Modelling the Solubility of H_2S and CO_2 in Ionic Liquids Using PC-SAFT Equation of State

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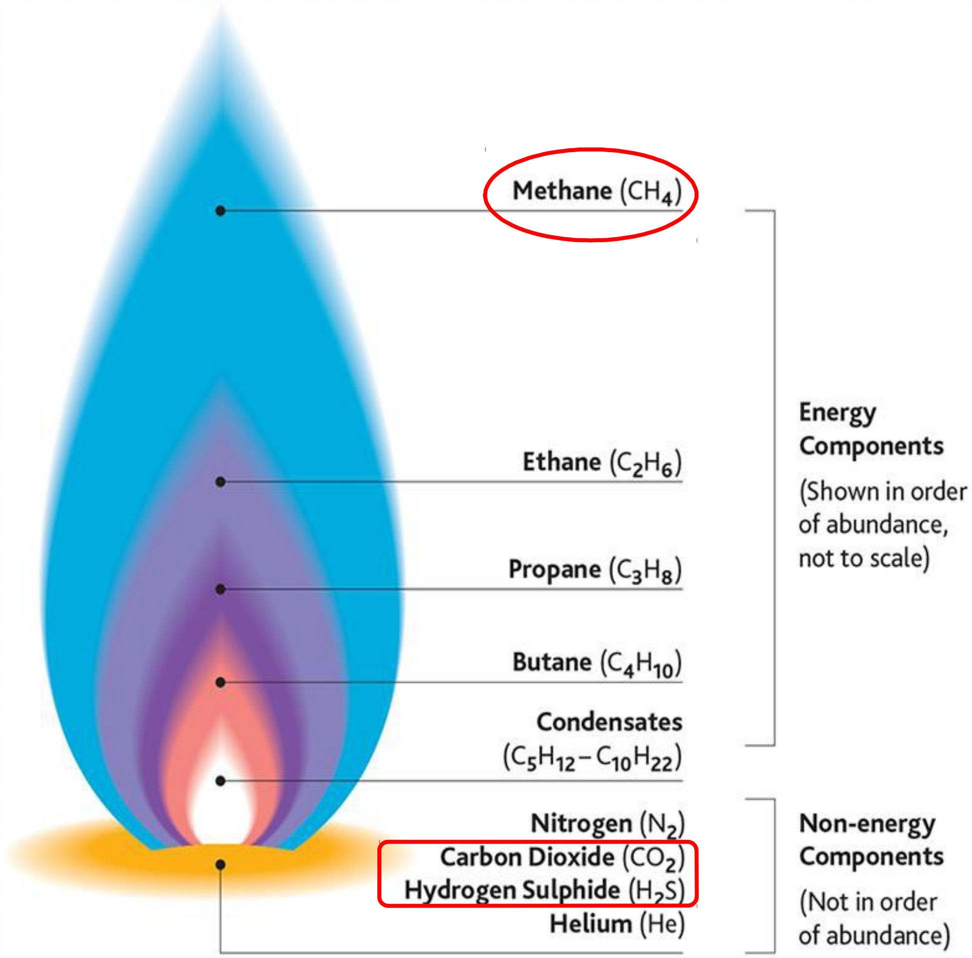
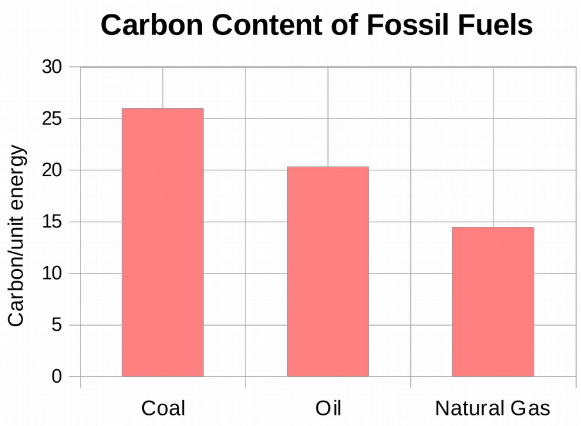
Natural Gas*



