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# Solubility of $CO_2$ in imidazolium-based tetrafluoroborate ionic liquids

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## Abstract

The solubility of $CO_2$ in imidazolium ionic liquids (ILs), 1-butyl-3-methyl imidazolium tetrafluoroborate ([bmim][$BF_4$]), 1-hexyl-3-methyl imidazolium tetrafluoroborate ([hmim][$BF_4$]) and 1-octyl-3-methyl imidazolium tetrtafluoroborate ([omim][$BF_4$]) was determined at 305–25 K and pressures from 1 to 9 MPa. The influence of chain length of alkyl substituents on the imidazolium cation on the solubility of $CO_2$ was investigated. The differences in solubility with chain length are in the sequence [omim][$BF_4$] > [hmim][$BF_4$] > [bmim][$BF_4$]. The solubility data were correlated by the extended Henry's law, and enthalpy, Gibbs free energy and entropy changes were obtained.

*Keywords:* Imidazolium tetrafluoroborate; $CO_2$; Ionic liquids; Solubility; Correlation

## 1. Introduction

Ionic liquids (ILs) are organic salts that are liquids at ambient conditions. Recently, ILs have attracted much attention due to their unique properties [1], e.g. extremely low vapor pressure, non-flammablility, excellent solvent power for organic and inorganic compounds, and easily modified structure [2–5]. $CO_2$ is extremely soluble in ILs, whereas the reverse is not the case [6]. Investigation of $CO_2$ solubility in ILs can provide fundamental knowledge for developing reactions and separation technologies utilizing the unique properties of ILs.

Kroon et al. [7] and Costantini et al. [8] reported the solubility of $CO_2$ in [bmim][$BF_4$] and [hmim][$BF_4$] at temperatures from 293 to 368 K and pressures from 0.5 to 86 MPa. Blanchard et al. [3] reported the solubility of $CO_2$ in [omim][$BF_4$] at pressures from 0.1 to 9.8 MPa and temperatures from 313 to 333 K. In this paper, the solubility of $CO_2$ in imidazolium ILs, 1-butyl-3-methyl-imidazolium tetrafluoroborate ([bmim][$BF_4$]) and 1-hexyl-3-methyl imidazolium tetrafluoroborate ([hmim][$BF_4$]) and 1-octyl-3-methyl imidazolium tetrtafluoroborate ([omim][$BF_4$]) at temperatures from 305 to 325 K and pressures from 1 to 9 MPa is presented. The influence of chain length of alkyl substituents on the imidazolium ring on the solubility of $CO_2$ in ILs was investigated. Henry's law constants and enthalpy, Gibbs free energy and entropy of solution of $CO_2$ in ILs, are discussed and compared with those reported in the literature [3,7,8].

## 2. Experimental

### 2.1. Synthesis of ILs

The imidazolium ILs ([bmim][$BF_4$], [hmim][$BF_4$] and [omim][$BF_4$]) were synthesized according to the literature [9]. The synthesized ILs were dried under vacuum at 80 °C for 48 h before use. The water content of ILs after drying was less than 200 ppm by Karl–Fisher titration method. Residual chloride in the ILs was 0.002 mol $L^{-1}$ by method in [10]. $CO_2$ was purchased from Beijing Analytical Instrument Factory with a purity of 99.995%.

### 2.2. Solubility measurement

The apparatus used for $CO_2$ solubility measurement consists of a high-pressure stainless steel cell with a volume scale win-

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dow, a gas storage tank, a pressure gauge, a magnetic stirrer and a constant temperature water bath. The measurement of solubility was done by a gravimetric method similar to that described in [11]. An accurate amount of IL was loaded in the high-pressure cell and degassed for 12 h in the constant temperature water bath. Then, a fixed mass amount of $CO_2$ was added to the storage tank. The equilibrium condition was judged when the pressure was unchanged for about 90 min. After equilibrium was reached, the amount of $CO_2$ in the gas storage tank was measured by analytical balance with accuracy of $\pm 0.001$ g and the amount of $CO_2$ in gaseous phase calculated. $CO_2$ dissolved in IL was obtained by difference. Temperature was measured by a thermometer with accuracy of better than $\pm 0.01$ K and pressure by a pressure transducer (FOXBORO/ICT Model 93) with accuracy of $\pm 0.025$ MPa. The estimated uncertainty of the solubility is $\pm 0.8\%$.

