LULEÅ UNIVERSITY OF TECHNOLOGY

HIGHBIO2 2011-2013
Biomass to Energy and Chemicals

Recovery of CO_2 through ionic liquids from syngas (gasified woody biomass)

Xiaoyan Ji

Division of Energy Science/Energy Engineering

Outline

- Introduction
- Modelling
- Results
- Conclusions

Introduction (1)

- CO_2 separation or removal is required in biomass gasification
  - to obtain products
  - to improve the efficiency of the subsequent process
  - Examples:
    - In production of synthetic hydrocarbons with Fischer-Tropsch technology, the inert CO_2 is removed to increase the efficiency and selectivity of higher hydrocarbons (C_{5+}).
    - In methanol production, CO_2 removal is made to obtain a favourable ratio of the gas mixture in order to increase the production yield.
    - hydrogen production, CO_2 is removed to purify hydrogen

Introduction (2)

- CO_2 separation technologies
  - Commercial technology: amine technology
    - High cost: $50 to $100 per ton carbon
    - Environmental affect: volatility (amine goes to environment)
  - New technology: ionic liquids*
    - Environment benign
    - Low cost: down to $20 per ton carbon
    - Designable solvents (properties depend on the constitution)

Design a proper type of ionic liquid for a specific process

* Ionic liquid: a molten salt consisting of cation and anion

Introduction (3)

- Current work:
  - Focus on the synthesis of new ILs, data are limited to gas solubility
  - Transport property is very limited
  - No systematic research from synthesis to application

Large gap to application

Introduction (4)

- A proper ionic liquid:
  - CO_2 solubility and selectivity
  - Diffusivity (viscosity and mass transfer, adsorption and desorption)
  - Low price
  - Corrosion and the effect of water (material choice)
  - Efficiency for adsorption/desorption
    - Several steps or one step, driving force and efficiency
    - Design of adsorption tower
  - CO_2 separation simulation
    - Aspen Plus
    - Techno economic evaluation (cost and energy consumption)
  - Process integration and evaluation
    - Choose a specific process and integrate the CO_2 process
    - Effects of CO_2 separation process on whole process

Planned and previous work

- Goal of this project:
  - to have a systematic study from fundamental modelling to process simulation and integration
  - to implement a CO_2 separation process into gasifier model (developed in highbio1)
- Previous work:
  - Development of a model to represent CO_2 solubility and selectivity in ionic liquids (ILs)

Modelling

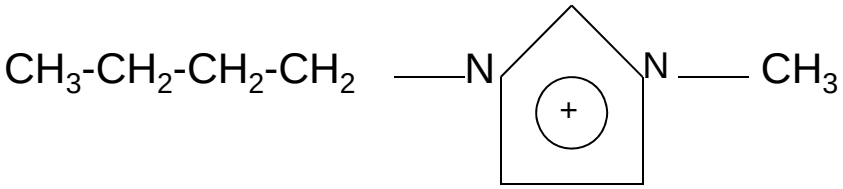
- Research review
  - Experimental work
    - Less than adequate (properties of Ils depends on the combination of cation and anion)
    - Time-consuming and expensive
  - Theoretical work
    - Excess Gibbs energy models and cubic EOS
      - an IL molecule was modelled as a single molecular species or assumed to completely dissociate into cation and anion
    - Statistical associating fluid theory (SAFT)-based models
      - an IL molecule was modelled as a neutral ion pair with one set of parameters
    - Heteronuclear square-well chain fluids, group-contribution non-random lattice fluid EOS, and group contribution EOS
      - imidazolium ring-anion pair was modelled as one segment or functional group

Parameters are not completely transferable

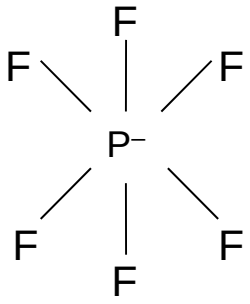
Modelling

- A model that can predict the properties of ILs based on the information of their alkyl substituents, cation head, and anion
- Hetero-segmented statistical association fluid theory (SAFT)
  - One molecule consists of different groups representing the alkyls, cation head, and anion
  - Each with one kind of segment and certain segment and bond numbers

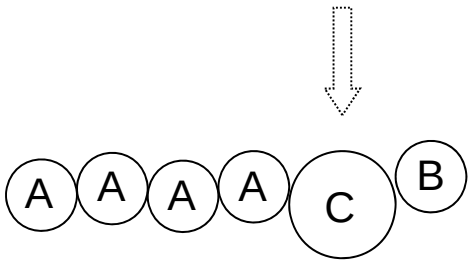
Heterosegmented SAFT EOS

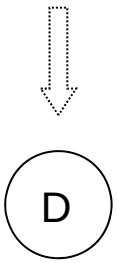


[bmim]$^+$



$[PF_6]^-$





A & B: alkyls; C: cation head; D: anion

Heterosegmented SAFT EOS

- Interaction between segments:
  - Hard sphere; Dispersion interaction;
  - Chain
  - Association (to account for the electrostatic/polar interactions)
- Parameters for ILs:
  - For alkyls:
    - Estimated from n-alkanes
  - For cation head and anion:
    - from fitting of the density for a group of IL data
    - $[C_n mim][Tf_2N]$, $[C_n mim][BF_4]$, and $[C_n mim][PF_6]$

