

Measurement and correlation of vapor-liquid equilibria for a binary system containing 1-butyl-3-methylimidazolium tridecafluorohexylsulfonate and carbon dioxide

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Abstract—Using a high-pressure variable-volume view cell, the vapor-liquid equilibria of the binary system CO₂ and 1-butyl-3-methylimidazolium tridecafluorohexylsulfonate ([BMIM][TDFO]) were determined. The CO₂ mole fraction ranged from 0.104 to 0.952 over a temperature range of 298.2–323.2 K. Both the Peng-Robinson and Soave-Redlich-Kwong equations of state were applied with two different mixing rules to correlate with the experimentally obtained results. Increasing the alkyl chain length in perfluorinated sulfonate anion mother structure from methyl to hexyl markedly increased the CO₂ solubility. To investigate the effect of the number of fluorine atoms in the anion on the phase behavior of imidazolium-based ionic liquid, these experimental results were then compared with those reported in previous experimental studies of 1-alkyl-3-methylimidazolium cations-including ionic liquid+CO₂ binary system.

Keywords: Carbon Dioxide, Phase Equilibrium, 1-Alkyl-3-methylimidazolium Tridecafluorohexyl Sulfonate, VLE

INTRODUCTION

There have been many different tactics proposed to capture CO₂, which is a primary cause of global warming, generated from various sources [1]. While aqueous amine solutions have been considered an appropriate means to trap CO₂ produced by power plants, there is still room for improvement because the amine solutions are very corrosive and extremely expensive to regenerate. Owing to their unique characteristics, ionic liquids (ILs) are considered as an alternative replacement. Not only do ILs have low volatility and high conductivity, but they can also be synthesized task-specifically by simply varying the cations and anions.

In general, the molecular affinity [2] between CO₂ and CO₂-philic functional group-containing ILs plays a significant role in CO₂ solubility in ILs. For example, Brennecke's group [3] reported that the CO₂ solubility in bis(trifluoromethylsulfonyl)imide (Tf₂N) anion-including ILs is higher than that in nitrate (NO₃) anion-containing ILs. The higher CO₂ solubility of Tf₂N-containing ILs may be attributed to the fact that the fluorine atoms in Tf₂N have a strong affinity for CO₂ [4–6].

Although the effects of molecular structure and the alkyl chain length in the anion on CO₂ solubility seem to be far more important than those of the cation counterpart in the ILs, there are some studies on the influence of alkyl chain length in 1-alkyl-3-methylimidazolium cation-containing IL on CO₂ solubility. As an example, Shin and Lee [7] reported that CO₂ solubility monotonically increases as the alkyl chain length in the imidazolium cation increases from ethyl to octyl. One possible explanation for this CO₂ solubility enhancement may be that a longer alkyl chain length increases the dispersion force, resulting in increased interaction with CO₂

[8–10].

As a continuation of our earlier studies [11–13], the effect of the perfluorinated alkyl chain length in the anion on the solubility of CO₂ was investigated. Specifically, the vapor-liquid phase equilibria of the 1-butyl-3-methylimidazolium tridecafluorohexylsulfonate ([BMIM][TDFO])+CO₂ binary system were determined experimentally at temperatures from 298 K to 323 K at interval of 5 K. The phase equilibria of [BMIM][TDFO]+CO₂ binary system were compared with those of 1-butyl-3-methylimidazolium nonafluorobutylsulfonate ([BMIM][NFO]), 1-butyl-3-methylimidazolium trifluoromethylsulfonate ([BMIM][TFO]), and other fluorine atom-containing ILs. The experimental phase equilibria data were then correlated using the Peng-Robinson (PR) as well as Soave-Redlich-Kwong equation of state (SRK-EoS) and two different mixing rules.

EXPERIMENTAL

1. Chemicals

1-Methylimidazole (≥99%), 1-bromobutane (99%), hexane (95%), toluene (99.8%), ethyl acetate and acetone were purchased from Sigma-Aldrich (St. Louis, MO, USA). Potassium tridecafluorohexylsulfonate (98%) was purchased from Wuhan Bright Chemical Co. (Hubei, China). The supercritical fluid chromatography-grade carbon dioxide (99.999%) was purchased from Sebotech Inc. (Daejeon, Korea). All chemicals were used as supplied without further purification.