## 3. Modelling

Due to the negligible vapor pressure of ILs [3,4], the gaseous phase is assumed to be pure $CO_2$. Applying the vapor–liquid equilibrium condition to $CO_2$ results in the extended Henry's laws equation:

$$K_{\mathrm{H,CO_2}}(T)\exp\left(\frac{V^{\infty}_{\mathrm{CO_2}}P}{RT}\right)a_{\mathrm{CO_2}}(T,m_{\mathrm{CO_2}})=f_{\mathrm{CO_2}}(T,P) \qquad (1)$$

where $K_{\mathrm{H,CO_2}}(T)$ is the Henry's law constant at the vapor pressure of the solvent ($P^{\mathrm{sat}}_{\mathrm{IL}}$) and $V^{\infty}_{\mathrm{CO_2}}$ is the partial molar volume of the gas at infinite dilution.

$a_{\mathrm{CO_2}}(T,m_{\mathrm{CO_2}})$ is the activity of $CO_2$ in the liquid:

$$a_{\mathrm{CO_2}}=\frac{m_{\mathrm{CO_2}}}{m^{\circ}}\gamma^{*}_{\mathrm{CO_2}} \qquad (2)$$

where $m^{\circ}=1\,\mathrm{mol\,kg^{-1}}$ and $\gamma^{*}_{\mathrm{CO_2}}$ is the activity coefficient of $CO_2$.

The fugacity of $CO_2$ at the equilibrium temperature and pressure, $f_{\mathrm{CO_2}}(T,P)$, is calculated from:

$$f_{\mathrm{CO_2}}(T,P)=P\phi_{\mathrm{CO_2}}(T,P) \qquad (3)$$

where $\phi$ is fugacity coefficient, which can be obtained by use of SRK EOS [12].

The Henry's law constant of $CO_2$ can be calculated from the VLE data according to Eq. (4).

$$K_{\mathrm{H,CO_2}}(T)=\lim_{P\to P^{\mathrm{S}}_{\mathrm{IL}}=0}\left[\frac{f_{\mathrm{CO_2}}(T,P)}{m_{\mathrm{CO_2}}/m^{\circ}}\right] \qquad (4)$$

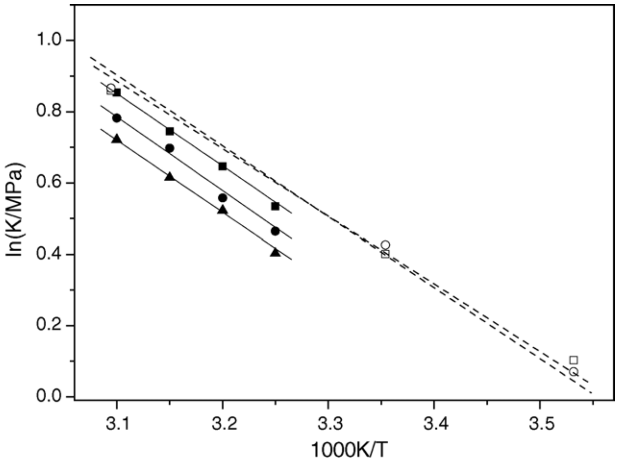

Fig. 1. Effect of temperature on Henry's constant on molalilty scale for $CO_2$ in ILs (■); [bmim][$BF_4$] in this work (●); [hmim][$BF_4$] in this work (▲); [omim][$BF_4$] in this work (□); [bmim][$BF_4$] in literature [30] (○); [bmim][$BF_4$] in literature [15] (–); regression of this work (- - -); regression of literature work.

The thermodynamic properties of the system are related to the Henry's constant as Eqs. (5)–(7).

$$\Delta_{\mathrm{sol}}H=R\left(\frac{\partial\ln(K_{\mathrm{H}}(T,P)/P^{\circ})}{\partial(1/T)}\right)_{P} \qquad (5)$$

$$\Delta_{\mathrm{sol}}G=RT\ln(K_{\mathrm{H}}(T,P)/P^{\circ}) \qquad (6)$$

$$\Delta_{\mathrm{sol}}S=\frac{\Delta_{\mathrm{sol}}H-\Delta_{\mathrm{sol}}G}{T} \qquad (7)$$

## 4. Results and discussions

The solubility of $CO_2$ in [bmim][$BF_4$], [hmim][$BF_4$] and [omim][$BF_4$] was measured at 322.15, 317.45, 312.45 and 307.55 K and pressures from 1 to 9 MPa. The solubility of $CO_2$ in all the studied ILs decreases with increasing temperature and increases with increasing pressure, which is similar to that in common organic solvents. With increasing chain length of alkyl substituents on the imidazolium ring, the solubility increases, but the differences are small.