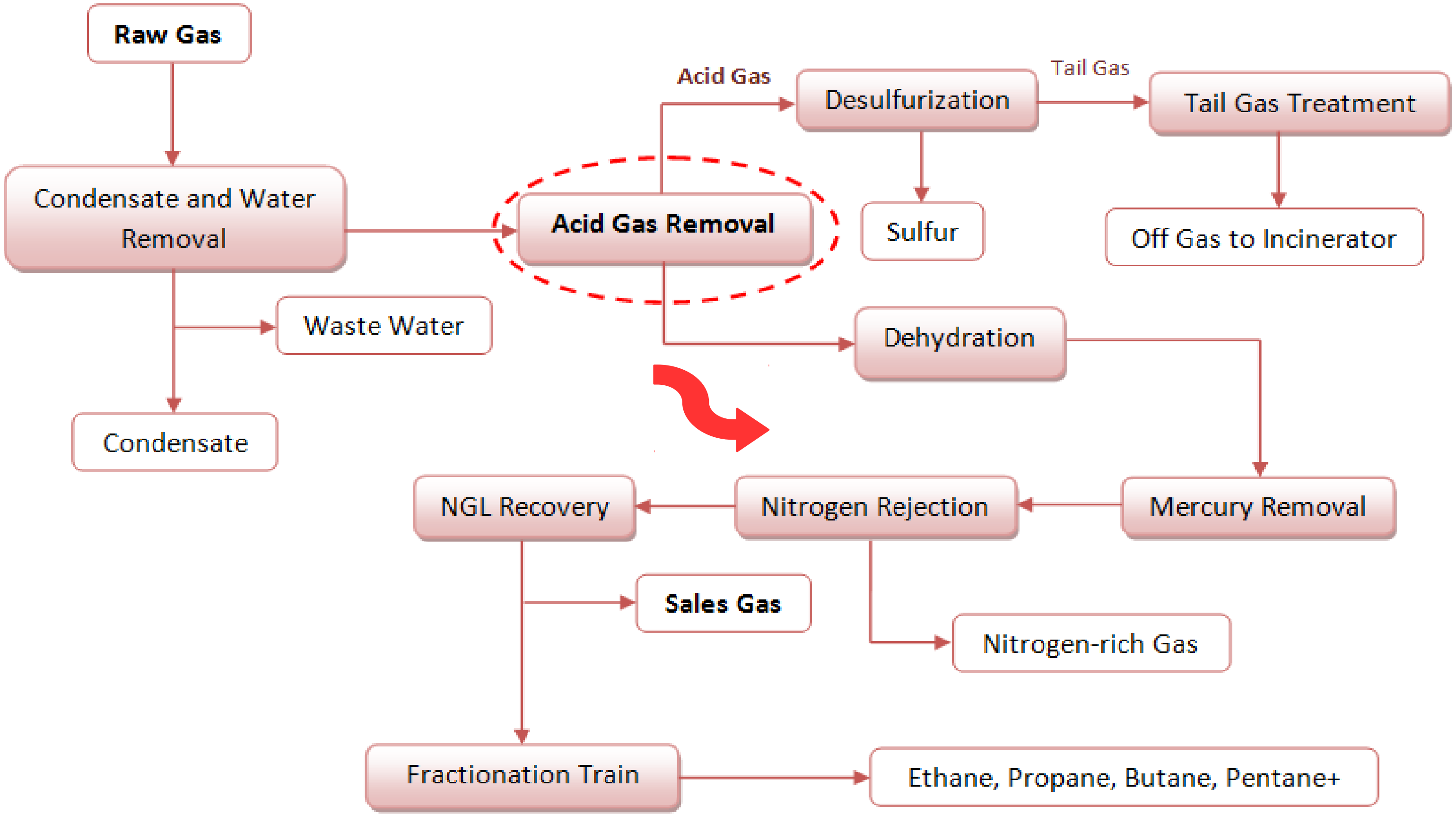


Carbon dioxide & Hydrogen sulfide

Acid Gases

** Reference: Canadian Centre for Energy Information*

Gas Processing



Sour Gas

- Sour gas = H_2S > 5.7 mg/m^3 of NG or (4 ppmv).
- Acid gas removal = 'gas sweetening'.
- Acid gases need to be removed for the following reasons:
  - Corrosion problems.
  - H_2S is toxic and flammable .
  - CO_2 may freeze and cause blockage of pipes.
  - CO_2 has poor heating value.
  - Environmental concerns over CO_2 and H_2S emissions .

40% of the **world's** natural gas reserves are sour.

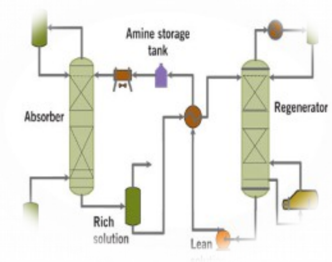
60% of the **Middle Eastern** natural gas reserves are sour.

34% of **Russia**'s reserves are sour *.

** Reference: Statistics from the International Energy Agency*

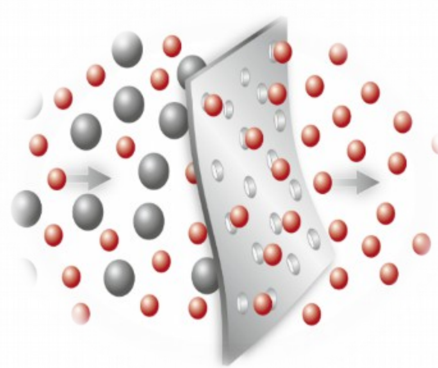
Acid Gas Removal Technologies

- Chemical absorption (Amine solvents: e.g. MEA, DEA, MDEA)
- Physical absorption (e.g. Selexol, purisol and ionic Liquids)
- Adsorption (e.g. Molecular sieve zeolite and activated charcoal)
- Membranes (polymer based e.g. cellulose acetate, polyamides)
- Cryogenic Distillation (CFZ, Sprex)
- Hybrid Technologies



Amine processes

Molecular sieve zeolite



Membranes

Cryogenic separation

