The Solubility of Carbon Dioxide in Ionic Liquids

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Introduction

- Ionic Liquids
  - Organic salts composed of cation and anion
  - Low melting points– near the room temperature
  - Negligible vapor pressure
  - Environmentally favorable solvents

- Motivation
  - Accuracy in equilibrium data is sometimes questioned
  - Few studies have been published on the modeling of equilibria

Experimental Apparatus

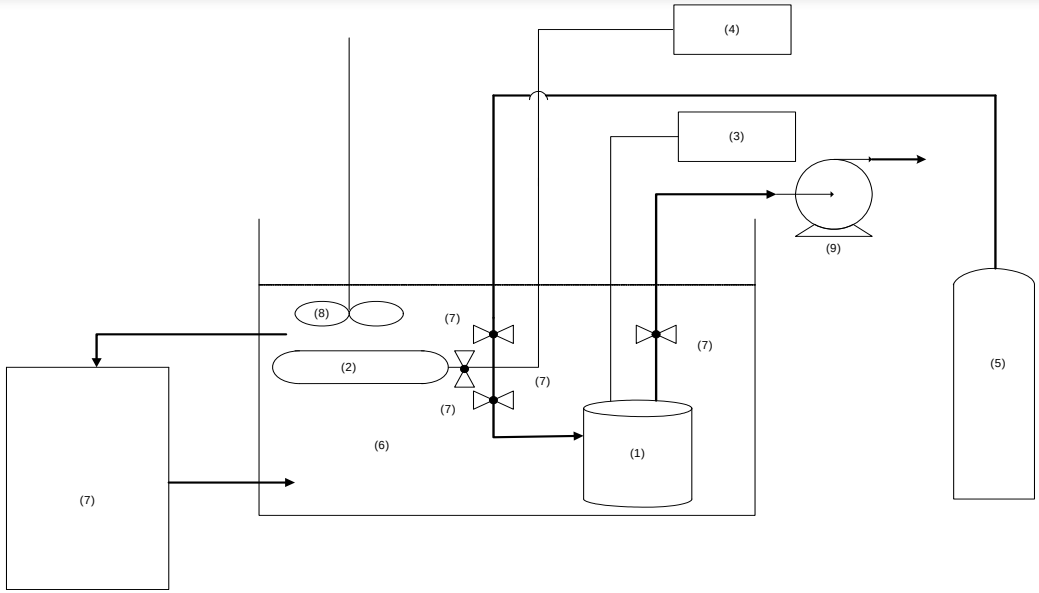

Figure 1. Schematic diagram of experimental apparatus

(1)equilibrium cell (2)CO_2 storage (3)pressure transducer
(4) thermocouple (6)water bath (5) CO_2 bomb (7) valve (8) agitator
(9) vacuum pump (10) circulator

Experimental

- Procedure
  - Solubilites can be measured as a vapor adsorption on solids
    - ILs have negligible vapor pressure
  - Amount in vapor phase is measured using PVT relation
- Accuracy
  - Temperature
    - Accuracy : $\pm$0.02K
  - Pressure
    - Range : 0 ~ 10 bar accuracy : 0.02 bar
  - Solubility
    - Mole fraction : ± 0.002
- Ionic Liquids
  - Amounts of halogen and water less than 30ppm

Model

- Nonrandom Lattice fluid hydrogen-bonding model

  (You et al., Fluid Phase Equilib., 93(1994) 193)

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  - ILs exist as ion-pairs
  - The specific interactions such as hydrogen bond did not exist (Haiware et al. J.Fluor.Chem.105(2002) 2437)

CO_2-ILs system can be modeled with physical interactions

Pure Parameter

- Segment number and interaction energy parameter
  - Parameter determined by using density and vapor pressure
    - For ionic liquids have no detectable vapor pressure

