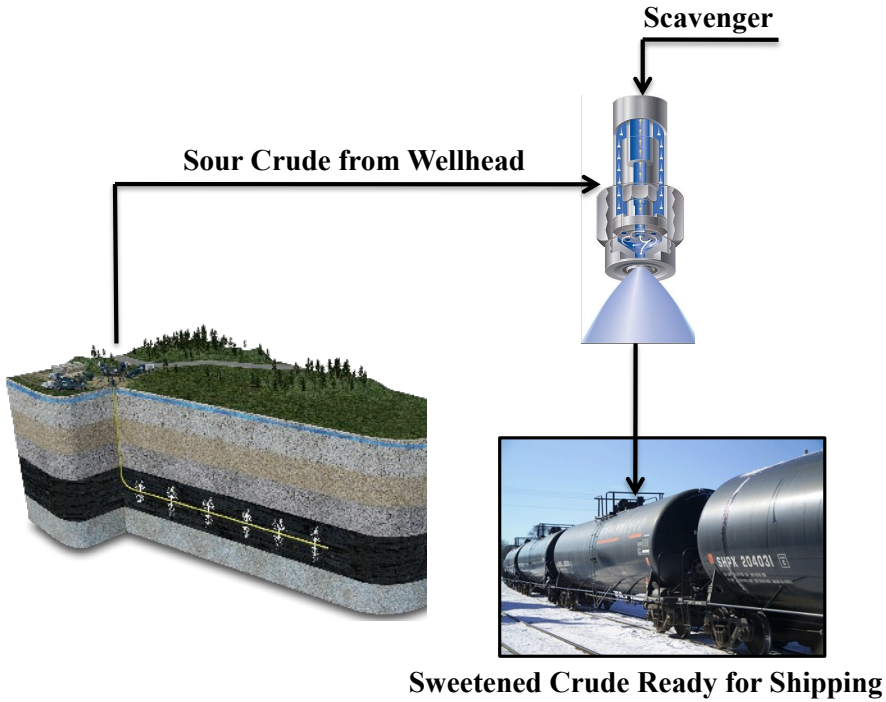
Thermodynamic Properties of Amine-Type and Ionic Liquid H_2S Scavengers

Tracy Benson, Ph.D.

College of Engineering
LAMAR UNIVERSITY
Dan F. Smith Department of Chemical
& Biomolecular Engineering



Background of H_2S Hazards

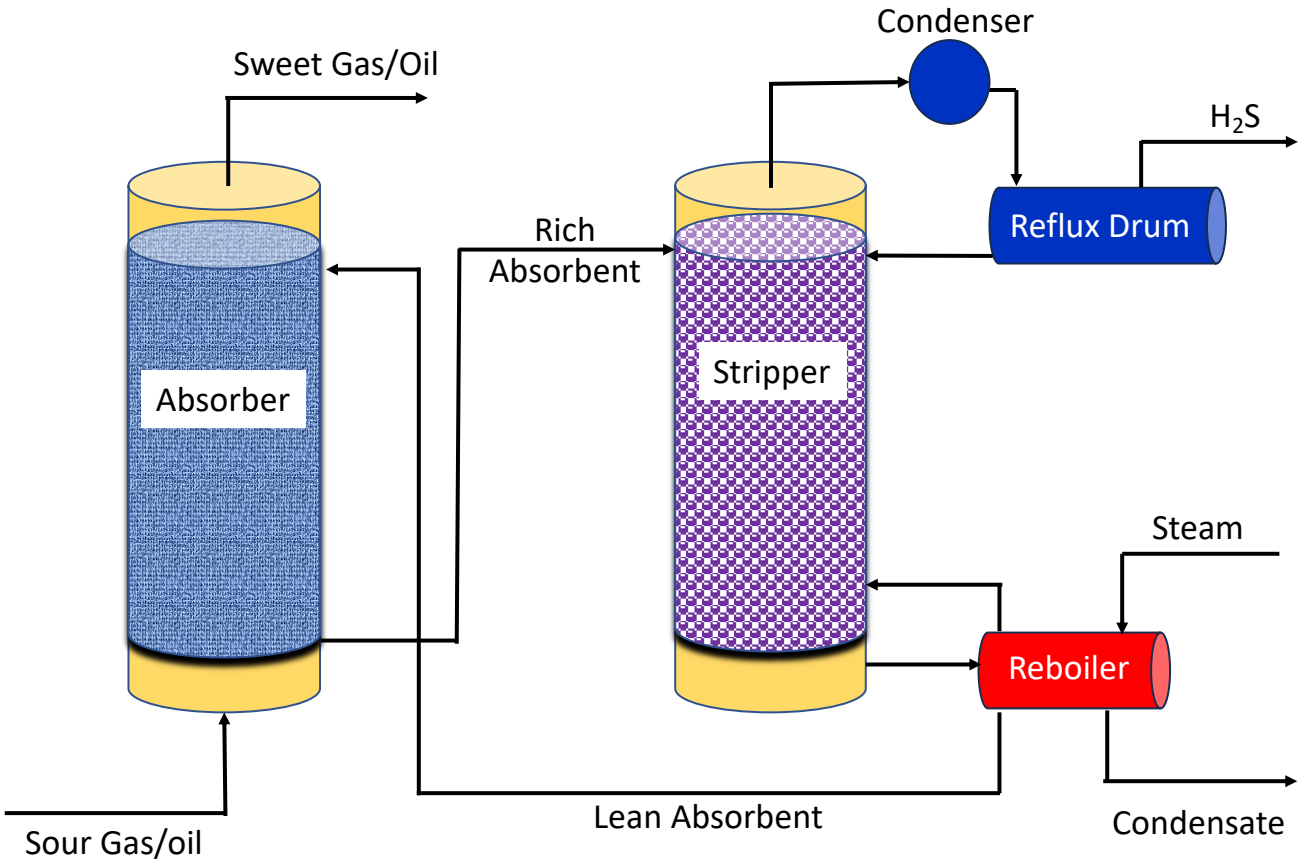
- **Naturally occurring, soluble in water, alcohols, oils, and ethers**
- **Colorless, Volatile, Toxic**
- **Characterized by a "rotten egg" smell**