Heterosegmented SAFT EOS

- For CO_2-IL system
  - Mixing rules for CO_2-segement in IL

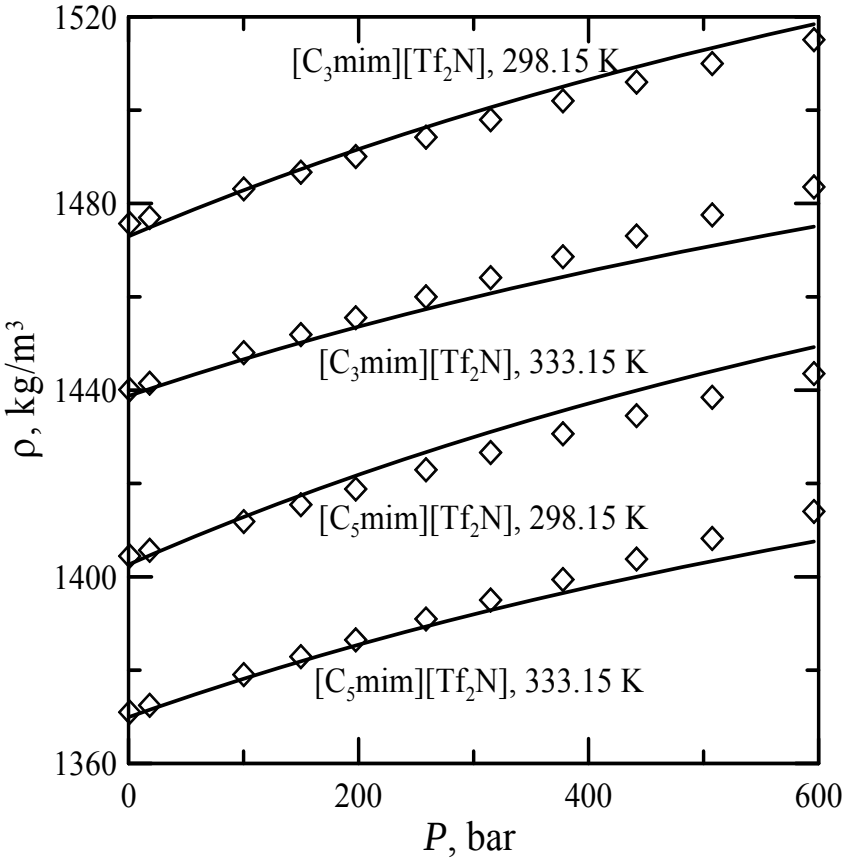
$$u_{\alpha\beta} = u_{\beta\alpha} = \sqrt{u_\alpha u_\beta}\left(1 - k_{\alpha\beta}\right)$$

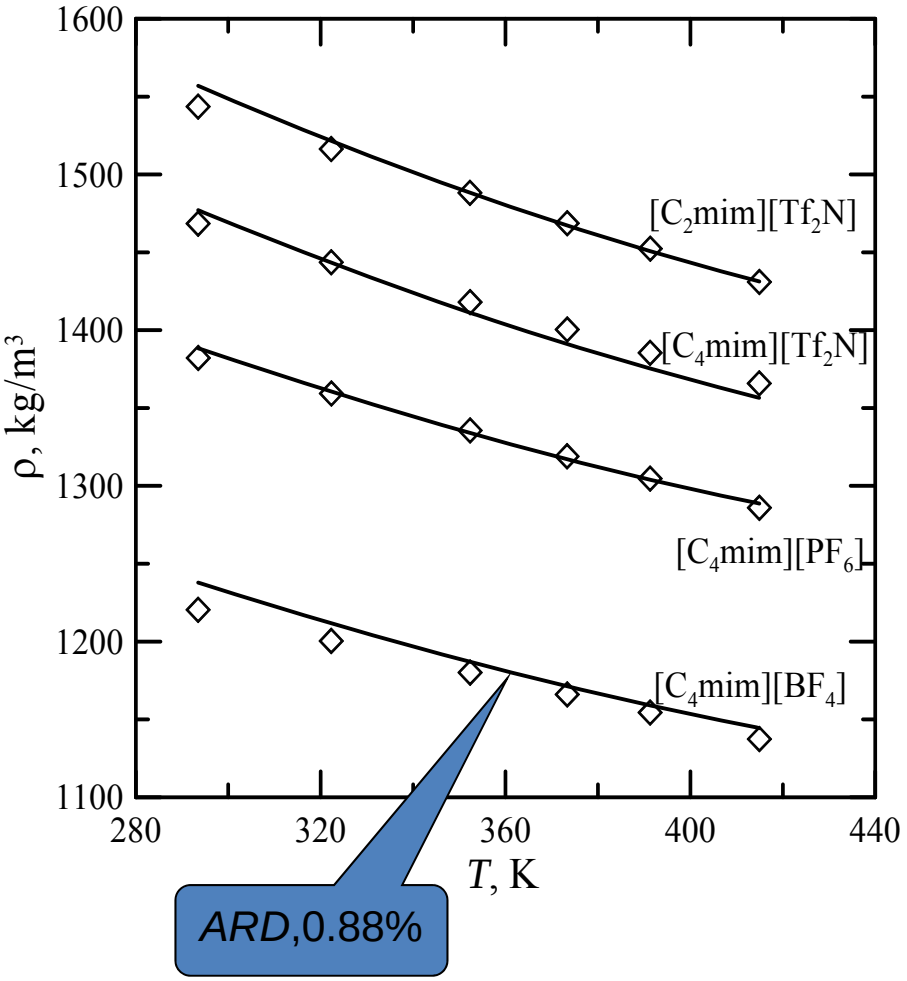
    where $k_{\alpha\beta}$: temperature-dependent
  - Parameters fitting:
    - Gas (CO_2) solubility
  - Prediction for other properties
    - molar volumes of CO_2/IL mixtures,
    - partial molar volume of CO_2 in CO_2/IL mixtures
    - the partial molar volume of CO_2 at infinite dilution in an IL