The Henry's law constants at different temperatures are shown in Table 1. Henry's law constants increase with increasing temperature. At a given temperature, the Henry's constant follows the sequence of [bmim][$BF_4$] > [hmim][$BF_4$] > [omim][$BF_4$].

Table 1
Henry's law constants of $CO_2$ in [bmim][$BF_4$],[hmim][$BF_4$] and [omim][$BF_4$]

| [bmim][$BF_4$] | | | [hmim][$BF_4$] | | | [omim][$BF_4$] | | |
|---|---|---|---|---|---|---|---|---|
| $T$ (K) | $K_{\mathrm{H}}$ (MPa) | S.D.[a] | $T$ (K) | $K_{\mathrm{H}}$ (MPa) | S.D.[a] | $T$ (K) | $K_{\mathrm{H}}$ (MPa) | S.D.[a] |
| 322.15 | 2.35 | 0.033 | 322.15 | 2.19 | 0.035 | 322.15 | 2.06 | 0.024 |
| 317.45 | 2.11 | 0.023 | 317.45 | 2.01 | 0.033 | 317.45 | 1.85 | 0.019 |
| 312.45 | 1.91 | 0.014 | 312.45 | 1.75 | 0.032 | 312.45 | 1.69 | 0.026 |
| 307.55 | 1.71 | 0.014 | 307.55 | 1.59 | 0.018 | 307.55 | 1.50 | 0.012 |

[a] Standard deviation.

Table 2
The standard enthalpy, Gibbs free energy and entropy of solution of $CO_2$ in ionic liquids

| Ionic liquids | $\Delta_{\text{sil}}H^\circ$ (kJ mol$^{-1}$) | $\Delta_{\text{sil}}G^\circ$ (kJ mol$^{-1}$) | $\Delta_{\text{sil}}S^\circ$ (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|
| [bmim][$BF_4$] | −15.8 | 0.94 | −55.8 |
| [hmim][$BF_4$] | −17.3 | 0.72 | −60.0 |
| [omim][$BF_4$] | −18.3 | 0.64 | −63.0 |

In Fig. 1, the logarithm of Henry's law constants are plotted against the inverse temperature. The Henry's constant of $CO_2$ in [bmim][$BF_4$] reported in the literature [13,14] is also presented in Fig. 1. There are no reported Henry's constants for $CO_2$ in [hmim][$BF_4$] and [omim][$BF_4$]. The agreement of Henry's constant for $CO_2$ in [bmim][$BF_4$] between this work and the literature [13,14] is fairly good considering the deviations between [13] and [14].

The standard enthalpy, standard Gibbs free energy and standard entropy are presented in Table 2. The negative enthalpy values show that $CO_2$ exhibits stronger molecular interactions with ILs than with the common organic molecules, e.g. −9.667 kJ mol$^{-1}$ in heptane, −5.556 kJ mol$^{-1}$ in cyclohexane, and −9.337 kJ mol$^{-1}$ in benzene [15]. However, the negative entropy values indicate a higher ordering degree when $CO_2$ dissolves in the ILs. The standard Gibbs free energy shows small positive values.

Comparing the data from this work with those reported in the literature [3,7,8], the solubility tendency are similar although the temperature ranges and pressure are somewhat different. The enthalpy and entropy changes for $CO_2$ dissolving in [bmim][$BF_4$] is −15.8 kJ mol$^{-1}$ and −55.8 J K$^{-1}$ mol$^{-1}$ in this work, which is quite close to the previously reported values of enthalpy and entropy changes $-13.9 \pm 1$ kJ mol$^{-1}$, $-45.6 \pm 3.2$ J K$^{-1}$ mol$^{-1}$ [13] and $-15.9 \pm 1.3$ kJ mol$^{-1}$, $-52.4 \pm 4.3$ J K$^{-1}$ mol$^{-1}$ [14].

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2005.11.023.

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