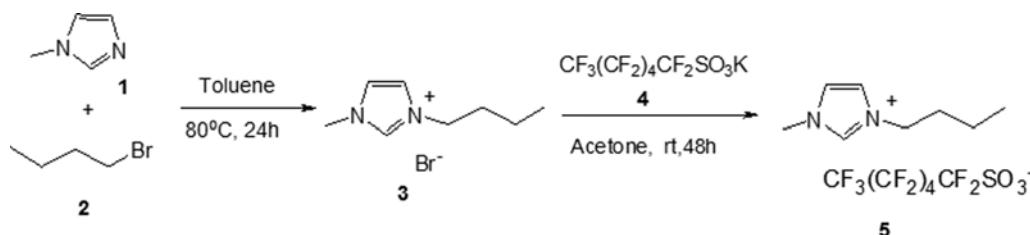
2. Synthesis

The syntheses of 1-butyl-3-methylimidazolium bromide [BMIM][Br] and [BMIM][TDFO] involved a similar method to the one we reported earlier [13]. Briefly, 10 mol% excess of 1-bromo butane was slowly added to a vigorously stirred solution of 1-methylimidazole in toluene at 0 °C. The quaternization reaction was carried out at 80 °C for 24 h, after which the solution was placed in a freezer at 0 °C for 4 h. The toluene was decanted and the remaining vis-

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Scheme 1.

cous oil repeatedly washed with ethyl acetate to yield a yellow oil, which was dried in vacuum to give [BMIM][Br] in approximately 90% yield.

[BMIM][Br] was dissolved in acetone and 10 mol% excess of potassium tridecafluorohexylsulfonate was added. The reactants were reacted at room temperature for 48 h using magnetic stirrer and magnetic bar. The suspension was filtered to remove the precipitated bromide salt and the solvent evaporated under reduced pressure, after which it was dissolved in dichloromethane/chloroform and washed with small volumes of water until no further AgBr precipitated in the aqueous phase on addition of a silver nitrate solution. The organic phase was then washed with water several times to ensure complete removal of the bromide salt. The solvent was removed in vacuum until no visible signs of either the organic solvents or water remained, resulting in a 65% yield of the corresponding IL. The water content of [BMIM][TfO] product was measured as <300 ppm by Karl Fischer moisture analysis. Scheme 1 for this synthesis is given below.

Spectral data for IL: ^1H NMR (CDCl_3 , 400 MHz): δ 0.73–0.77 (t, 3H), 1.15–1.20 (q, 2H), 1.66–1.70 (t, 2H), 3.79 (s, 3H), 4.01–4.05 (t, 2H), 7.32–7.33 (d, 2H), 8.86 (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): 12.74, 19.08, 31.80, 35.92, 49.56, 122.37, 123.70, 136.31. ^{19}F NMR (CDCl_3 , 376 MHz): δ –81.58 to –81.63 (CF_3), –115.05 to –115.13 (CF_2), –121.05 to –121.13 (CF_2), –122.32 (CF_2), –123.30 (CF_2), –126.70 to –126.80 (CF_2); ^{19}F NMR (CDCl_3 , 376 MHz): –81.63 (CF_3), –115.05 to –115.13 (CF_2), –121.05 to –121.13 (CF_2), –122.32 (CF_2), –123.30 (CF_2), –126.70 to –126.80 (CF_2).

3. Experimental Apparatus and Method

The vapor-liquid equilibria (VLE) experiments were carried out using a high-pressure variable-volume view cell described in detail elsewhere [12]. The procedure used is summarized as follows. The accurately measured IL (precision of ± 0.1 mg) was inserted into the view cell with a syringe. The air, any dissolved gas and water from the IL were removed by evacuating the cell for at least several hours at room temperature. Once the upper portion of the view cell became entirely clear, a measured amount of CO_2 was added at constant temperature and pressure by using a syringe pump. The mass of the CO_2 inserted was calculated based on the difference in the volume and density [14] of the gas in the syringe pump before and after the CO_2 was inserted into the cell. The bubble-point pressure was taken to be the pressure at which the first bubbles became visible. Every measurement was repeated at least four times for each condition and an averaged value reported. As suggested by the guidebook [15], the estimated uncertainties in temperature, pressure and calculated mole fraction in liquid were within 0.1 K, 0.047 MPa, and 0.01, respectively.