Summary of model performace

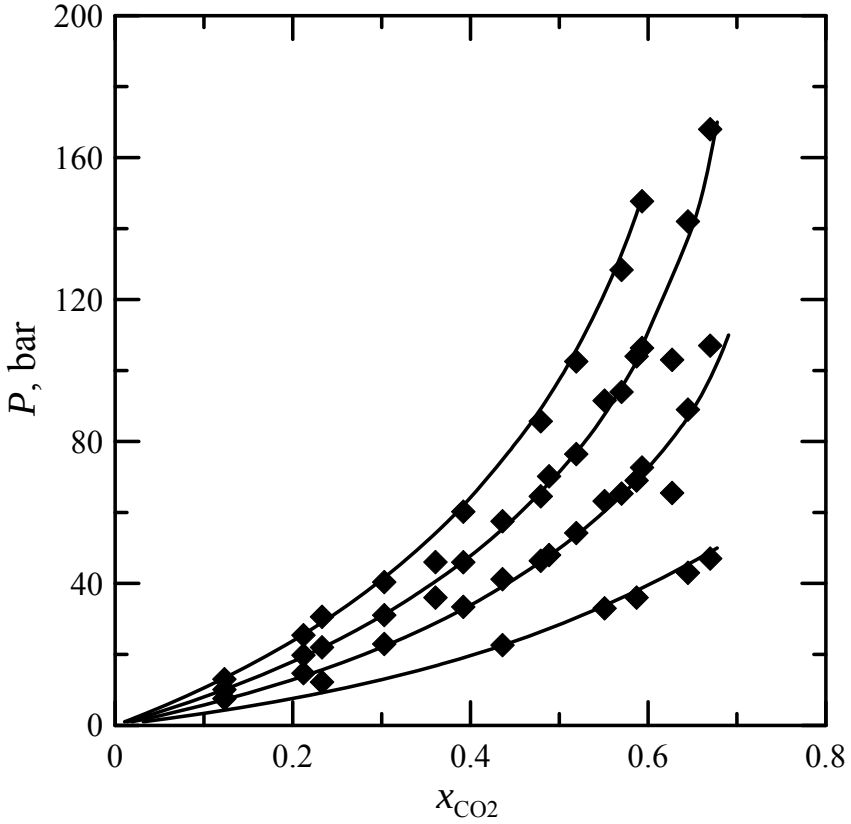
	T, K	P_{max}	ARD (%)
$[C_2mim][Tf_2N]$	293-415	400	0.24
$[C_3mim][Tf_2N]$	298.15-333.15	600	0.17
$[C_4mim][Tf_2N]$	293-415	400	0.31
	298.15-328.20	591	0.19
$[C_5mim][Tf_2N]$	298.15-333.15	600	0.16
$[C_6mim][Tf_2N]$	298.15-333.15	600	0.30
	293.15-338.15	650	0.23
$[C_4mim][BF_4]$	293-415	400	0.88
	298-333	600	0.52
$[C_4mim][PF_6]$	295-335	200	0.08
	293-415	400	0.24
$[C_6mim][PF_6]$	295-335	200	0.10
$[C_8mim][PF_6]$	295-335	200	0.11