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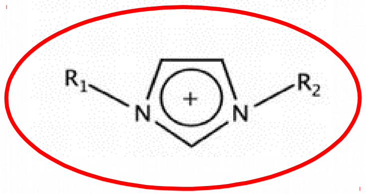
Aims

- Improve the pre-existing amine units for sour gas treatment
- Explore the use of Ionic liquids as an alternative solvent
- Thermodynamic model
- Represent the solubility of CO_2 and H_2S in ILs
- Effect of accounting for ILs association and charge on the solubility
- Find the best strategy and association scheme

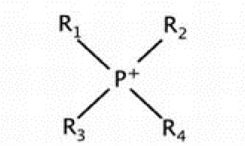
Ionic Liquids (ILs): Common cations and anions

ILs are materials consisting of ions and are liquid below 100°C. They are salts in the liquid state.

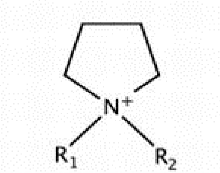
Cations



Imidazolium

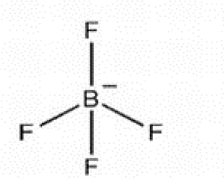


Phosphonium

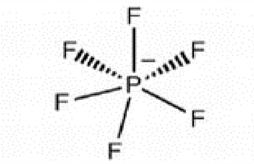


Pyrrolidinium

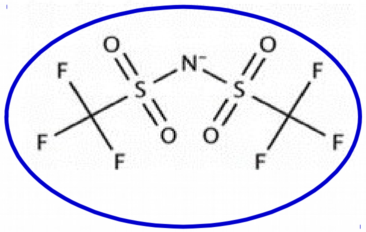
Anions



Tetrafluoroborate
BF4



Hexafluorophosphate
PF6



Bis(trifluoromethanesulfonyl)amide
NTf2

** Reference: Somers, A.E.; Howlett, P.C.; MacFarlane, D.R.; Forsyth, M. Lubricants 2013, 1, 3-21.*

Ionic Liquids (ILs): Features

- Easy to separate
- Very low vapour pressure (negligible volatility)
- Non-flammable
- High thermal stability
- Low toxicity
- Structural tunability
- Recyclable and reusable