CORRELATION

ILs have a negligible vapor pressure, so it is quite logical to presume that there is no IL present in the vapor phase. At constant temperature and pressure, the fugacity of CO_2 (1) in the gas phase and that in the IL (2) phase are the same at equilibrium.

$$f_1^v = f_1^{IL} \quad (1)$$

where f_1^v and f_1^{IL} are the fugacity of CO_2 in the vapor phase and in the IL phase, respectively. In this study we decided to use both the PR-EoS and the SRK-EoS for correlation because these two cubic equations are widely used for the correlation of binary mixture experimental data. However, in terms of accuracy, the correlation strongly depends on the characteristics of the system investigated [16]. In addition, the choice of mixing rule is crucial to obtain high accuracy. We chose the van der Waals (VDW) mixing rule because it is simple and quite straightforward compared with other rigorous mixing rules. To investigate the effect of choice of different mixing rules on the correlation, the Mathias-Klotz-Prausnitz (MKP) mixing rule was also chosen for correlation because the MKP mixing rule is known not to suffer from the Michelsen-Kistenmacher effect [17]. The VDW mixing rules are expressed in Eqs. (2) and (3):

$$a_m = \sum_{i=1} \sum_{j=1} x_i x_j \sqrt{a_i a_j} (1 - k_{ij}^{VDW}) \quad (2)$$

$$b_m = \sum_{i=1} \sum_{j=1} x_i x_j \frac{b_i + b_j}{2} (1 - l_{ij}^{VDW}) \quad (3)$$

The parameters in Eqs. (2) and (3), k_{ij}^{VDW} and l_{ij}^{VDW} , are the binary interaction parameters in the VDW mixing rule. The MKP mixing rules are expressed in Eqs. (4) and (5).

$$a_m = \sum_{i=1} \sum_{j=1} x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \left(\sum_{i=1} x_i \left(\sum_{j=1} x_j (\sqrt{a_i a_j} \lambda_{ij})^{1/3} \right)^3 \right) \quad (4)$$

$$b_m = \sum_{i=1} \sum_{j=1} x_i x_j \frac{b_i + b_j}{2} (1 - l_{ij}) \quad (5)$$

The parameters in Eqs. (4) and (5), k_{ij} , l_{ij} , and λ_{ij} are the binary interaction parameters in the MKP mixing rule.

The critical properties of CO_2 are available in the literature [14] and those of [BMIM][TfO] were calculated using those reported earlier [18] before use in correlation. The experimentally obtained bubble-pressure data for the CO_2 + [BMIM][TfO] binary system were correlated with the PR-EoS at each temperature. The software package PE 2000 [19] was used to approximate the VLE. The objective function (OF) defined in Eq. (6) was used to optimize binary interaction parameters in terms of the average absolute deviation (AAD) for the liquid mole fraction.

Table 1. Physical properties of chemicals

| | Formula | Mw [g/mol] | T_c /K | P_c /MPa | ω | Ref. |
|-----------------|-----------------------------|------------|----------|------------|----------|-------------------------|
| [BMIM][TDfO] | $C_{14}H_{15}N_2O_3F_{13}S$ | 538.3 | 1040.4 | 1.35 | 0.6024 | This study ^a |
| CO ₂ | CO ₂ | 44.01 | 304.2 | 7.38 | 0.239 | [14] |

^aThe critical properties of ionic liquids are estimated by using a method in the literature [18]

$$OF = \frac{1}{N} \sum_{i=1}^N \frac{|x_i^{exp} - x_i^{cal}|}{x_i^{exp}} \cdot 100 \quad (6)$$

where x_i^{cal} is the calculated mole fraction in the liquid phase, x_i^{exp} is the experimentally measured mole fraction in the liquid phase for a given temperature, and N is the number of data points.

RESULTS AND DISCUSSION

1. Phase Equilibria of CO₂+ [BMIM][TDfO] Binary Mixture

The bubble point pressures for [BMIM][TDfO] and CO₂ binary system were measured over the temperature range 298.2–323.2 K at intervals of 5 K, as shown in Table 2. Fig. 1 shows the bubble-point pressure versus CO₂ mole fraction in liquid phase, along with the correlation results obtained by applying the SRK-EoS and MKP mixing rules for comparison. The correlation results and the experimental data are, in general, in good agreement. Overall, as the temperature increases, the pressure must also be increased so as to dissolve a given amount of CO₂ in [BMIM][TDfO]. As expected, the solubility of CO₂ in [BMIM][TDfO] increases with pressure at constant temperature. For example, at 308.2 K CO₂ solubility was increased from 0.202 at 2.73 MPa to 0.597 at 5.64 MPa.