Density prediction for ILs

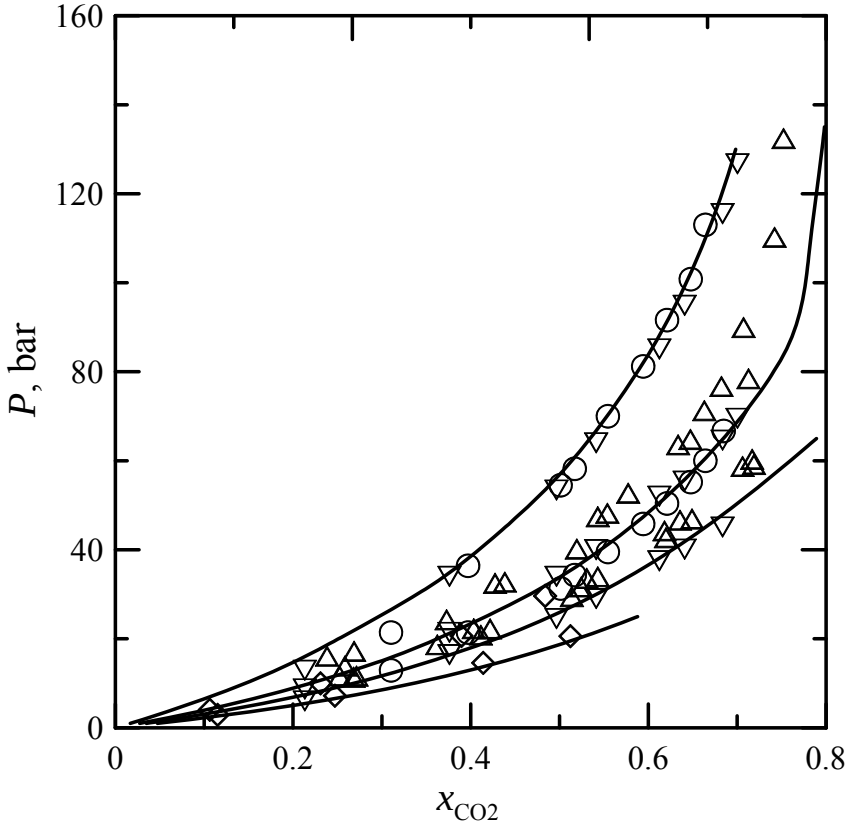




CO_2 solubility in IL

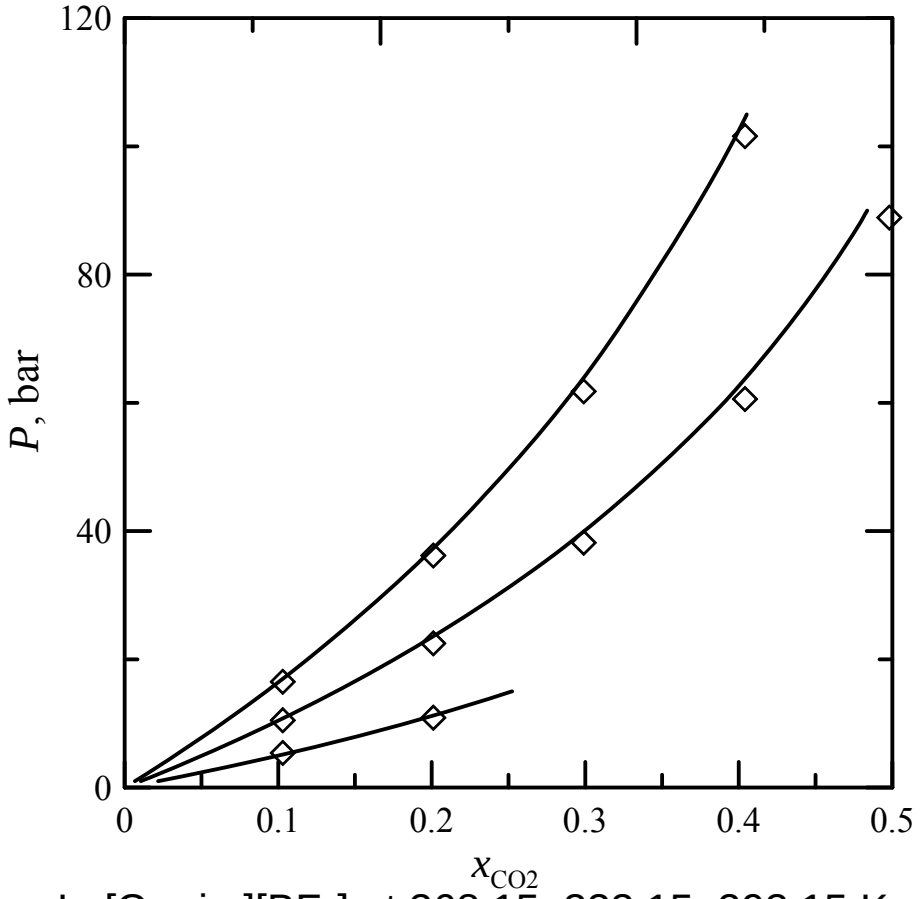


In $[C_2mim][Tf_2N]$ at 363.15, 344.55, 324.15, and 293.15 K (from left to right). ◆, experimental data; —, calculated

