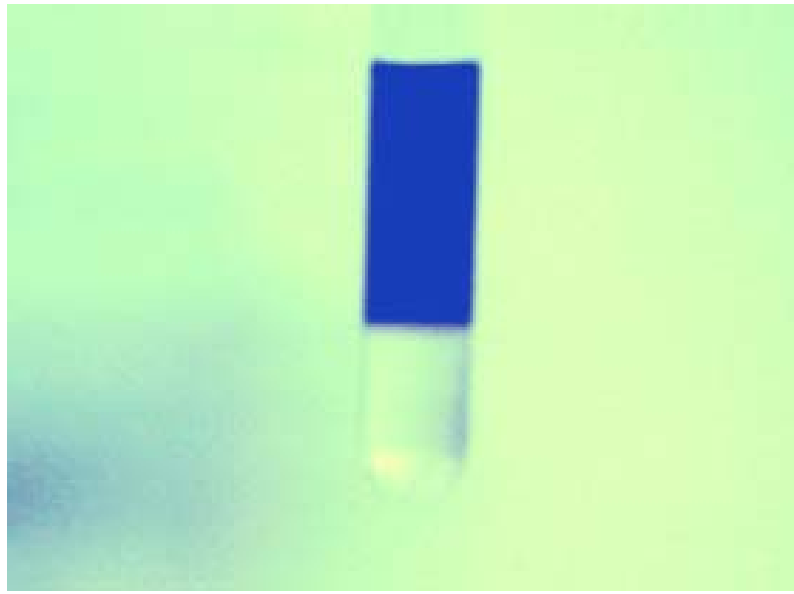
bis[(trifluoromethyl) sulfonyl]amide (Tf_2N^-)

tetrafluoroborate (BF_4^-)

Hexafluorophosphate (PF_6^-)

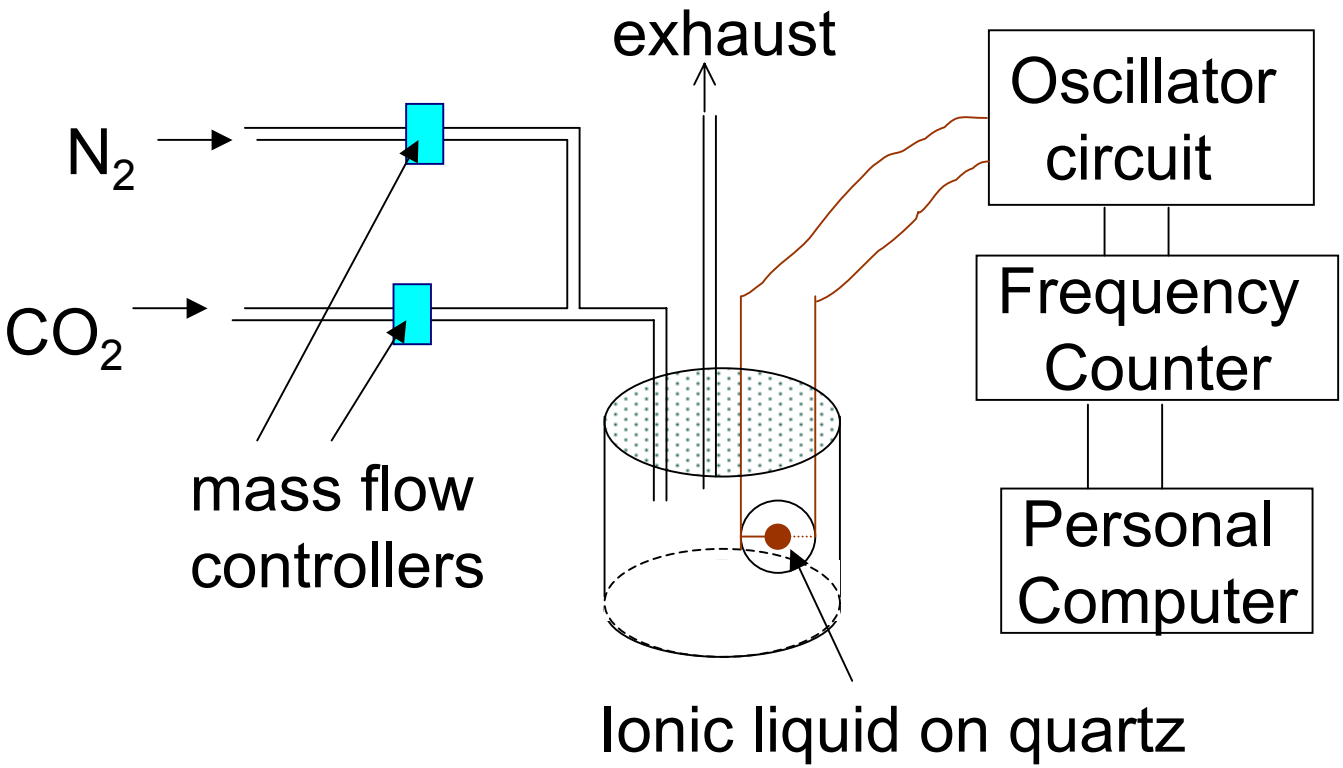
Criteria for Solvents Used for Separation of Organics from Produced Water

- Water insoluble
- High affinity for WSO
- Physical properties
- Regeneration
- Stability
- Low losses
- Few chemical interferences
- Cost effective
- Low toxicity