Thermodynamic Modelling: Previous models

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Cubic equations of state

- PR
- SRK

Activity coefficient methods

- NRTL
- UNIQUAC
- UNIFAC

Quantum chemistry calculations

- COSMO-RS

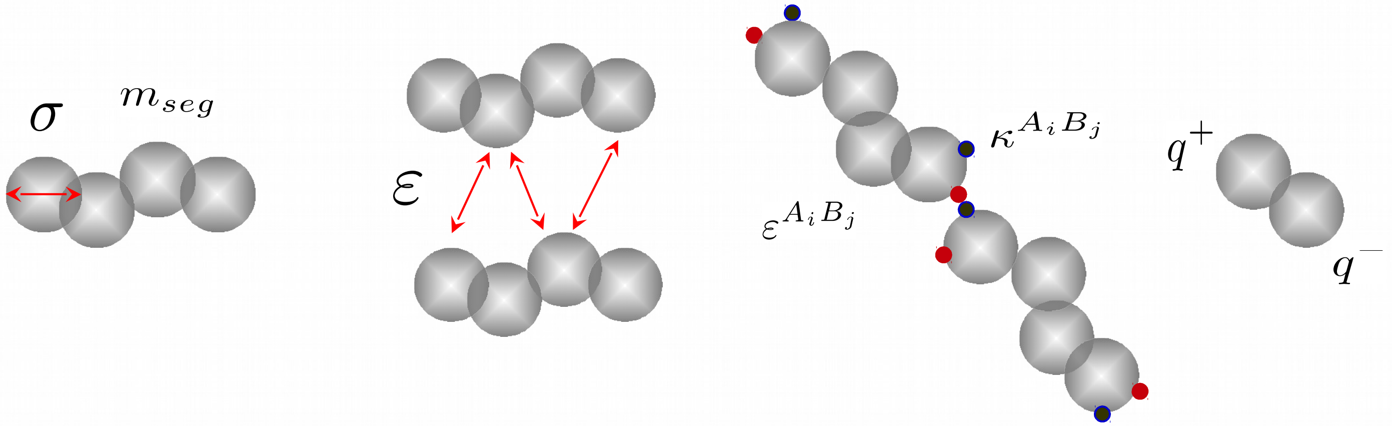
Statistical mechanics-based molecular approaches

- SAFT
- SAFT-VR
- PC-SAFT
- PC-PSAFT

Thermodynamic Modelling:

Perturbed-Chain Statistical Associating Fluid Theory

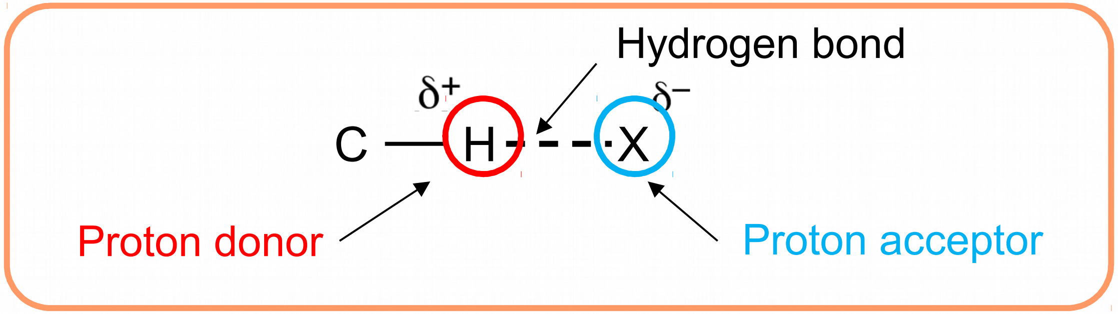
PC-SAFT

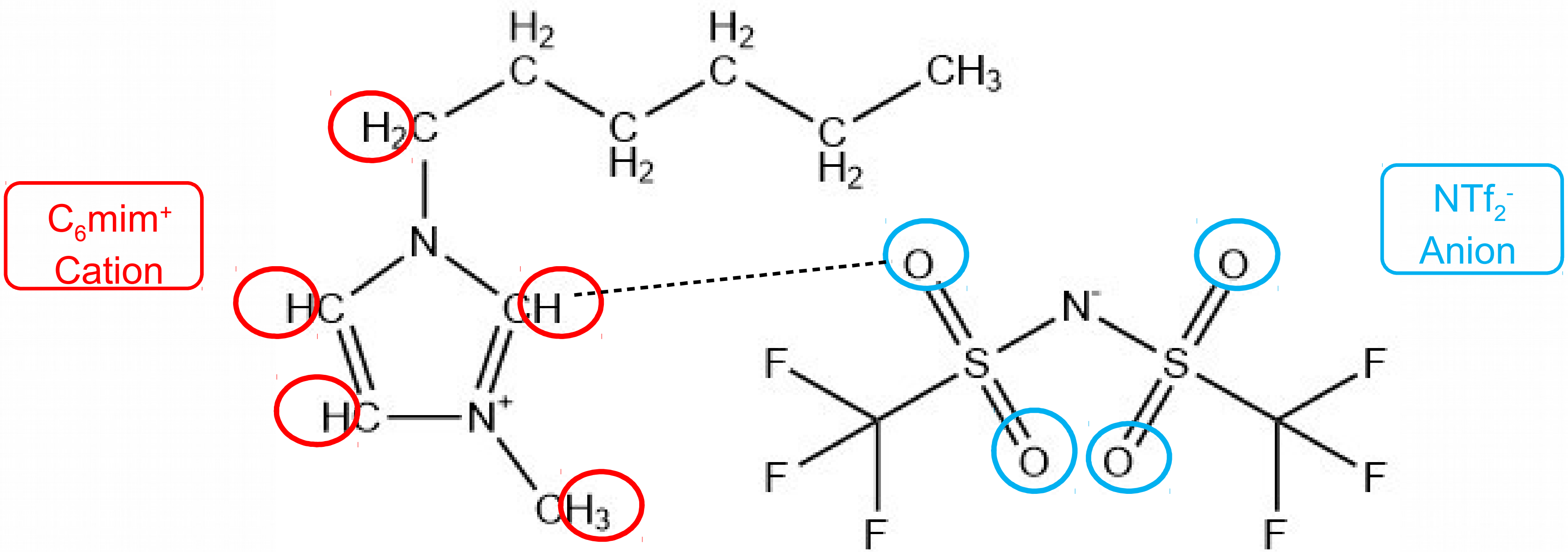


$$a^{residual} = a^{hardchain} + a^{dispersion} + a^{association} + a^{electrolyte}$$

* Reference : J. Gross, G. Sadowski, Ind. Eng. Chem. Res. 40 (4) (2001) 1244–1260.