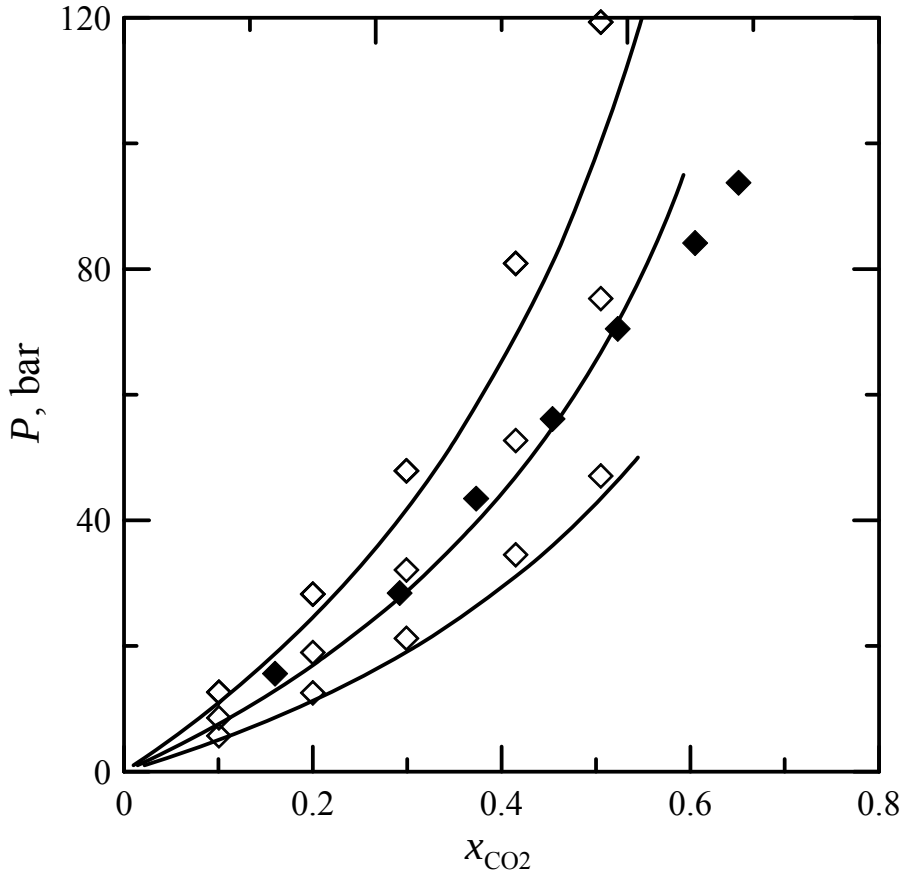


In $[C_4mim][Tf_2N]$ at 344.5, 313, 298, and 280 K (from left to right). Symbols, experimental data; —, calculated

CO_2 solubility in IL

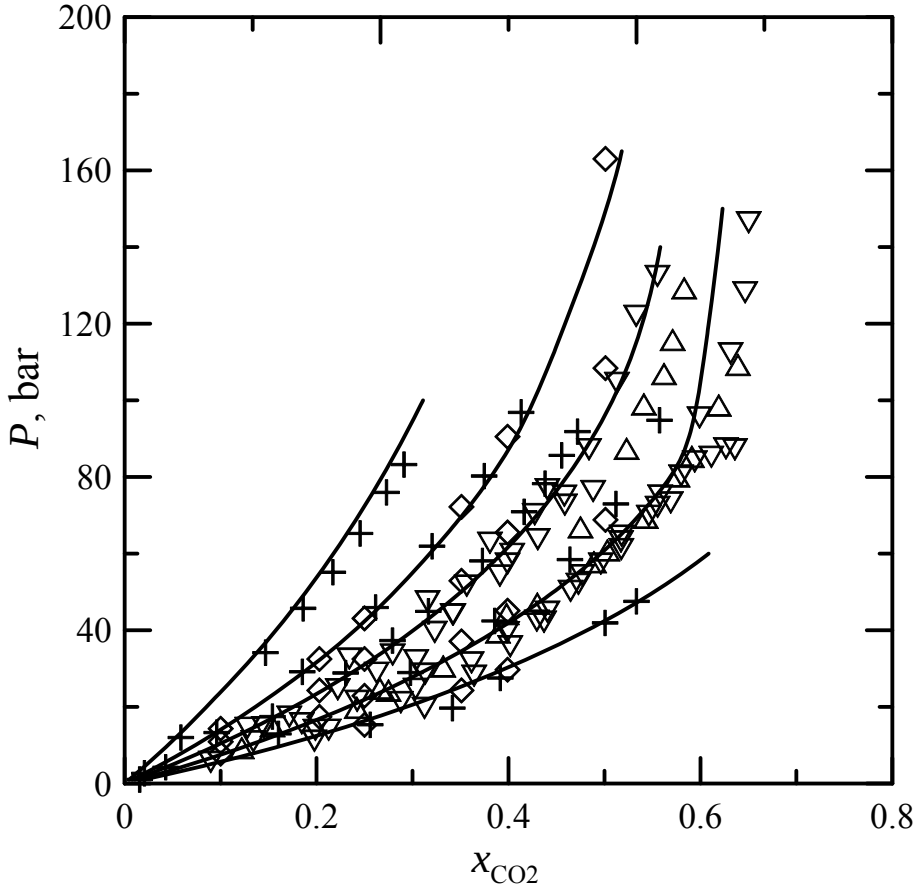


In $[C_6mim][BF_4]$ at 368.15, 333.15, 293.15 K (from left to right). ◇, experimental data; —, calculated.