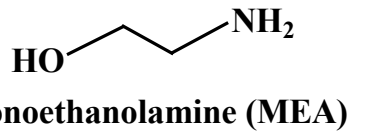
Concentration (ppm)	Effects
0.003 - 0.02	Clearly detectable by smell
3 – 10	Very unpleasant smell
20 – 100	Distinct smell of rotten eggs
50 – 100	Stinging pain in eyes and irritation of respiratory organs
100 – 200	Sedation of olfactory sense
250 – 500	Fluids in lungs, cyanosis, bloodstained cough, pneumonia
500	Headache, vertigo, paralysis of respiratory muscles, unconsciousness
500 – 1000	Stop for respiration, immediately collapse, death

Background of H_2S Hazards

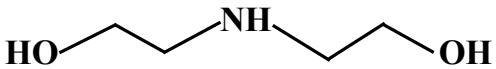
Source Data: TX Railroad Commission

Regenerative H_2S Absorbents

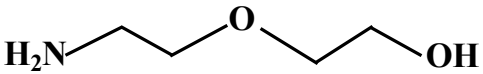




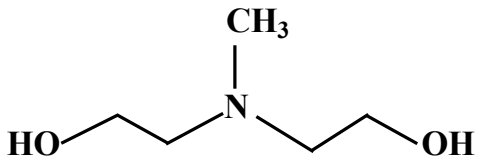
Monoethanolamine (MEA)



Diethanolamine (DEA)



Diglycolamine (DGA)



Methyldiethanolamine (MDEA)

Non-Regenerative Scavengers

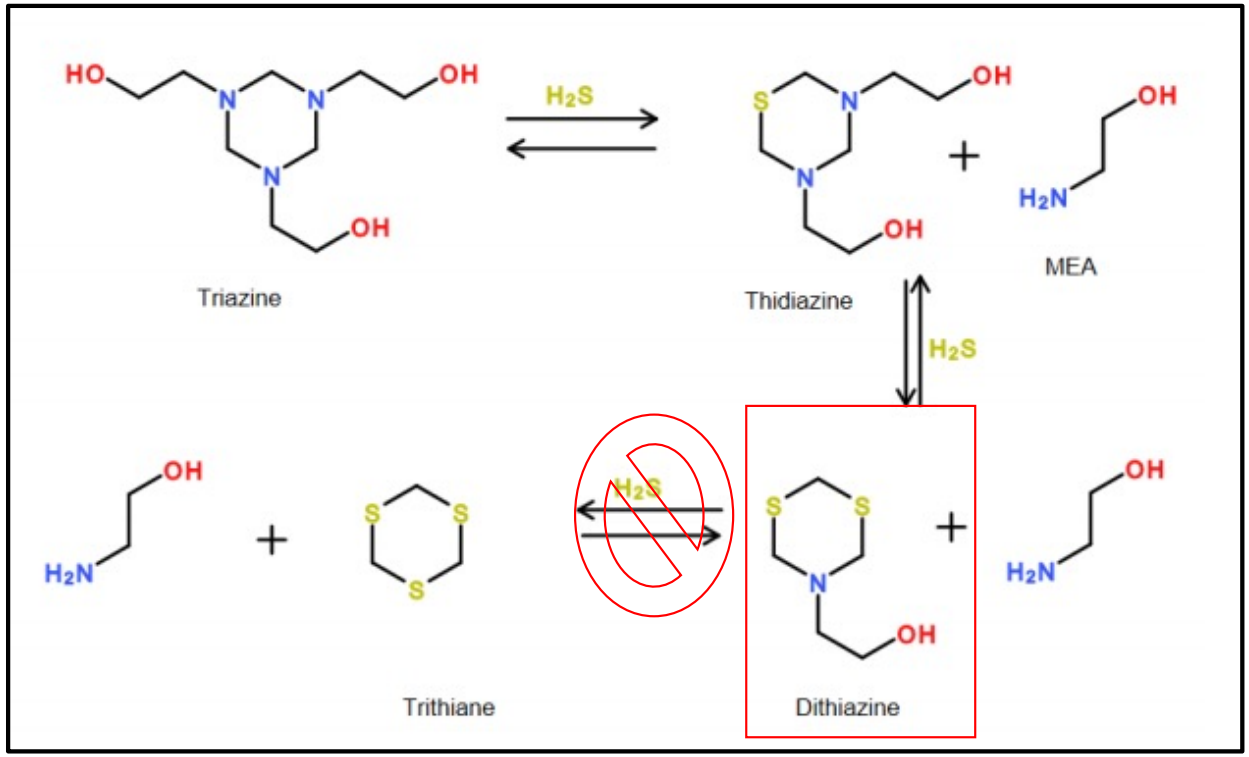
- Form irreversible reactions with H_2S
- Solids and liquids
- Better for H_2S > 100 ppm
- More ideal for smaller well-head facilities

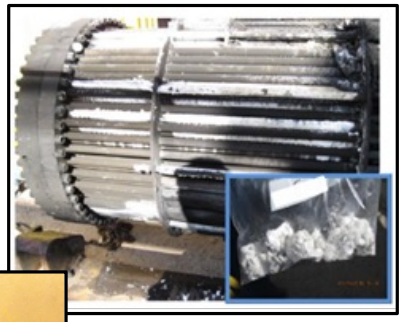
- Oxidizers
- Metal Carboxylates and Chelates
- Aldehydes, Ethers, and Amines
- Triazines

Key Perspectives

- Minimize number of additives
- Reduce product rejections and shipping delays
- Reduce additive odor, corrosion, and safety problems