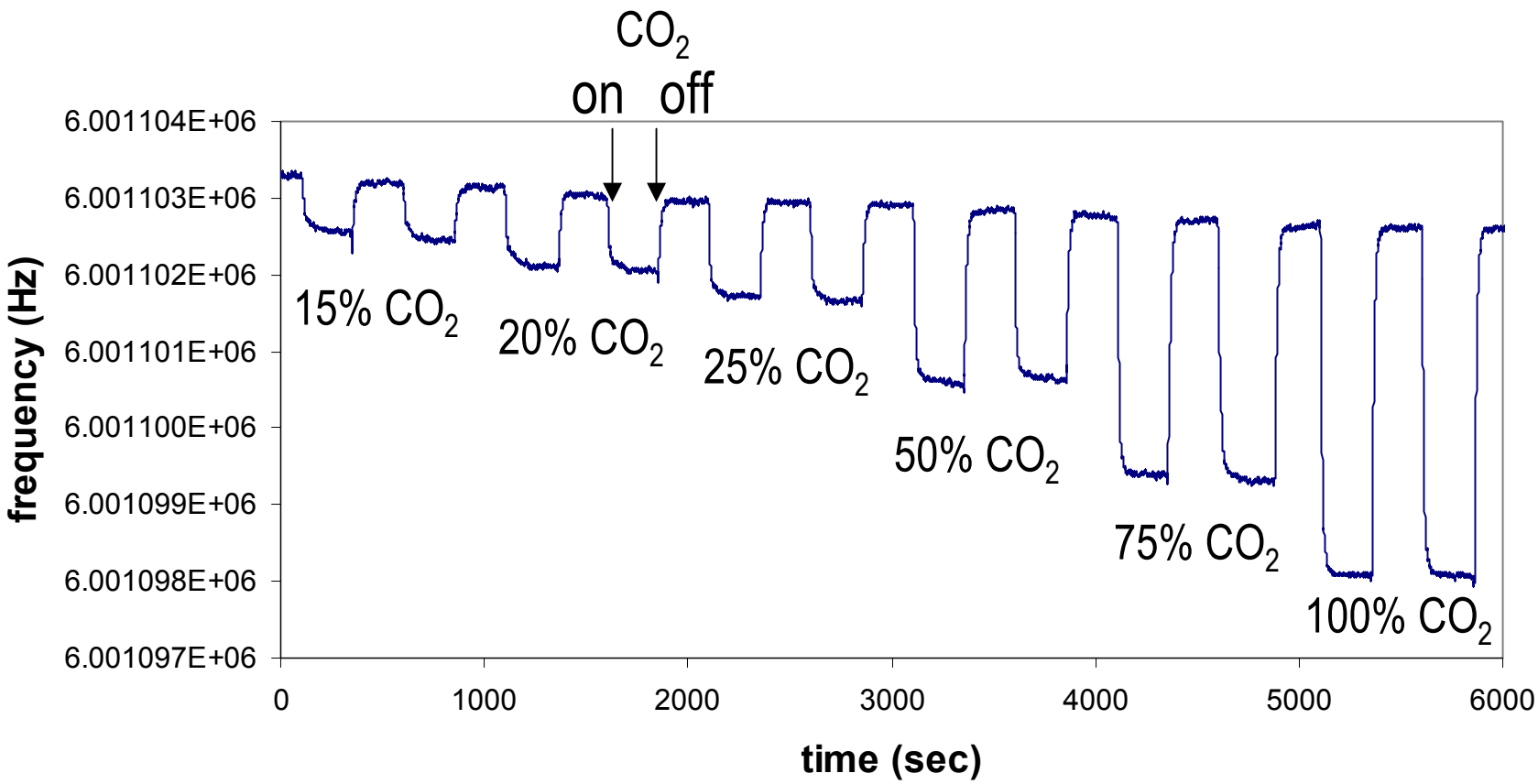
Photographic picture of the phase separation between an ionic liquid (molten salt) and an aqueous solution containing Cu(II) dye.

Determining Organic Solubility in Ionic Liquids Using a Quartz Crystal Microbalance



Small change in mass on the quartz resulting from organic uptake yields measurable frequency change

Previous Work: Quartz Crystal Microbalance Response to CO_2



Evaluation of Ionic Liquids

- **Liquid-liquid extraction followed by conventional methods of organic analysis:**
  - **GC-FID, UV spectroscopy, Ion chromatography for acids, HPLC**
  - **Performance as a function of organic type, salinity, pH, temperature**
- **Performance of quartz crystal microbalance detection of organics**
  - **Sensor coated with ionic liquid or supported ionic liquid films**
  - ***In-situ* aqueous phase monitoring**
- **Comparison of results to models of solubility based on thermodynamic equilibrium**

Liquid-Phase Extraction

K_d	*IL1*	*IL2*	*IL3*	*IL4*	*IL5*	*IL6*
acetic acid	189	1	32	350	1141	7074
toluene	315	197	58	65	136	112
butane diol	319	161	67	36	104	64
hexanoic acid	316	191	105	37	114	63
1-nonanol	2711	909	360	458	1128	569

$$K_d = \frac{[IL]}{[H_2O]}$$

Project Schedule

- **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 feasibility of separation technology in targeted produced water remediation.***

Industry Participation

- Project planning and oversight
- Produced water samples
- Test/field conditions

Project Budget ($x 10^3)

	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
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 liquids are 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 solving environmental problems