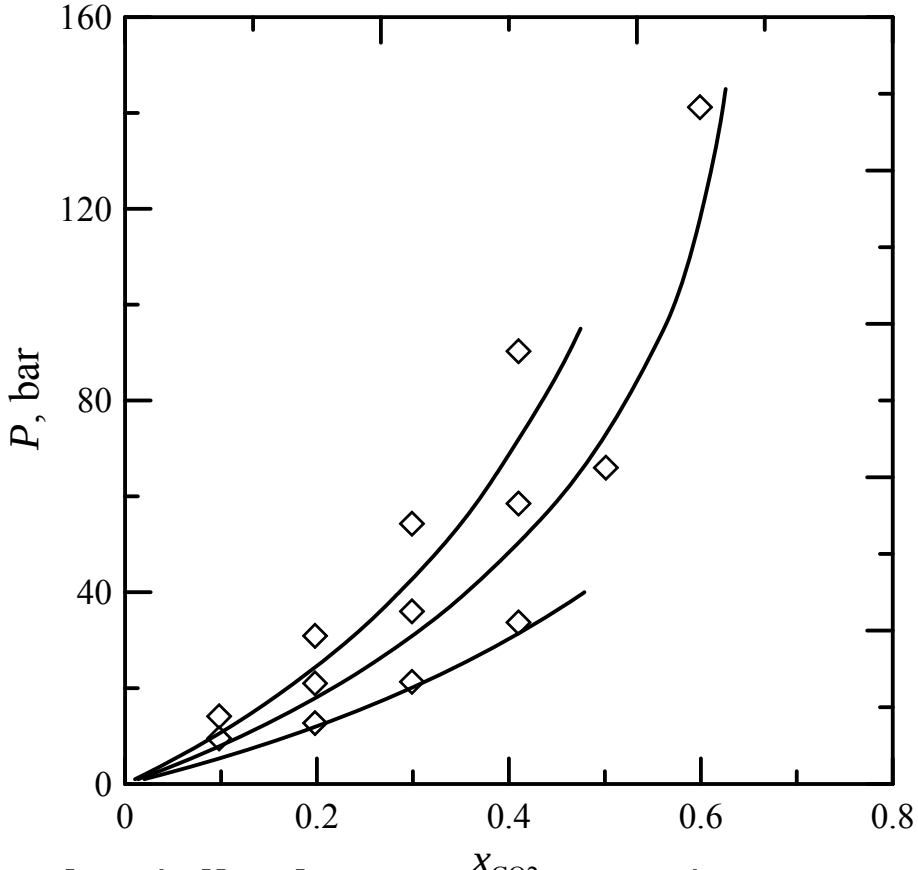


In $[C_8mim][BF_4]$ at 363.15, 333.15, and 308.15 K (from left to right). Symbols, experimental data; —, calculated

CO_2 solubility in IL

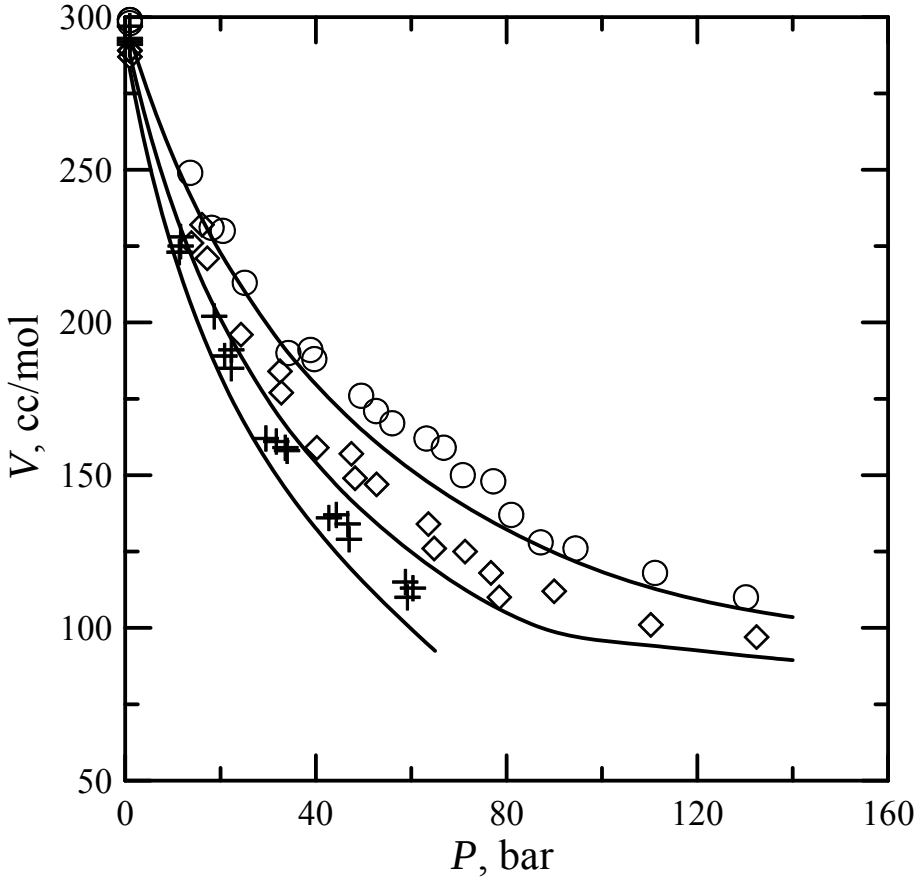


In $[C_4mim][PF_6]$ at 395.05, 354.35, 333.3, 313.3, and 293.55 K (from left to right). Symbols, experimental data; —, calculated.