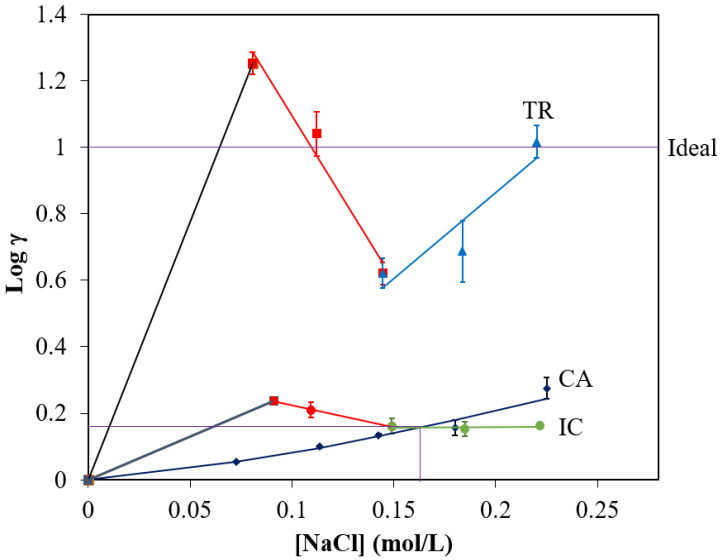
Non-Regenerative Scavengers

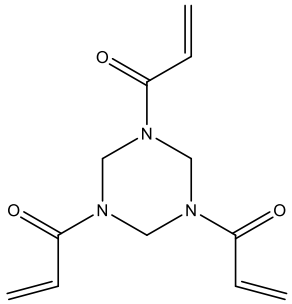




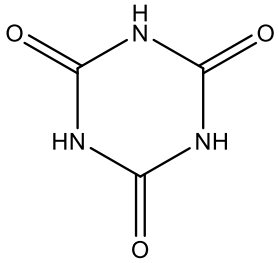
Solubility is key to effectiveness

Solubility of Triazines in Aqueous Solutions

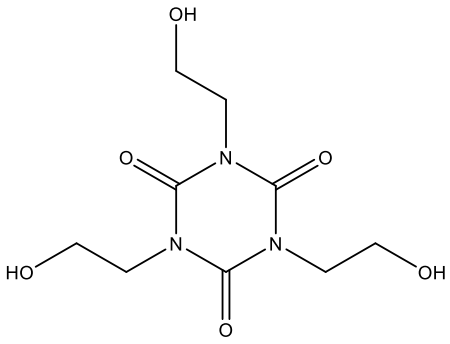




1,3,5-Triacryloylhexahydro
-1,3,5-triazine (triazine)



Cyanuric Acid (CA)



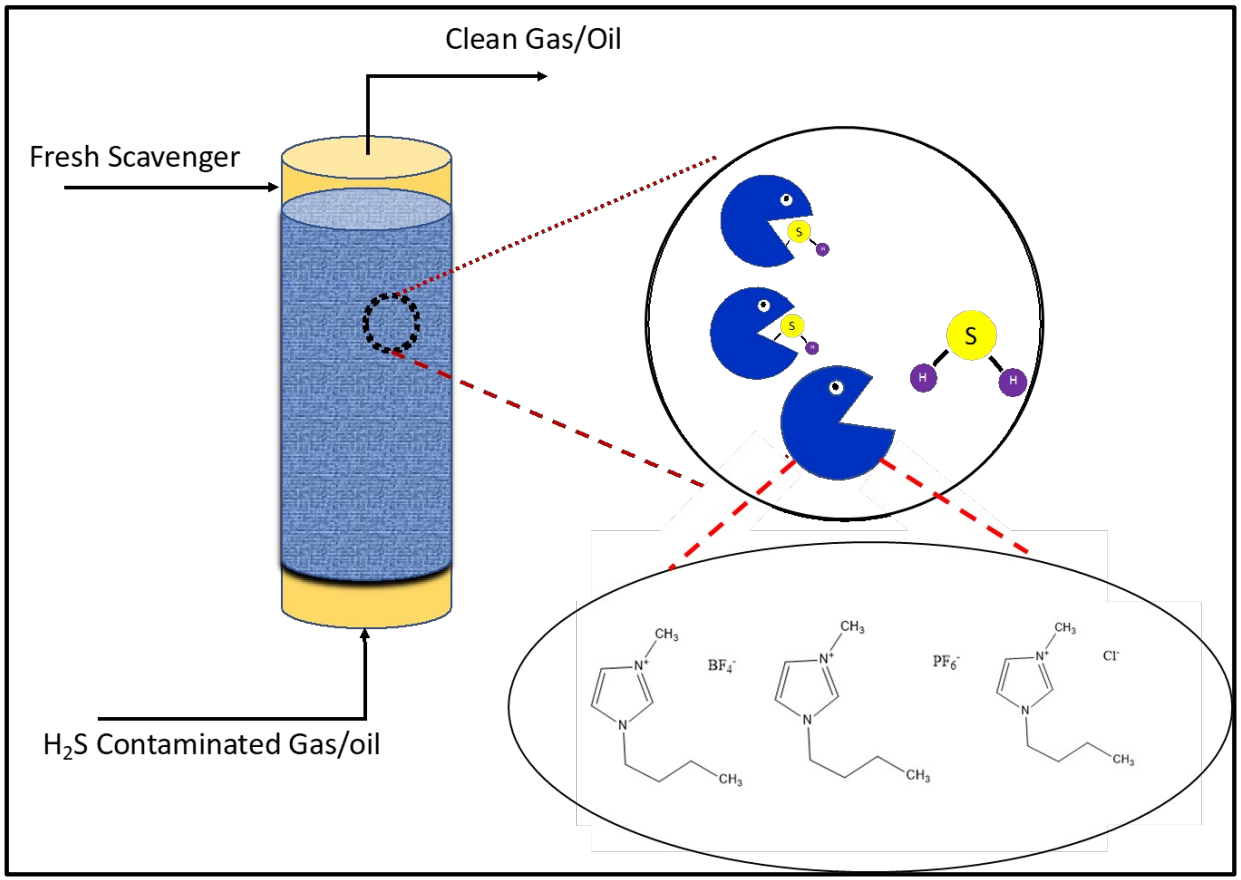
1,3,5-Tris(2-hydroxyethyl)
cyanuric acid (IC)

Linh Doan and Tracy Benson (2020) Journal of Chemical & Engineering Data, 65, 2325 – 2331.

