Calculation of Phase Equilibria of Ionic Liquids and CO_2 using GC-NLF EoS

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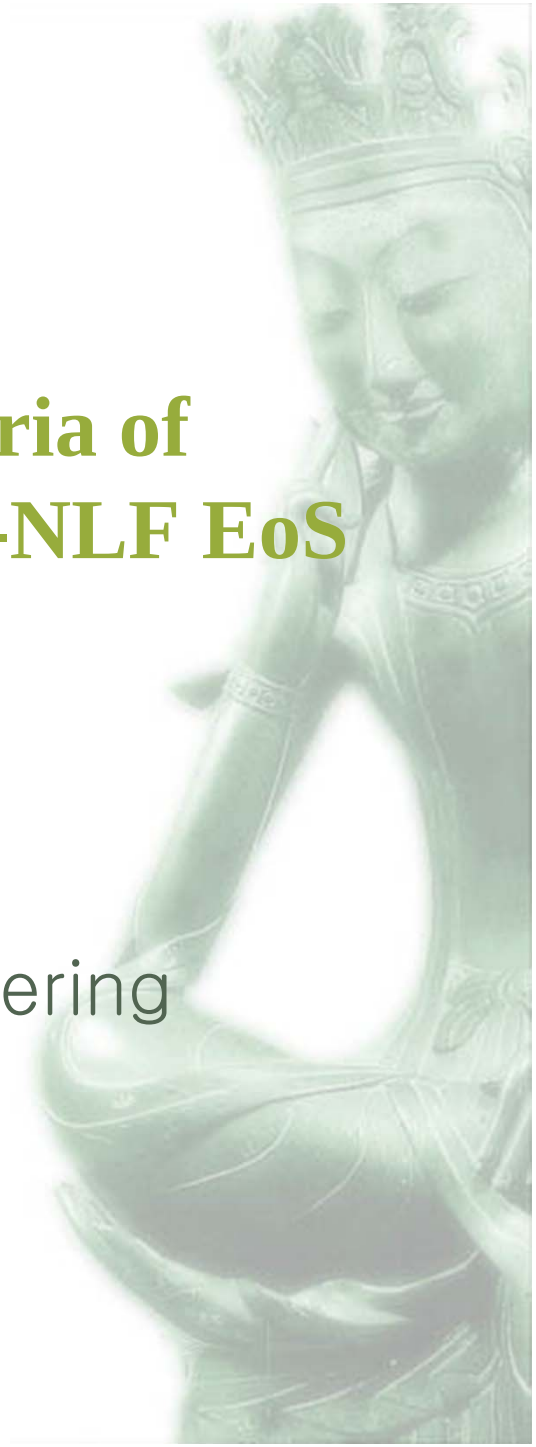
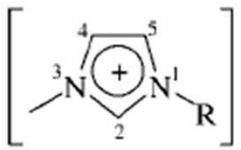


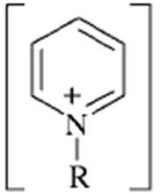
What Are Ionic Liquids?

- Organic salts composed of cations and anions
- Usually liquid state in near room temp.

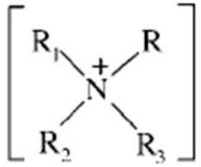
Most commonly used cations:



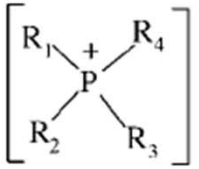
1-alkyl-3-methyl-imidazolium



N-alkyl-pyridinium



Tetraalkyl-ammonium



Tetraalkyl-phosphonium ($R_{1,2,3,4}$ = alkyl)

Some possible anions:

water-insoluble

$[PF_6]^-$

$[(CF_3SO_2)_2N]^-$

$[BR_1R_2R_3R_4]^-$

$[BF_4]^-$

$[CF_3SO_3]^-$

water-soluble

$[CH_3CO_2]^-$

$[CF_3CO_2]^-$, $[NO_3]^-$

Br^-, Cl^-, I^-

$[Al_2Cl_7]^-$, $[AlCl_4]^-$ (decomp.)