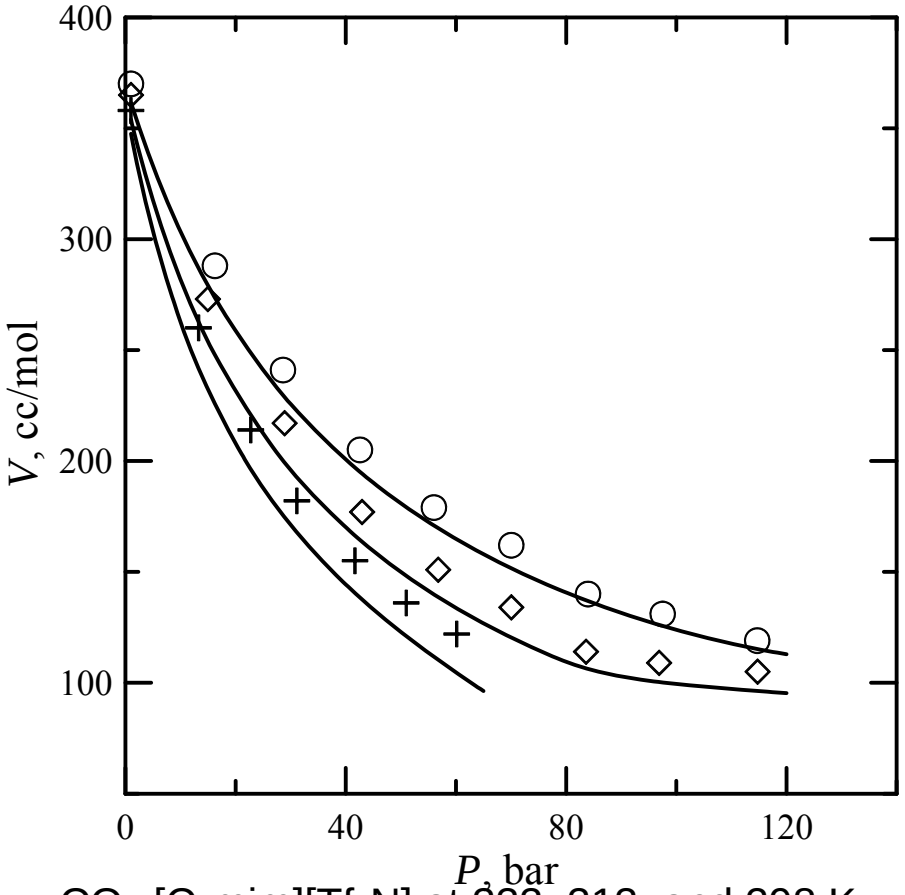


In $[C_6mim][PF_6]$ at 363.4, 333.3, and 303.35 K (from left to right). Symbols, experimental data; —, calculated