2. Effect on CO₂ Solubility of the Alkyl Chain Length in the Perfluorinated Anion

As mentioned earlier, the effect of alkyl chain length in the cation on the CO₂ solubility is relatively well understood. Specifically, Shin and Lee [7] reported the solubility of CO₂ in 1-alkyl-3-methylimidazolium trifluoromethanesulfonate, [AMIM][TfO], suggest-

ing that as the alkyl chain length in the imidazolium cation was systematically increased, the CO₂ solubility was correspondingly

Table 2. Experimentally determined bubble-point pressures for CO₂ (1)+[BMIM][TDfO] (2)

| T [K] | x_1 | P [MPa] |
|-------|--------|---------|
| 298.2 | 0.1043 | 1.91 |
| | 0.2024 | 2.12 |
| | 0.2949 | 2.30 |
| | 0.4041 | 2.89 |
| | 0.5039 | 4.08 |
| | 0.5971 | 4.97 |
| | 0.7001 | 5.95 |
| | 0.8010 | 7.03 |
| | 0.9008 | 8.52 |
| | 0.9516 | 10.75 |
| 303.2 | 0.1043 | 2.20 |
| | 0.2024 | 2.42 |
| | 0.2949 | 2.761 |
| | 0.4041 | 3.38 |
| | 0.5039 | 4.46 |
| | 0.5971 | 5.32 |
| | 0.7001 | 6.42 |
| | 0.8010 | 7.48 |
| | 0.9008 | 8.99 |
| | 0.9516 | 9.76 |
| 308.2 | 0.1043 | 2.53 |
| | 0.2024 | 2.73 |
| | 0.2949 | 3.00 |
| | 0.4041 | 3.77 |
| | 0.5039 | 4.83 |
| | 0.5971 | 5.64 |
| | 0.7001 | 6.74 |
| | 0.8010 | 7.81 |
| | 0.9008 | 9.54 |
| | 0.9516 | 11.79 |
| 313.2 | 0.1043 | 2.83 |
| | 0.2024 | 3.13 |
| | 0.2949 | 3.29 |
| | 0.4041 | 4.28 |
| | 0.5039 | 5.38 |
| | 0.5971 | 6.23 |
| | 0.7001 | 7.27 |
| | 0.8010 | 8.39 |
| | 0.9008 | 10.10 |
| | 0.9516 | 11.79 |

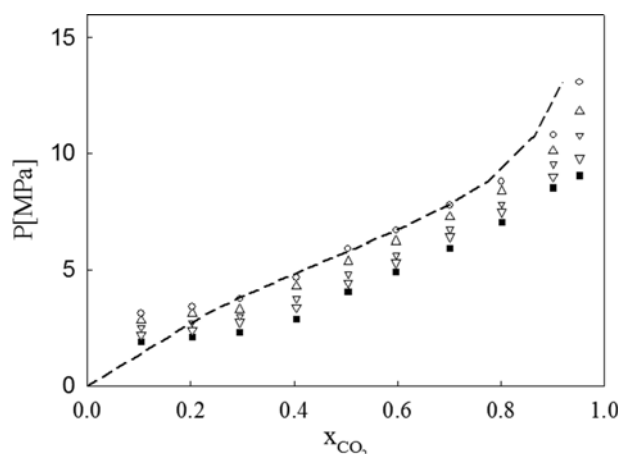


Fig. 1. P- x_1 diagram for the CO₂ (1)+[BMIM][TDfO] (2) system at different temperatures (■: 298.2 K; △: 303.2 K; ▽: 308.2 K; ◇: 313.2 K; ○: 318.2 K; the dotted black line represents the correlation results for VLE at 318.2 K).

Table 2. Continued

| T [K] | x_1 | P [MPa] |
|-------|--------|---------|
| 318.2 | 0.1043 | 3.12 |
| | 0.2024 | 3.42 |
| | 0.2949 | 3.77 |
| | 0.4041 | 4.67 |
| | 0.5039 | 5.91 |
| | 0.5971 | 6.69 |
| | 0.7001 | 7.76 |
| | 0.8010 | 8.79 |
| | 0.9008 | 10.79 |
| | 0.9516 | 13.13 |
| 323.2 | 0.1043 | 3.29 |
| | 0.2024 | 3.55 |
| | 0.2949 | 3.85 |
| | 0.4041 | 4.92 |
| | 0.5039 | 6.33 |
| | 0.5971 | 7.10 |
| | 0.7001 | 8.19 |
| | 0.8010 | 9.26 |
| | 0.9008 | 11.20 |
| | 0.9516 | 14.11 |

increased. A similar trend was observed for the perfluorinated anion-containing ILs, such as the [BMIM][TfO]₂+CO₂ binary mixture. The literature results show that the pressure required to dissolve 0.5367 CO₂ mole fraction in [BMIM][TfO] at 303.85 K is 4.9 MPa [7], and that to dissolve 0.531 CO₂ mole fraction in [BMIM][NfO] at 303.2 K is 4.45 MPa [13]. As can be seen in Table 2, at 303.2 K and 4.46 MPa, the CO₂ solubility in [BMIM][TfO] is only 0.5039.