Ionic Liquids as Regenerative H_2S Absorbents

- **Regenerative Absorbents**
- **Strong ionic interactions**
- **Negligible vapor pressures**
- **Tunable Properties**

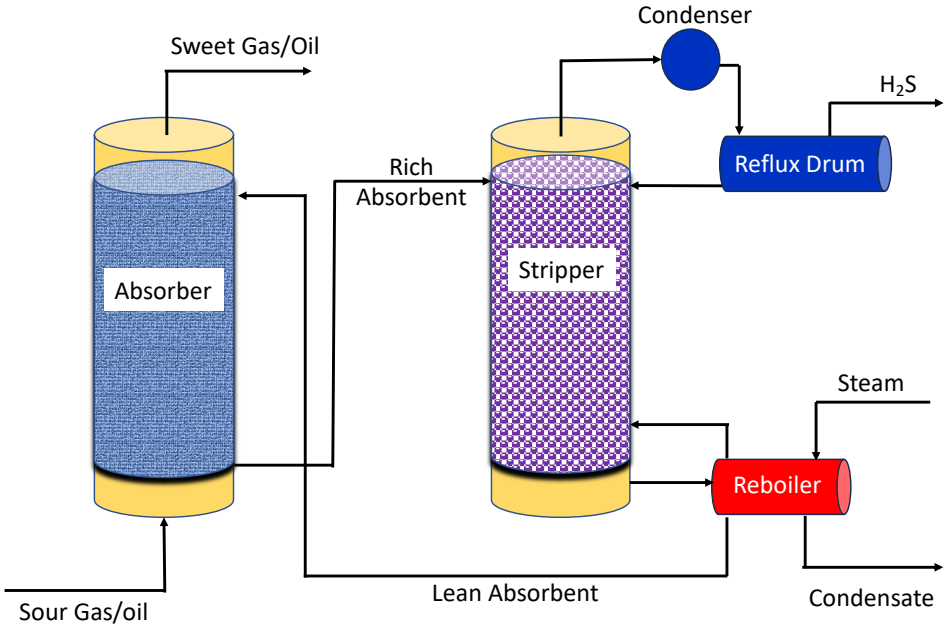
$[C_4mim][Cl]$
$[C_4mim][BF_4]$
$[C_4mim][PF_6]$



Research Objectives

Understanding chemical and physical characteristics for selecting ILs

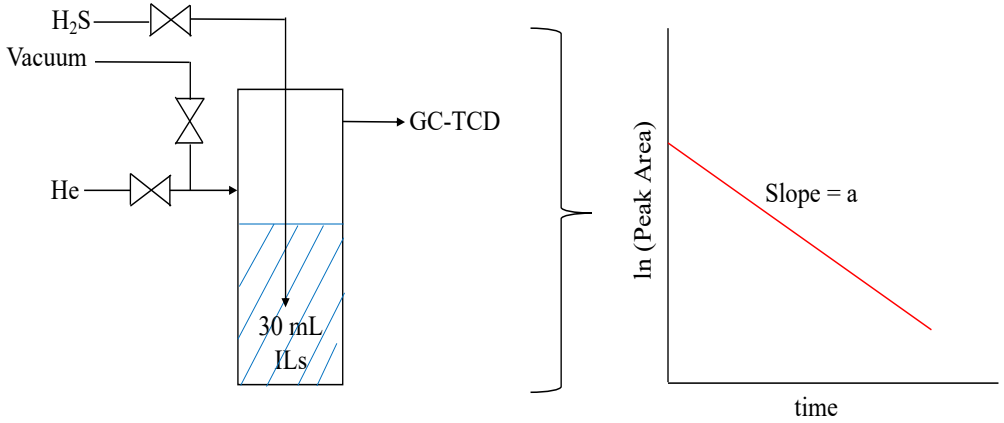
- ✓ **Infinite dilution activity coefficients of ILs**
- ✓ **Henry's constants, infinite dilution partial molar volume, mean ionic activity coefficients of ILs**

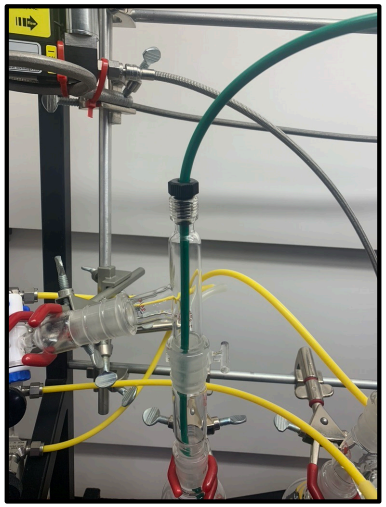


Safety Protocols:

- Training
- Fume hood
- H_2S signs
- Buddy system
- Scrubber
- Surveillance system
- Lapel Monitors

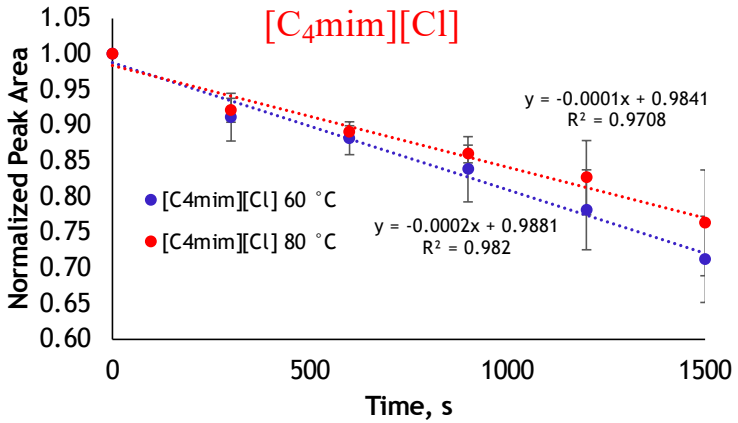
Infinite Dilution (Low Press) Experiments