Most commonly used alkyl chains:

ethyl octyl
butyl decyl
hexyl

Reprinted from Seddon et al., *Pure Appl. Chem.*, 72, 2275-2287, **2000**

Characteristics of Ionic Liquids

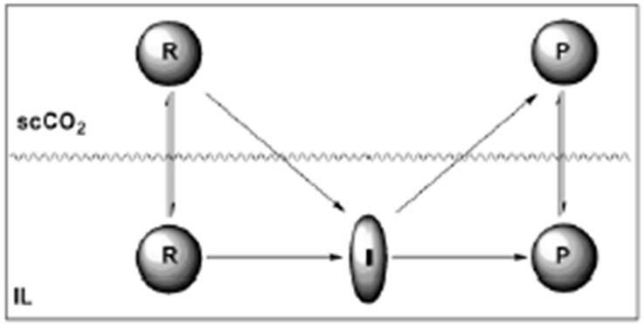
- Negligible vapor pressure
  - No fugitive emissions
- Wide liquidus range : 300 to 400℃
- Good sovents
  - Dissolving both polar and nonpolar species
- Modification of physical and chemical properties
  - The substituents on the cations (alkyl groups)
  - The choice of anion

Applications of Ionic Liquids I

- Reactions
  - Hydrogenation, hydroformylation, isomerization, alkylation, Diels-Alder reaction, etc...
  - Good or better reaction rates and selectivities
- Electrolyte/fuel cells
  - Wide electrochemical window, high conductivity, and a low dielectric constant
- Lubricants
  - High thermal stability and large liquidus range

Applications of Ionic Liquids II

- Combining of Ionic liqu
  - Recovery of organic solu using SCF CO_2
    - No contamination in SCF
  - Continuous catalytic processes using SCR CO_2 as mobile phase
- Liquid-Liquid extraction
- Gas separations
  - The solubility of CO_2 in [bmim][PF_6] is about 0.6-0.7 mole fraction at 100 bar.



Scheme 1 Pictorial illustration of a $scCO_2$/IL biphasic system **R** = reactant, **P** = product, **I** = polar intermediate (*e.g.* carbamate **4**).

Motive

- Studies on ionic liquids
  - Focused on the synthesis of ionic liquids and the application of catalytic reaction as solvents
  - Very few measurements and no modeling of the phase equilibria relating ionic liquids

- This work
  - Modeling of phase equilibria for ionic liquids and carbon dioxide
  - Application of group-contribution NLF theory

NLF-HB Theory

- *Nonrandom Lattice Fluid Hydrogen Bonding Theory*
  - NLF EOS by You et al. [1994 a, b]
  - Expansion to associating system using Veytsman statistics[1990] by Yeom et al. [1999]
  - A normalization of Veytsman statistics by Lee et al. [2001]
  - Application of amino acids using extended Veytsman statistics by Park et al. [2002, 2003]

GC-NLF Theory

- Calculations of parameters for group contribution
  - Connectivity relation : $zq_q^G = r_q^G(z-2) + 2(1-l_q^G)$
  - Group size parameters : $r_i = \sum_{j=1}^{G} v_{ij} r_j^G$
  - Group energy parameters :

$$\varepsilon_{ij} = \sum_{k=1}^{G}\sum_{l=1}^{G} \theta_{ik}^G \theta_{jl}^G \varepsilon_{kl}^G = \frac{\sum_{k=1}^{G}\sum_{l=1}^{G} v_{ik} v_{jl} q_k^G q_l^G \varepsilon_{kl}^G}{\sum_{k=1}^{G}\sum_{l=1}^{G} v_{ik} v_{jl} q_k^G q_l^G}$$

GC-NLF Theory

- The temperature dependency of size and energy parameters proposed by Kehiaian
  - Group size parameters

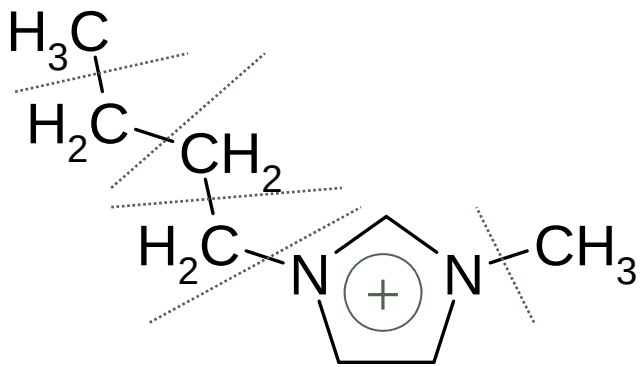
$$r_j^G = w_j^G + h_j^G (T - T_o) + c_j^G \left(T \ln(T_o/T) + T - T_o\right)$$