Molar volumes of CO_2/IL mixtures

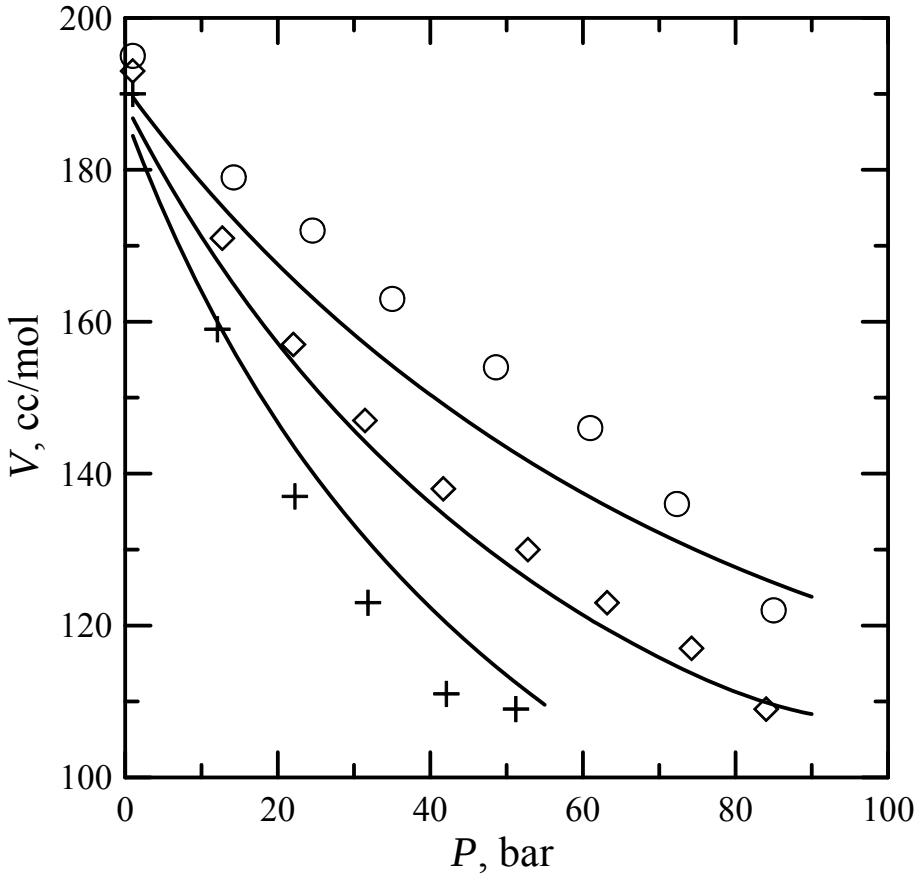


CO_2-[C_4mim][Tf_2N] at 333, 313, and 298 K (from top to bottom). Symbols, experimental data; —, predicted.

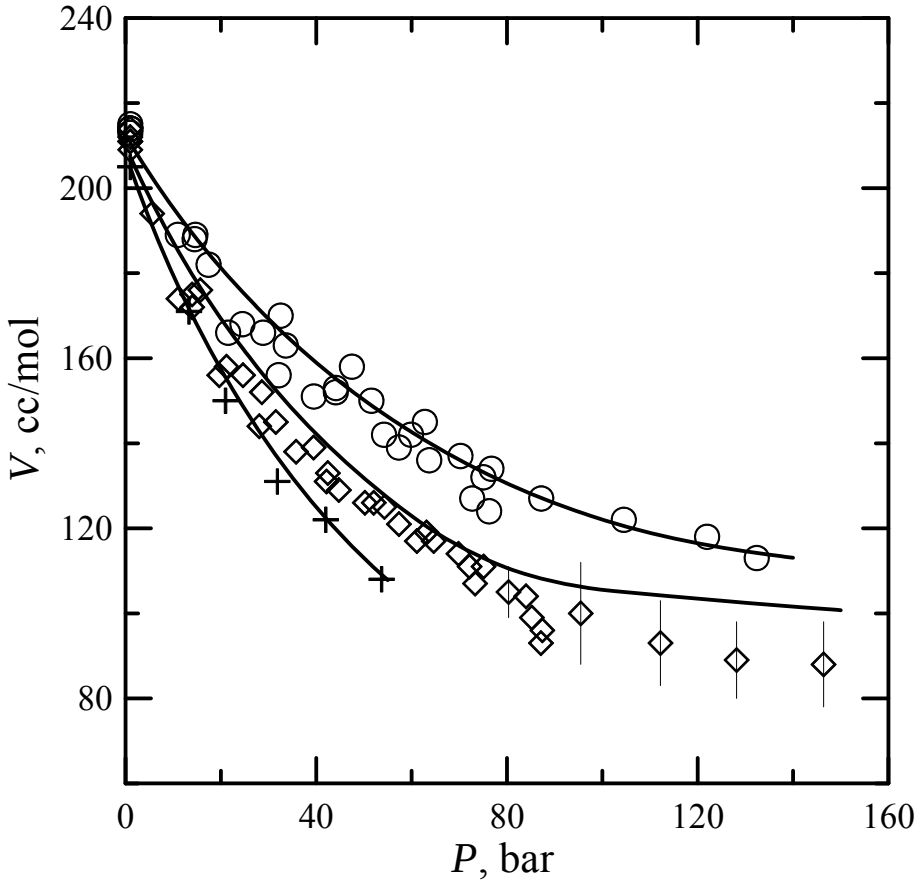


CO_2-[C_8mim][Tf_2N] at 333, 313, and 298 K (from top to bottom). Symbols, experimental data; —, predicted.

Molar volumes of CO_2/IL mixtures



CO_2-[C_4mim][BF_4] at 333, 313, and 298 K (from top to bottom). Symbols, experimental data; —, predicted.



CO_2-[C_4mim][PF_6] at 333, 313, and 298 K (from top to bottom). Symbols, experimental data; —, predicted.

Conclusions

- Heterosegmented SAFT can be used to represent
  - Properties (density) of imidazolium-based ionic liquids from 293.15 to 415 K and up to 650 bar
  - Phase equilibrium of CO_2-IL systems from 283 to 415 K and up to 200 bar
  - Thermodynamic properties can be predicted reliably
    - molar volumes of CO_2/IL mixtures,
    - partial molar volume of CO_2 in CO_2/IL mixtures
    - the partial molar volume of CO_2 at infinite dilution in an IL

Future Work

- A specific ionic liquid
  - Equilibrium modelling
    - Experimental data evaluation
    - New experimental data measurements
    - Model parameters
  - Kinetics
  - CO_2 separation Process simulation
  - Process integration
  - Process evaluation

Thanks all of you for kind attention!