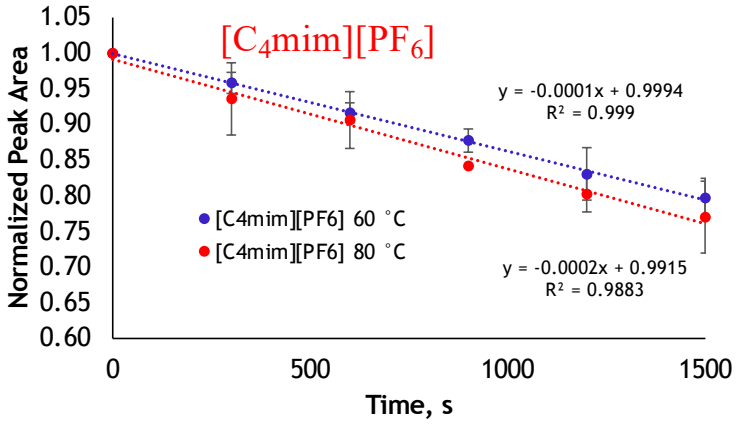


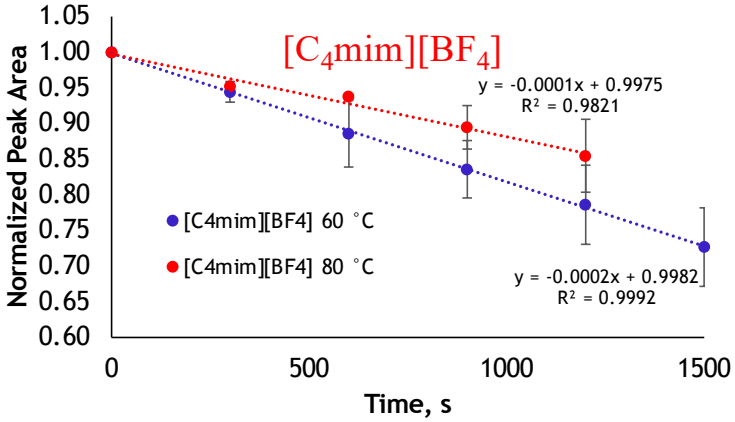


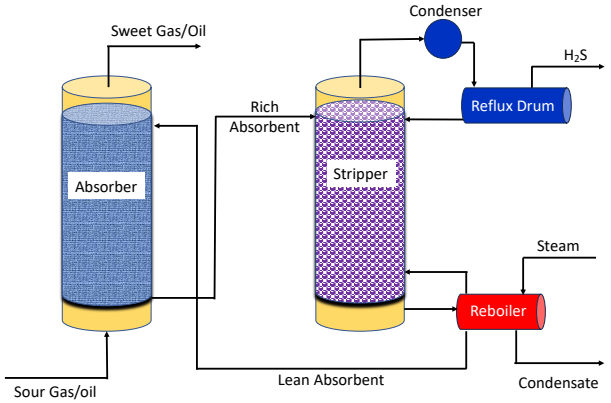
$$\gamma_i^{\infty} = -\frac{n_{IL}RT}{\varphi^s_{H_2S}P^s_{H_2S}\left(\frac{F_{He}}{a} + V_g\right)}$$

Infinite Dilution Activity Coefficients

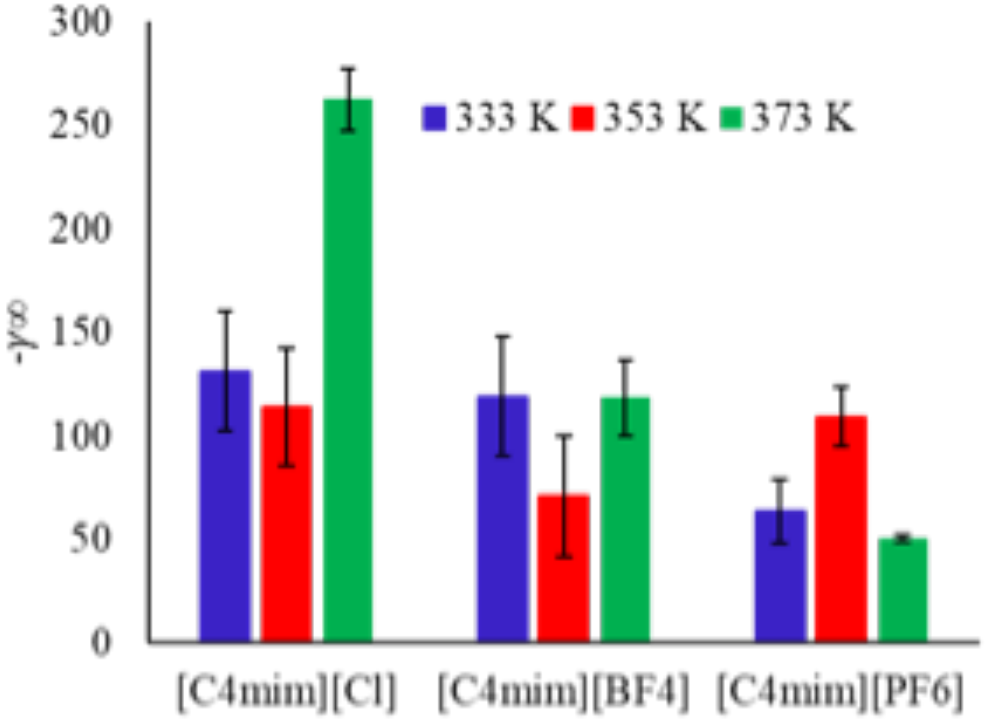


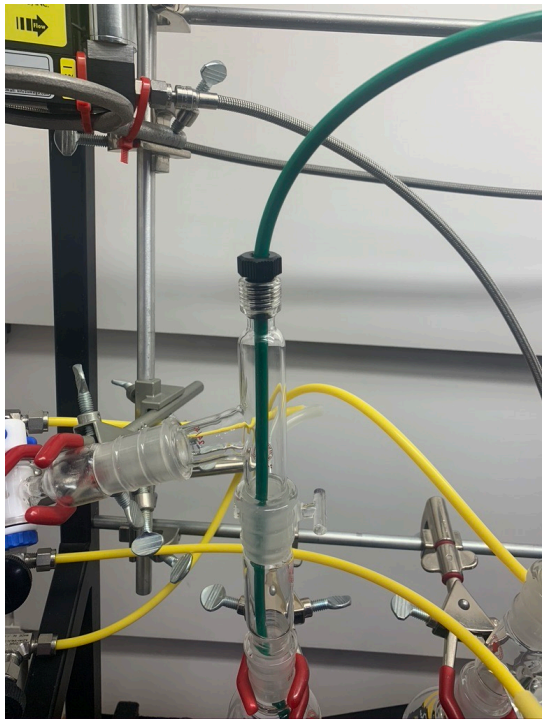






Infinite Dilution Activity Coefficients





Derivation of Henry's Constant

Ionic Liquid	Henry Const, $H_{2,1}$ (bar)	T (K)	P (bar)	Exp or Model
$[C_4mim][PF_6]$	14.3	298	10	Exp
	18.6	303	14	Exp
	10.0	298	1	Model
	7.1	298	14	Model
$[C_4mim][BF_4]$	15.5	303	14	Exp
	7.0	298	1	Model
	5.7	298	14	Model
$[C_4mim][Cl]$	3.54	298	1	Model
	2.7	298	14	Model