⇒ assumed that $P_v < 10^{-5}$ bar

$$\varepsilon_{ii}/k = \varepsilon_a + \varepsilon_b(T - T_0) + \varepsilon_c\left[T\ln(T_0/T) + (T - T_0)\right]$$

$$r_i = r_a + r_b(T - T_0) + r_c\left[T\ln(T_0/T) + (T - T_0)\right]$$

Table 1. Pure parameters for the NLF EOS

species	ε_a	ε_b	ε_c	r_a	r_b	r_c
[bmim][PF_6]	126.3448	−0.0387	−3.8358	20.0	0	0
[emim][BF_4]	155.0282	−0.2594	0.2810	15.3		
[C_6mim][BF_4]	118.457	0	0	21.0		
CO_2	84.0970	−0.0977	−0.4073	3.8322	0.0047	0.0053

Binary parameter

- Interaction between segments of carbon dioxide and ionic liquids

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}(1-\lambda_{ij})$$

$$\lambda_{ij} = \lambda_a + \lambda_b(T - T_0) + \lambda_c\left[T\ln(T_0/T) + (T - T_0)\right]$$

Table 2. Binary parameters for the NLF EOS

Species	λ_a	λ_b	λ_c
[bmim][PF_6]	0.0785	6.012×10^{-4}	0.0108
[emim][BF_4]	0.059	0	0
[C_6mim][BF_4]	−0.017	0	0

Results

Table 3. Solubility of CO_2 with $[C_6mim][BF_4]$ and $[emim][BF_4]$ at 298.15K

[C6mim][BF4]		[emim][BF4]	
Pressure [bar]	Mole fraction	Pressure [bar]	Mole fraction
2,09	0,042	1,62	0,039
2,70	0,053	2,05	0,047
3,19	0,071	2,52	0,056
3,61	0,076	2,95	0,062
3,95	0,081	3,27	0,070
4,43	0,089	3,70	0,076
4,92	0,100	3,99	0,080
5,41	0,109	4,45	0,088
5,88	0,115	4,89	0,097
6,22	0,119	5,39	0,102
6,67	0,127	5,67	0,107
7,11	0,133	5,93	0,111
8,12	0,144	6,39	0,117
		6,73	0,122
		7,15	0,125
		7,46	0,129
		7,96	0,134
		8,45	0,141

Comparison

Table 4. Comparison of experimental and calculated solubilities

Data ref.	T[K]	P range[bar]	AADx[%]	T[K]	P range[bar]	AADx[%]
[bmim][PF_6]	293.15	15.33-47.52	3.78	313.15	1.05-94.80	2.58
1	333.15	4.24-91.84	1.61	353.15	2.66-96.85	0.94
	373.15	2.29-91.91	0.54	393.15	11.99-83.24	0.34
3	283.15	0.50-12.99	3.00	298.15	0.50-12.99	2.34
	323.15	0.50-12.99	1.43			
2	313.15	15.17-95.67	9.07	323.15	17.38-92.46	11.1
	333.15	15.79-93.01	14.1			
This work	298.15	5.29-6.67	3.02			
[emim][BF_4]	298.15	1.62-8.45	0.54			
[C_8mim][BF_4]	298.15	2.09-812	0.31			

1 Kamps et al., J. Chem. Eng. Data, 48(2003) 746

2 Anthony et al., J. Phys. Chem. B, 106(2003) 7315

3 Blanchard et al., J. Phys. Chem. B, 105(2001) 2437

Discussion

- [Bmim][PF_6]
  - Solubility data of CO_2 is sometimes questioned
  - The measurement method is very accurate and the error is very likely associated with IL sample
  - Using physical model assuming ion pairs like molecular species obtained good agreements with exception of Blanchard et al.
  - The average deviation between data sets was 5.3% AAD in mole fraction
- [C_6mim][BF_4] [Emim][BF_4]
  - At low pressure, small effect of alkyl chain length was observed