Association: Hydrogen Bonding





1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, $[C_6mim]^+[NTf_2]^-$

Strategies and Association schemes for ILs

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Strategies: Two strategies were investigated

Molecule

$C_n$mimNTf$_2$

Electrolyte

$C_n$mim$^+$

Cation

NTf_2^-

Anion

Association schemes: The investigated association schemes

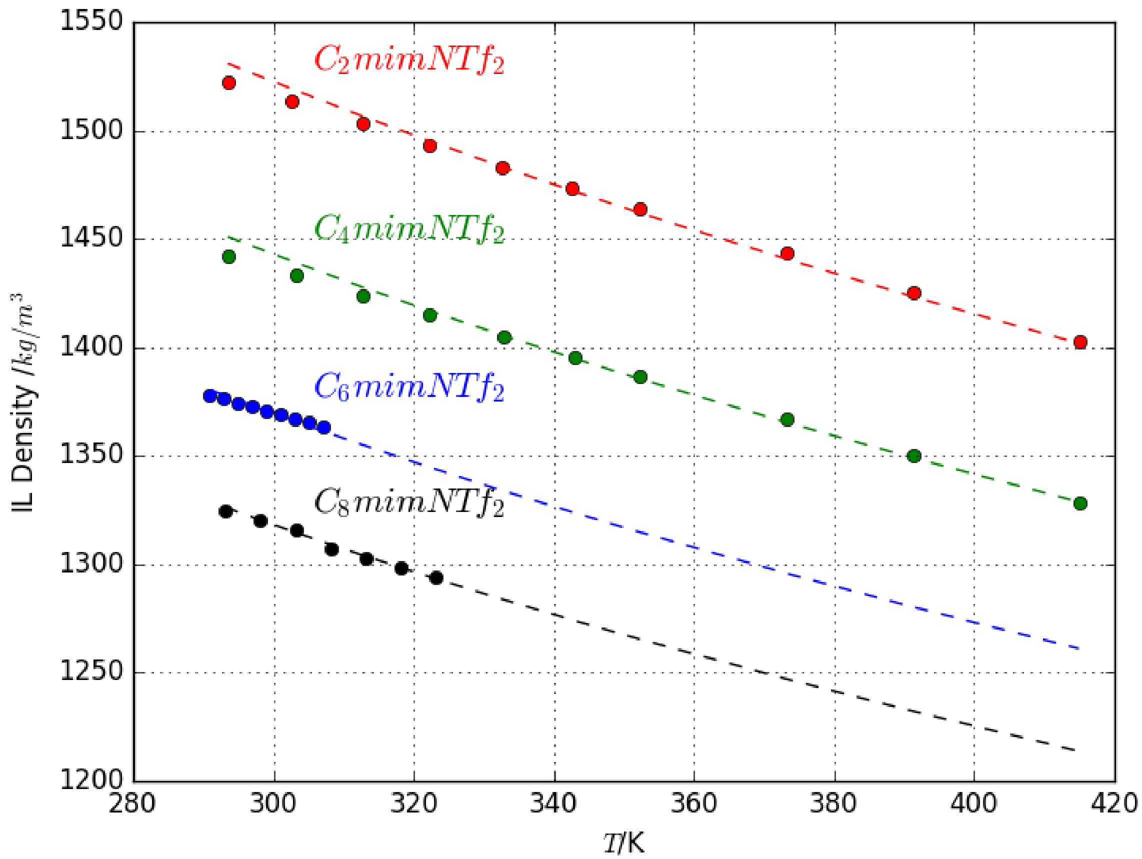
2-site association scheme 2(1:1) = One donor and one acceptor