$$P_i = y_i P = k x_i$$

$$f_i^g = f_i^l$$

$$f_i^l = k x_i$$

$$f_2^l = k x_2 = H_{2,1} x_2 = \gamma_2 x_2 f_2^\circ$$

$$k = H_{2,1} = \gamma_2 f_2^\circ$$

$$RT ln\gamma_2 = A(1 - x_2)^2 + B(1 - x_2)^3$$

$$RT ln\gamma_2 = A(1 - x_2)^2$$

$$ln\gamma_2 = \frac{A}{RT}$$

$$\left(\frac{\partial ln f_i^l}{\partial P}\right)_{T,x} = \frac{\bar{v}_i}{RT}$$

$$H_{i,solvent} = \lim_{x_i \to \infty} \frac{f_i^l}{x_i}$$

$$\left(\frac{\partial ln H_{i,solvent}}{\partial P}\right)_T = \frac{\bar{v}_i^\infty}{RT}$$

Krichevsky – Kasarnovsky

$$ln\frac{f_2}{x_2} = lnH_{2,1}^{P_1^s} + \frac{\bar{v}_2^\infty (P - P_1^s)}{RT}$$

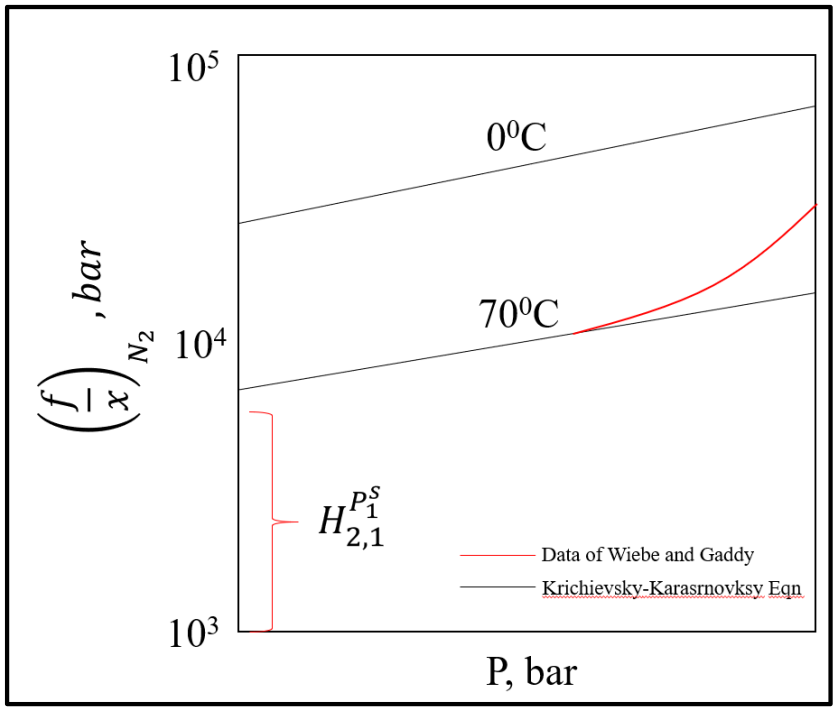
Derivation of Henry's Constant

Krichevsky – Kasarnovsky

$$ln\frac{f_2}{x_2} = lnH_{2,1}^{P_1^s} + \frac{\bar{v}_2^{\infty}(P - P_1^s)}{RT}$$

Krichevsky – Ilinskeya

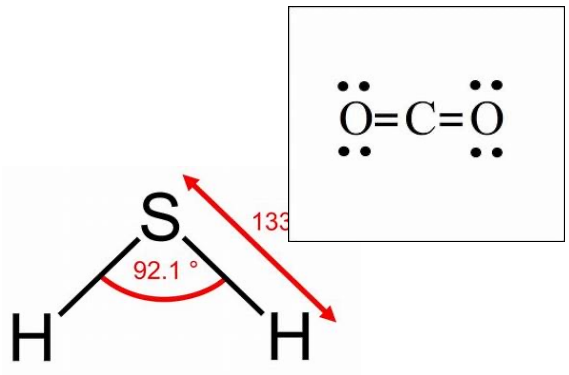
$$ln\frac{f_2}{x_2} = lnH_{2,1}^{P_1^s} + \frac{\bar{v}_2^{\infty}(P - P_1^s)}{RT} + \boxed{\frac{A}{RT}(x_1^2 - 1)}$$



Research Hypothesis

- ILs should be thermodynamically treated as electrolytes, having long-range electrostatic interactions

- H_2S has a strong dipole moment and can take part in dipole – dipole and dipole – induced dipole interactions