[BF_4] System

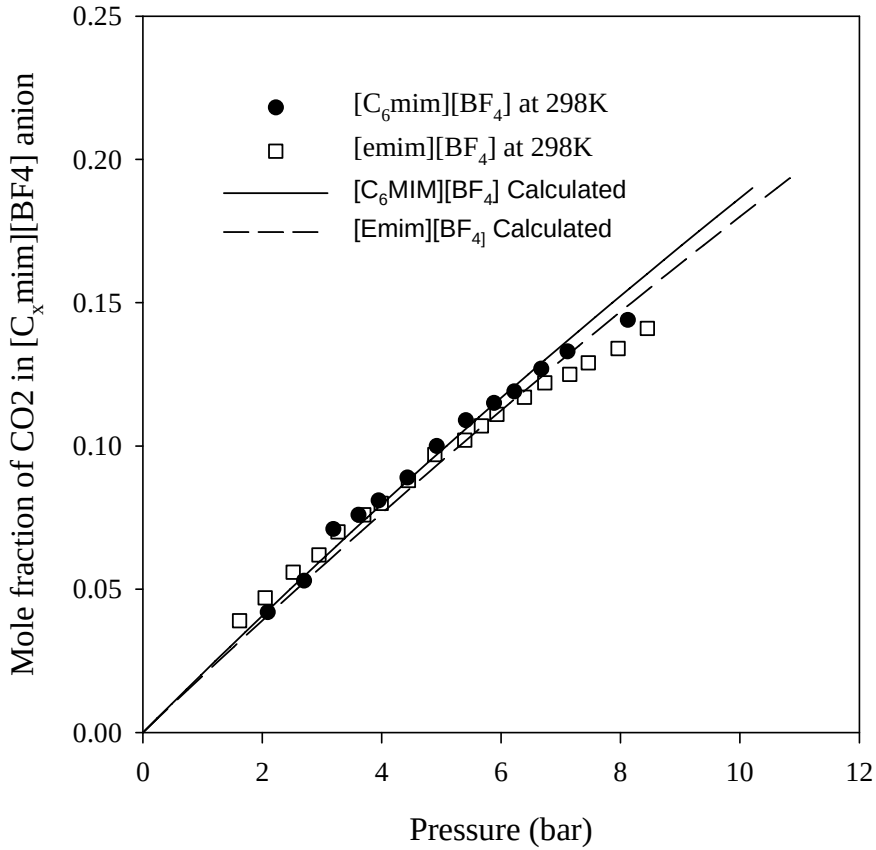

Figure 1. The solubility of carbon dioxide in [Cxmim][BF4]