3-site association scheme 3(2:1) = Two donor and one acceptor

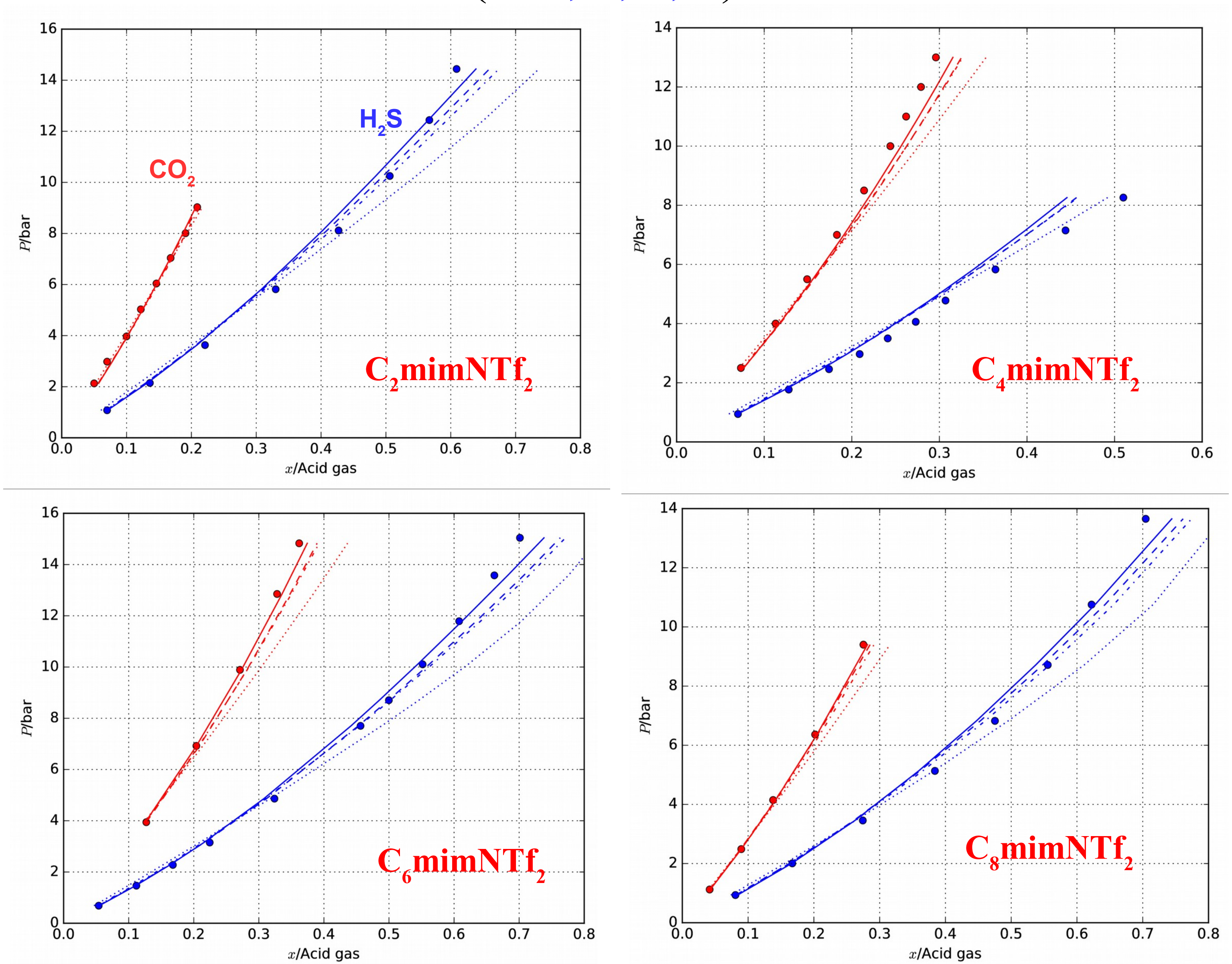
4-site association scheme 4(2:2) = Two donor and two acceptor