  - Group energy parameters

$$\varepsilon_{ij}^G = a_{ij}^G + b_{ij}^G (T - T_o) + d_{ij}^G \left(T \ln(T_o/T) + T - T_o\right)$$

Groups of Ionic Liquids

- Cations



- Anions
  - $[BF_4]^-$, $[PF_6]^-$, $[(CF_3SO_2)_2N]^-$

Determination of Group Parameters

- Methyl and ethyl group : from Kang's data
- Ionic liquids : Imidazolium and anions
  - Liquid density
  - Assuming that its vapor pressure is less than 10^{-5} bar.
- Carbon dioxide
  - Using PVT data
  - Conversion of values of You et al. [1994]
- Carbon dioxide and other groups
  - VLE data

Group size parameters

Group	w_a^G	h_b^G	c_c^G	l_i
CH3	2.6293	-3.5423e-4	3.0078e-3	0.5
CH2	1.5525	-7.0335e-5	6.0318e-4	1.0
Imim	5.3383	2.5610e-4	9.0646e-4	1.0
PF6	5.4475	-4.6293e-5	-0.0236	0.0
BF4	3.0153	4.3912e-3	-0.0596	0.0
CO2	3.8322	0.1044e-1	5.2964e-3	0.0

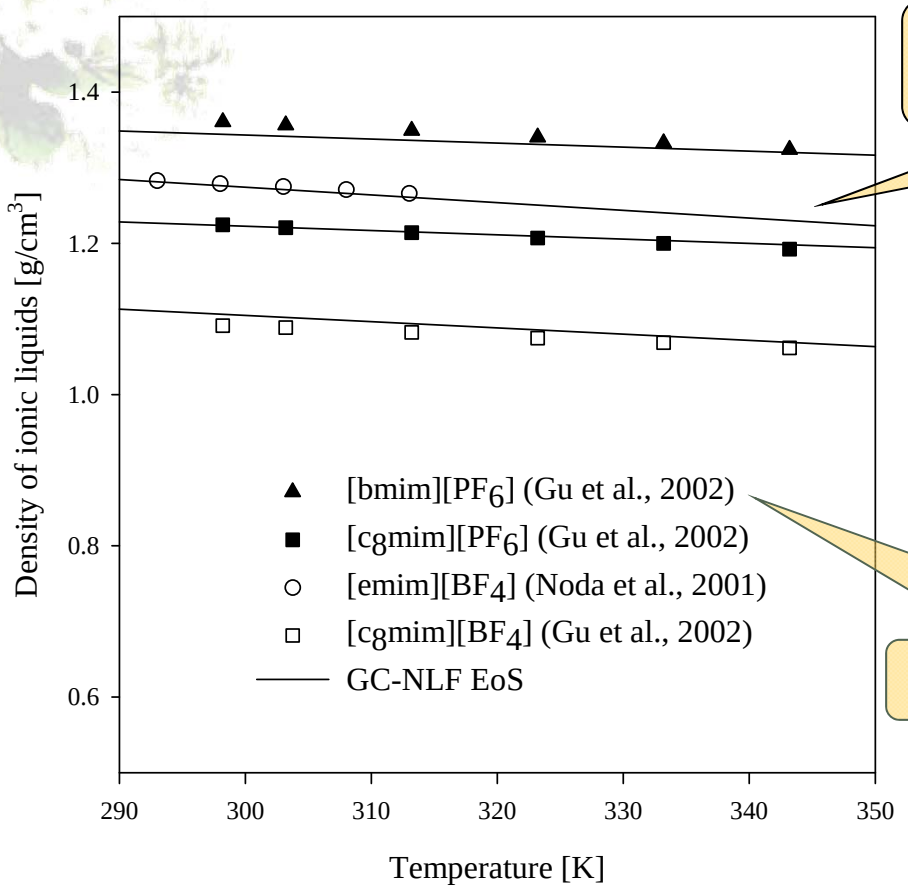
Group interaction parameters I

Group	a_{ij}^{G}	b_{ij}^{G}	d_{ij}^{G}
CH3-CH3	79.8206	0.0152	-0.0762
CH3-CH2	93.9827	0.0159	-0.0168
CH3-imim	142.6601	0.0264	-0.2391
CH3-PF6	69.5207	0.1965	0.5689
CH3-BF4	46.9115	0.2547	0.7097
CH3-CO2	73.5246	-0.0548	-0.0469
CH2- CH2	115.786	0.0546	0.0101
CH2-imim	178.1273	0.1418	0.3003
CH2-PF6	80.8913	0.1688	0.1415
CH2-BF4	55.5056	0.2267	-1.4049