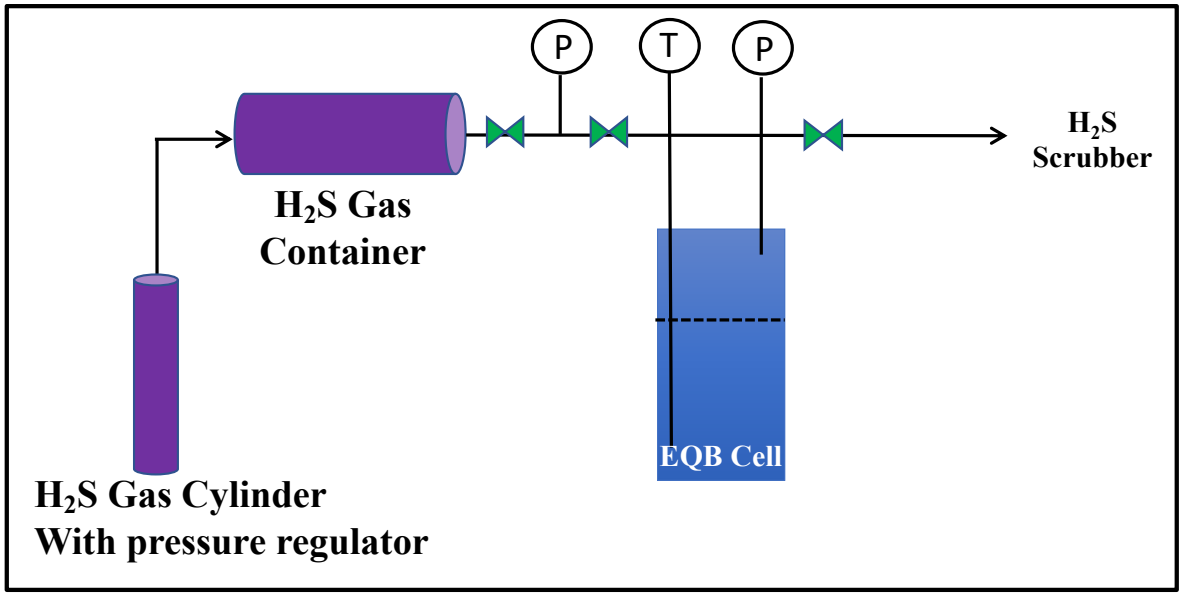


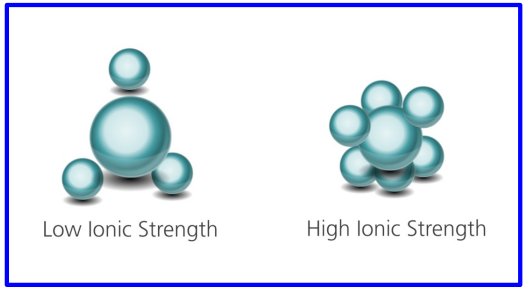
MIAC

$$ln\frac{f_2}{x_2} = lnH_{2,1}^{P_1^s} + \frac{\bar{v}_2^{\infty}(P - P_1^s)}{RT} + ln\gamma^{\pm}(x_1^2 - 1)$$

Proposed Model (Benson-Doan)

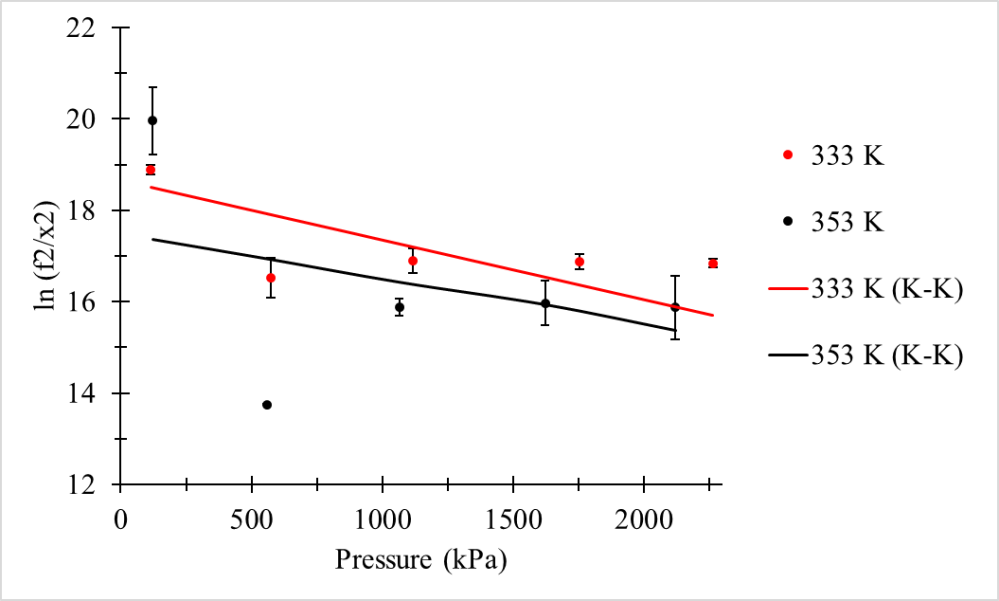
High Pressure Experimental Setup



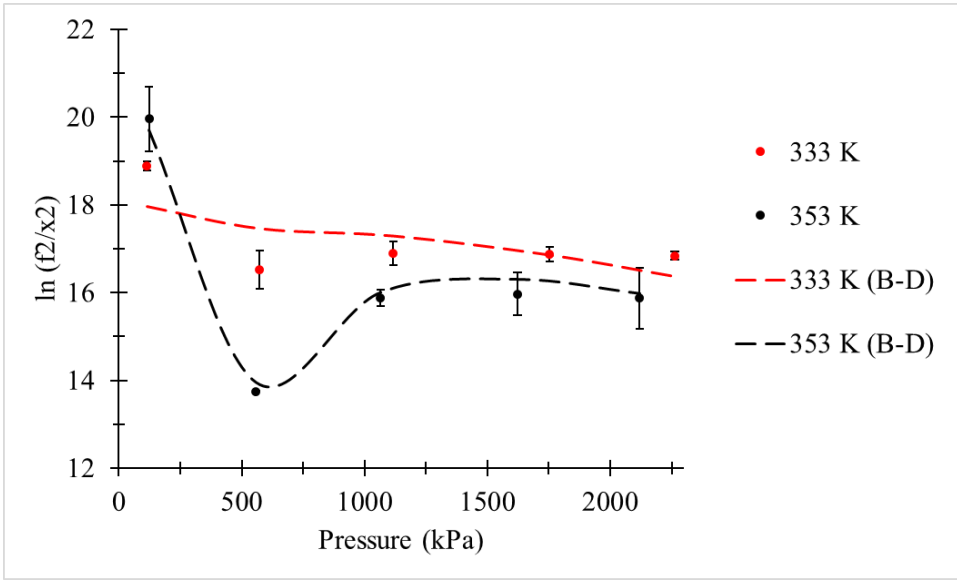


Testing Proposed Model

$$ln\frac{f_2}{x_2} = lnH_{2,1}^{P_1^s} + \frac{\bar{v}_2^{\infty}(P - P_1^s)}{RT}$$