ILs pure component parameters

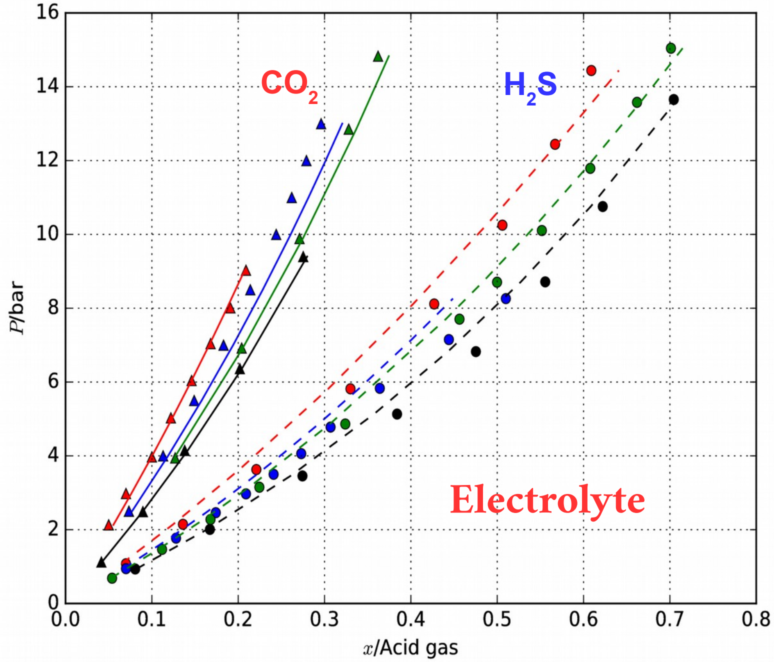
Experimental density fit

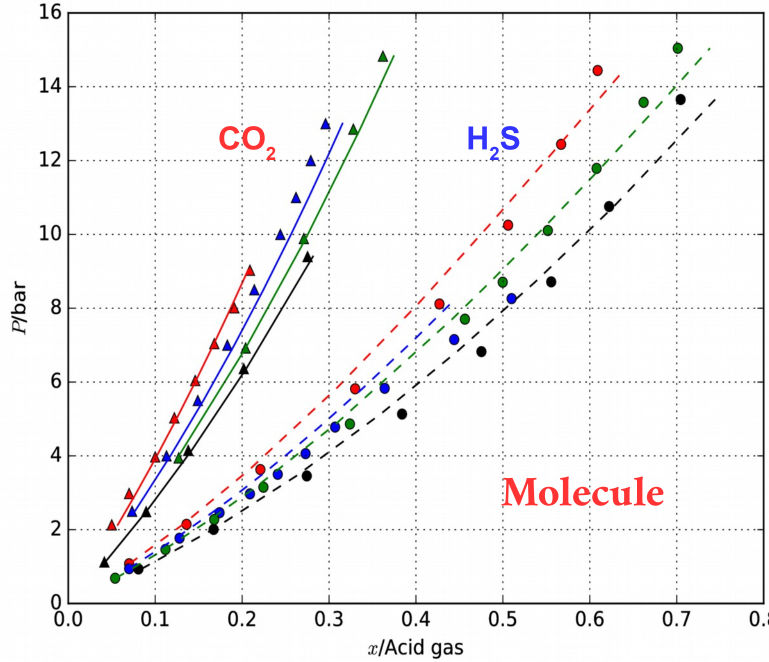


Solubility of acid gases in $C_n$mimNTf$_2$ ILs as a molecule (n=2, 4, 6, 8)



Solubility of acid gases in $C_n$mimNTf$_2$ ILs as a molecule and electrolyte (best association scheme)





Conclusions

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- ILs could contribute significantly to improving the economy and environmental sustainability of the AGR process.
- The solubility of acid gases in ILs can be accurately described using PC-SAFT by accounting for the self-association between IL molecules and selecting the proper association scheme.
- No binary interaction parameters are needed.
- Although no significant improvement has been achieved by treating ILs as electrolytes, the model predictive capability is enhanced.
- H_2S is about two times more soluble than CO_2 in the studied ILs.
- The solubility of acid gases in ILs increases by increasing the cation alkyl chain length of the ILs. Therefore, of the studied ILs; $[C_8mim][NTf_2]$ is the most promising solvent for AGR applications especially for high H_2S content NG.

Future Work

- Explore the applicability of PC-SAFT model for multicomponent natural gas systems (methane, acid gases, water, ethanolamines and ILs).
- Build IL-based gas treatment process simulation using our PC-SAFT parameters for the studied ILs.
- Evaluation of the proposed gas treatment process against current conventional techniques.

Acknowledgement

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Thank You