So this result may suggest that as the alkyl chain length in the perfluorinated anion increased from butyl to hexane the CO₂ solubility is not subsequently increased. As previously reported [13], in the case of fluorine atom-containing IL+CO₂ binary systems, as long as the anion contains the S=O functional group and the number of fluorine atoms in the anion is greater than a certain number, the CO₂ solubility in that type of IL is much higher than its solubility in other types of ILs.

3. Effect of Mixing Rule on the Correlation

The correlation between the experimental VLE data and the PR-EoS with VDW mixing rules was established and the binary interaction parameters determined at three different temperatures, as shown in Table 3. The PR-EoS has been proven to combine simplicity and accuracy required for the prediction and correlation [20]. In addition to the PR-EoS, SRK-EoS was also applied in the correlation by applying both VDW and MKP mixing rules. The AAD based on the PR-EoS and VDW mixing rules between experimental and correlated liquid-phase composition at 298.2, 308.2, and 318.2 K corresponded to 5.5, 4.8, and 3.2%, respectively, as can be seen in Table 3. The AAD based on the SRK-EoS and VDW mixing rule similarly corresponded. As long as the VDW mixing rule was applied in the correlation, the choice of EoS was insignificant in the binary system comprised of perfluorinated alkyl chains in the anion moiety-including IL and CO₂. While correlation outcomes based on the MKP mixing rule and PR-EoS resulted in unimproved results, those based on MKP mixing rule and SRK-EoS yielded much better correlation results. For example, the AAD is as small as 2.9% with the MKP mixing rule and SRK-EoS at 318 K.

CONCLUSIONS

This study reports the vapor-liquid phase equilibria of the CO₂+

Table 3. The binary interaction parameters for CO₂ (1)+[BMIM][TfO] (2) system

| EOS | Mixing rule | Parameter | 298 K | 308 K | 318 K |
|-----|-------------|----------------|---------|---------|---------|
| PR | VDW | k_{12}^{VDW} | 0.0633 | 0.0502 | 0.0317 |
| | | l_{12}^{VDW} | -0.0118 | -0.0194 | -0.0325 |
| | | AAD (%) | 5.5 | 4.8 | 3.2 |
| | MKP | k_{12} | 0.1132 | 0.0355 | 0.0423 |
| | | l_{12} | -0.0007 | -0.0237 | -0.0294 |
| | | l_{12} | -0.1016 | -0.0256 | 0.0184 |
| | | AAD (%) | 13.2 | 5.4 | 3.2 |
| | VDW | k_{12}^{VDW} | 0.0419 | 0.0624 | 0.0420 |
| | | l_{12}^{VDW} | -0.0293 | -0.0150 | -0.0330 |
| | | AAD (%) | 6.1 | 5.0 | 2.9 |
| SRK | MKP | k_{12} | 0.0633 | 0.0621 | 0.0324 |
| | | l_{12} | -0.0127 | -0.0189 | -0.0357 |
| | | l_{12} | -0.0315 | 0.0032 | -0.0169 |
| | | AAD (%) | 5.2 | 4.4 | 2.9 |

AAD (%): Average absolute deviation, which is defined as,

$$\text{AAD (\%)} = \frac{1}{N} \sum_{i=1}^N \frac{|x_i^{\text{exp}} - x_i^{\text{cal}}|}{x_i^{\text{exp}}} \times 100$$

where N is the number of data and 10 in this study

[BMIM][TfO] binary system using a high-pressure variable-volume view cell. Compared with other ILs containing a perfluorinated alkyl chain-including anion and CO₂ binary system, CO₂ solubility tended to increase as the alkyl chain length increased from methyl to butyl. However, when the alkyl chain length in the perfluorinated alkyl anion increased from butyl to hexyl, the effect of alkyl chain length produced an insignificant increase. In general, the correlation results applying the Peng-Robinson EoS along with VDW mixing rules showed good correlation with the experimental data. However, the Soave-Redlich-Kwong EoS along with MKP mixing rules yielded a better correlation with the experimental data. Therefore, use of the SRK-EoS with the MKP mixing rule would be a better correlation method for the perfluorinated anion-containing IL+CO₂ binary system.

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