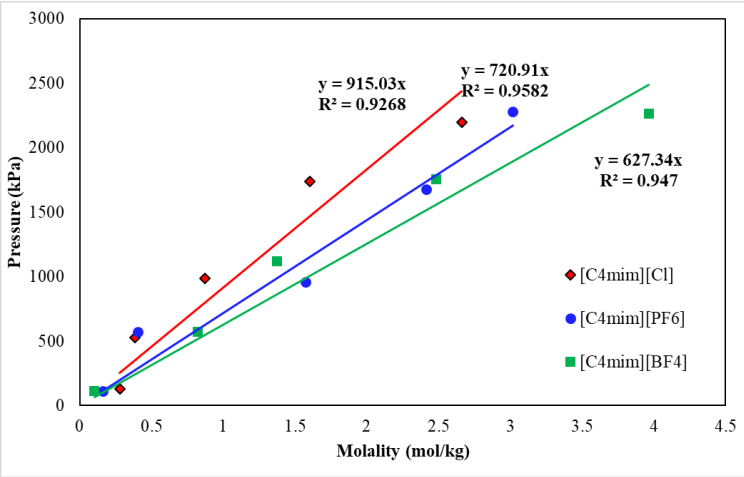


$$ln\frac{f_2}{x_2} = lnH_{2,1}^{P_1^s} + \frac{\bar{v}_2^{\infty}(P - P_1^s)}{RT} + ln\gamma^{\pm}(x_1^2 - 1)$$

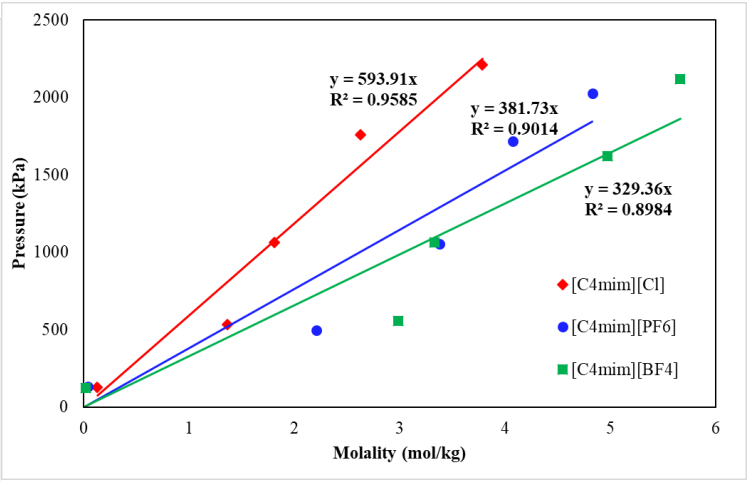


Thermodynamic Properties

60 °C

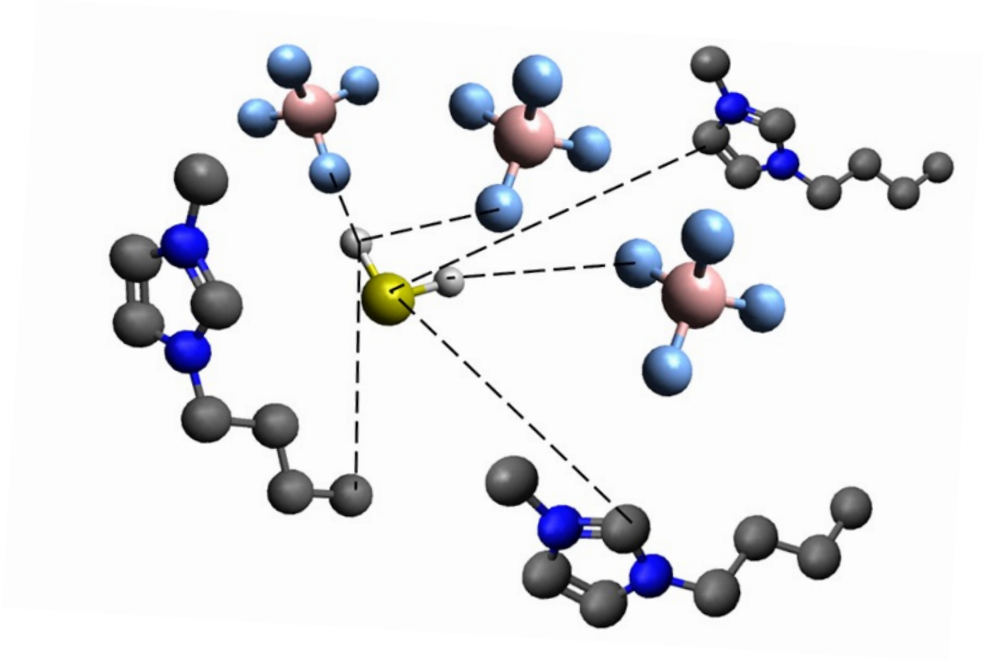


80 °C



- T = 60 °C : $[C_4mim][BF_4]$ = 1.18 $[C_4mim][PF_6]$ = 1.42 $[C_4mim][Cl]$
- T = 80 °C : $[C_4mim][BF_4]$ = 1.04 $[C_4mim][PF_6]$ = 1.51 $[C_4mim][Cl]$
- Highest Absorption: $[C_4mim][BF_4]$ at T = 80 °C and P = 2,000 kPa

H_2S/IL Interactions

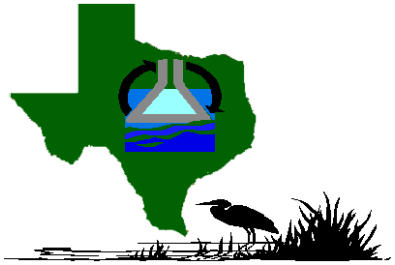


Acknowledgements

CENTER FOR MIDSTREAM MANAGEMENT & SCIENCE
LAMAR UNIVERSITY

Students:
Linh Doan, Ph.D.
Obakore Agbroko
Emily Brown
Kelvin Elgar

Collaborators:
Dr. Sylvestre Twagirayezu
Dr. Clayton Jeffryes
Dr. James Henry



Texas Hazardous Research Center