Group interaction parameters II

Group	a_{ij}^{G}	b_{ij}^{G}	d_{ij}^{G}
CH2-CO2	87.5626	0.0226	-0.0721
Imim-Imim	190.0152	0.1664	0.8805
Imim-PF6	246.5117	0.1732	0.1498
Imim-BF4	266.4575	0.2438	0.1316
Imim-CO2	101.3528	-0.0217	-0.2436
PF6-PF6	266.8880	0.1626	-0.0239
PF6-CO2	158.8124	-0.1864	-1.3339
BF4-BF4	282.0467	0.2505	0.1148
BF4-CO2	183.1955	0.1039	-2.2597
CO2-CO2	84.097	-0.0977	-0.4073

Result – Density of Ionic Liquids

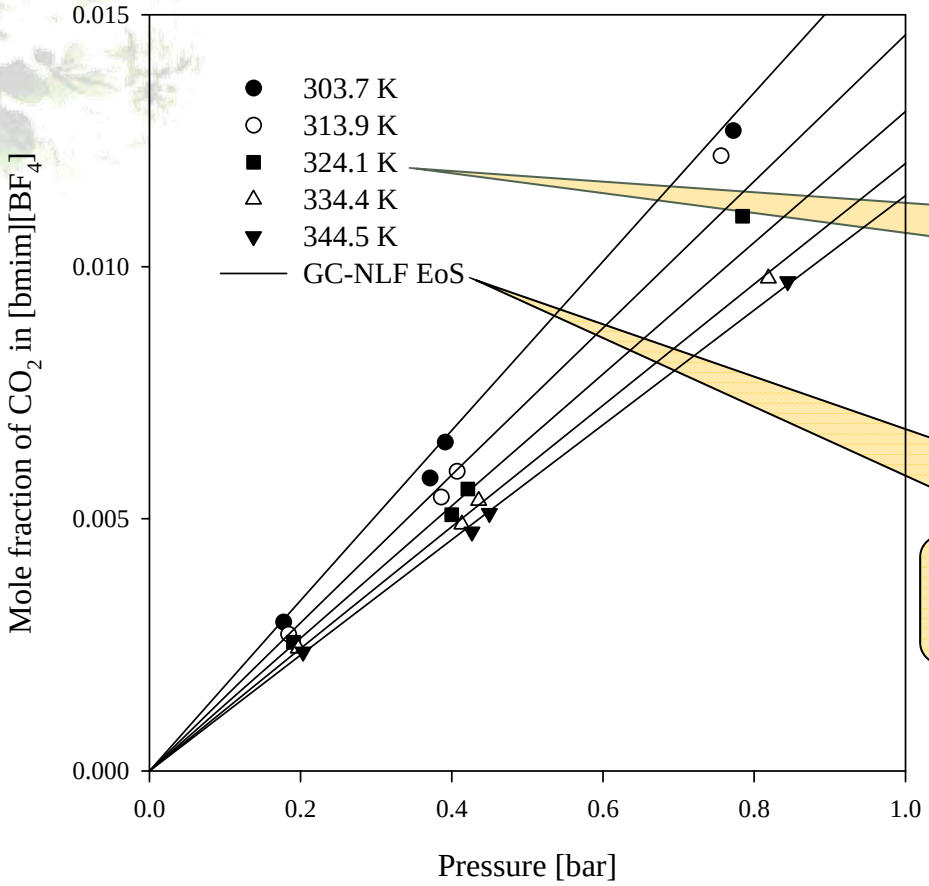


Average deviation with experimental data is ± 0.55 %

Experimental accuracy ± 0.60 %

The comparions of experimental and calculated densities of ionic liquids at various temperatures

Result – Low Pressure for [bmim][BF_4]