[PF_6] System

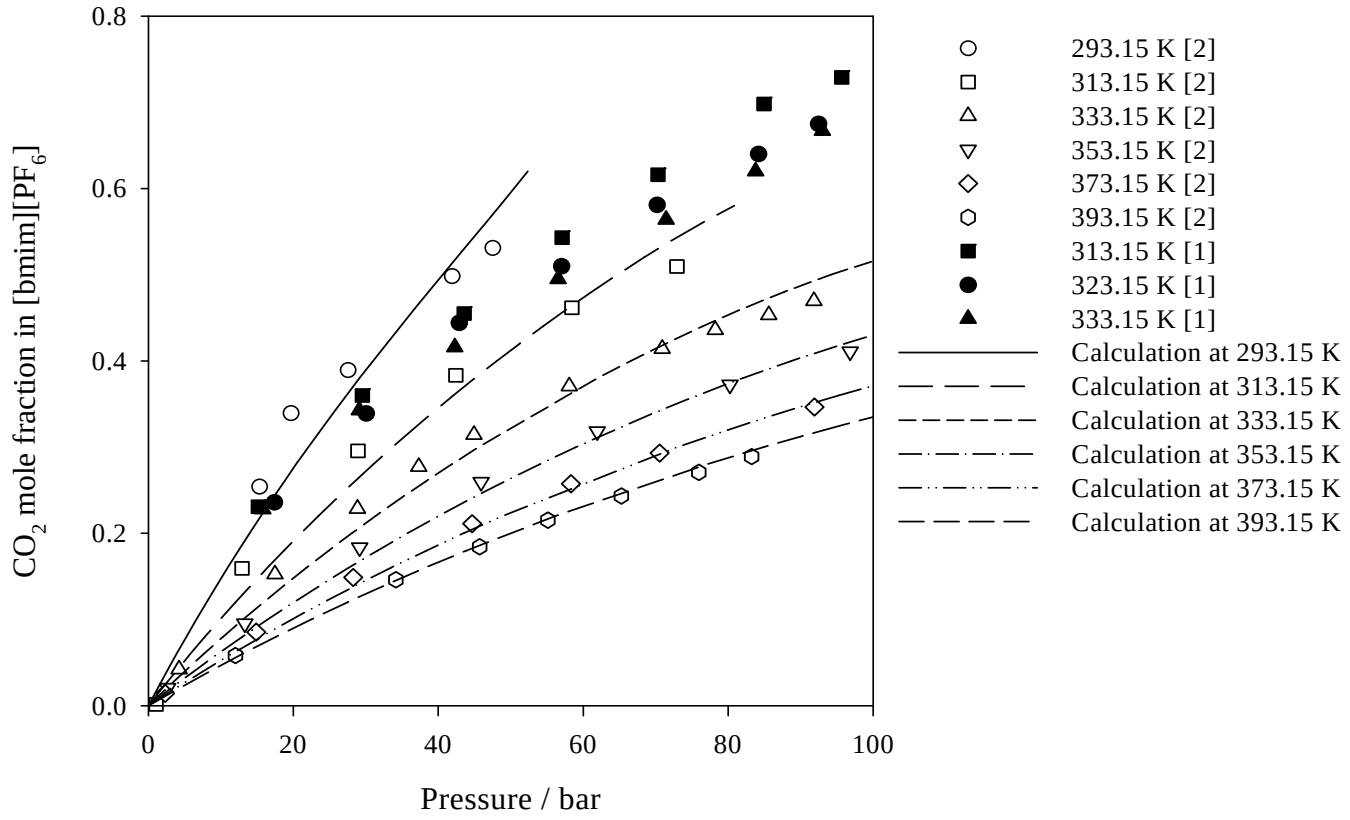

Figure 2. Comparison of the solubility of carbon dioxide in [bmim][PF_6]

[PF_6] System

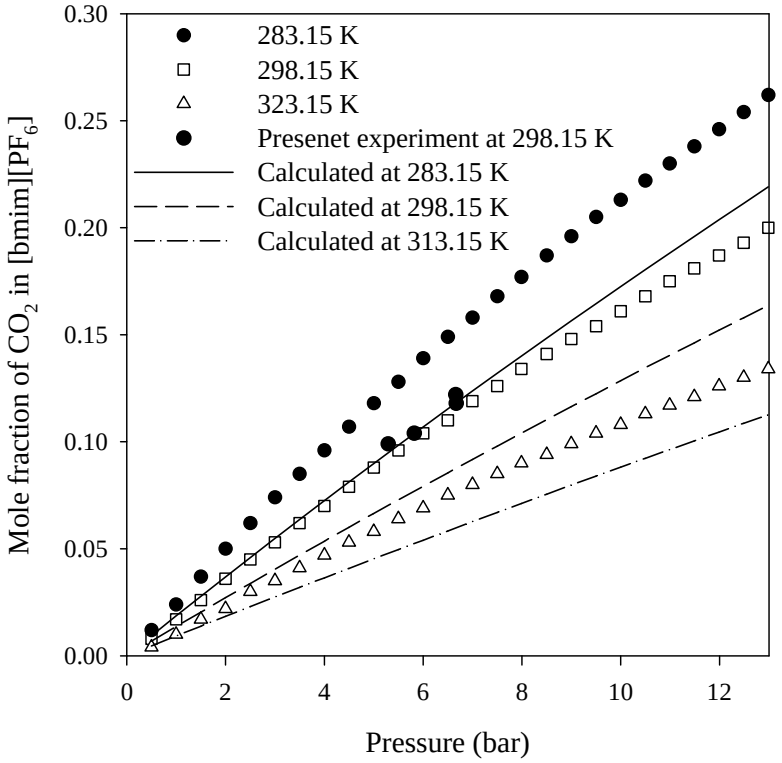

Figure 3. Comparison of the solubility of carbon dioxide in [bmim][PF_6]

Conclusion

- The solubility of CO_2 in ionic liquids were experimentally measured
  - [Bmim][PF_6], [C_6mim][BF_4], [Emim][BF_4]
  - An estimated accuracy is 0.002 mole fraction
- NLF EOS was adopted for phase equilibria of carbon dioxide and ionic liquids
- The calculated results were good with and exception of Blanchard et al.