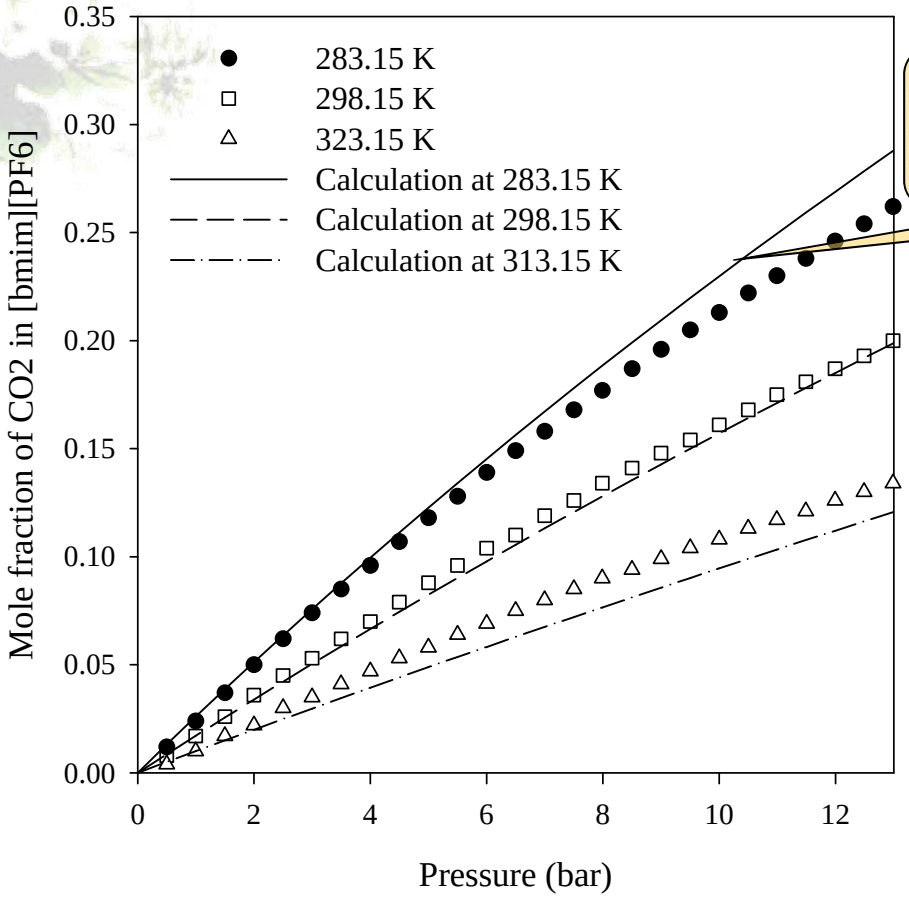


Experimental accuracy ± 1.0 % in mole fraction

Average deviation with experimental data is ± 2.6 %

The solubility of carbon dioxide in [bmim][BF_4] [Husson-Borg et al., 2003]

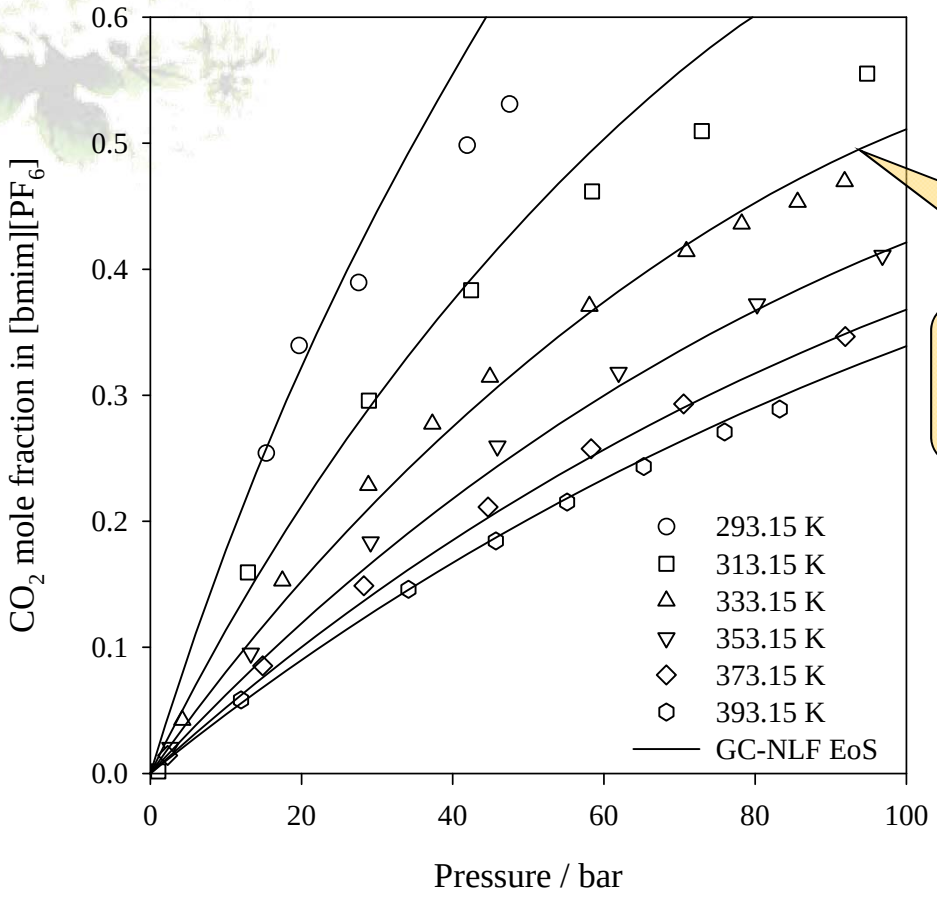
Result – Medium Pressure for [bmim][PF_6]



Average deviation with experimental data is ±0.0079 in mole fraction.

The solubility of carbon dioxide in [bmim][PF_6] [Anthony et al. 2002]

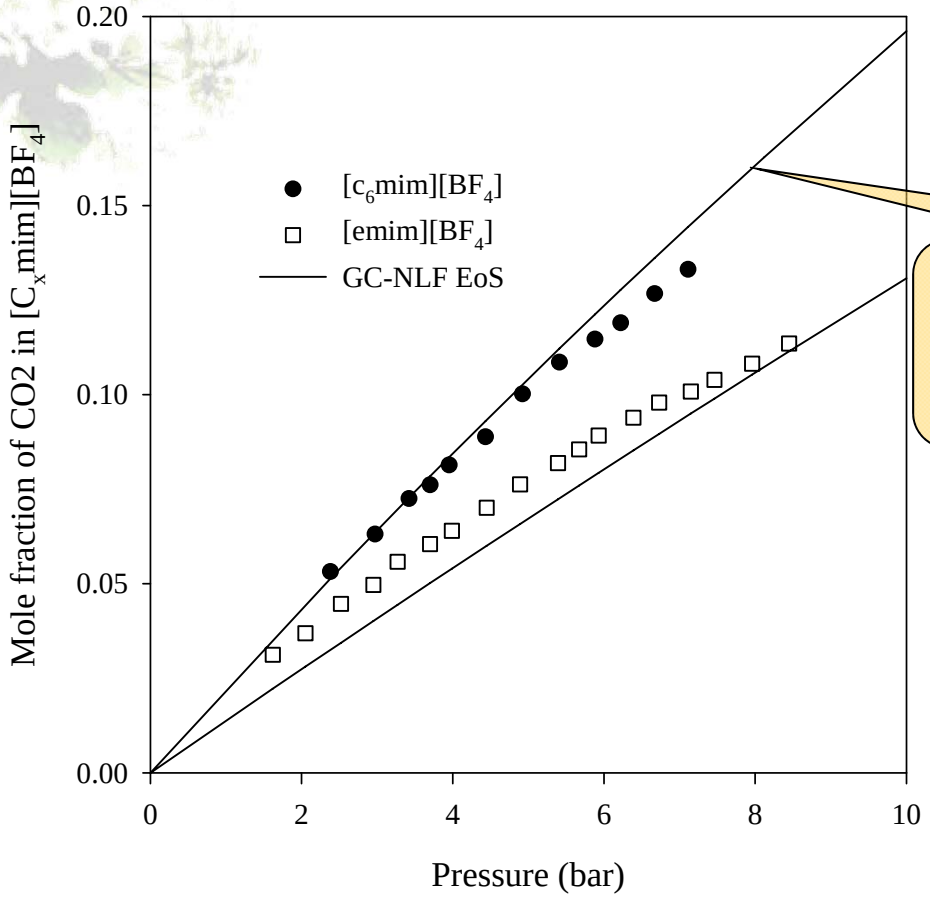
Result – High Pressure for [bmim][PF_6]



Average deviation with experimental data is ±0.017 in mole fraction.

The solubility of carbon dioxide in [bmim][PF_6] [Kamps et al. 2003]

Result – Length of Alkyl Chains



The solubility of CO2 increase with length of alkyl chain substituted on imidazolium ring.

The solubility of carbon dioxide in [$C_x$mim][BF_4] at 298.15 K

Conclusions

- GC-NLF equation of state was found to be effective to predict the phase equilibria of carbon dioxide and ionic liquids.
  - For wide range of pressure and temperature
  - The effect of the length of alkyl chain in imidazolium ring on the solubility of carbon dioxide in ionic liquids