INVESTIGATION OF CO_2 AND METHANOL SOLUBILITY AT HIGH PRESSURE AND TEMPERATURE IN THE IONIC LIQUID [EMIM][BF_4] EMPLOYED DURING METHANOL SYNTHESIS IN A MEMBRANE-CONTACTOR REACTOR

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ABSTRACT: In this paper, the solubility properties of the ionic liquid (IL), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]) were studied using a high-pressure, high-temperature set-up employing the pressure-drop technique. [EMIM][BF_4] was selected for study because it is used as the sweep liquid in a membrane reactor (MR)-based methanol synthesis (MR-MeS) process recently proposed and studied by our group. The MR-MeS studies indicated high methanol (MeOH) solubilities in the IL under typical MeS reaction conditions, which then motivated this study to measure such solubilities directly under non-reactive conditions to validate the findings of the MR study. In addition, during the MR-MeS studies a concern existed about the solubility of CO_2 in [EMIM][BF_4], since it is a reactant in the MeS process and its dissolution in the sweep liquid would be detrimental for reactor performance. Studies, therefore, were also

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carried out to investigate the solubility of CO_2, in addition to MeOH, in the IL. Our investigation indicates that though CO_2 solubilities in the [EMIM][BF_4] are high at room temperature, they become negligible at the typical MeS operating conditions (i.e., temperatures above 200 ºC).

KEYWORDS: Solubility, Carbon dioxide, Membrane reactor, Ionic liquid, [EMIM][BF_4]

1. INTRODUCTION

Ionic liquids (ILs) have been studied extensively during the last decade or so due to their unique characteristics such as high thermal stability, high electrical conductivity, very low vapor pressure, and good solvation properties[1-4]. These favorable properties make ILs good potential 'green' alternatives to conventional organic solvents. One of the promising applications of the ILs in the chemical industry is to use them as absorption media for gas separations. This has, then, spurred significant interest in studying the solubility of various gases into ILs in order to optimally design such absorption processes.

Recently, we used an IL, specifically, 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]), in our studies of methanol synthesis (MeS) in a high pressure and temperature membrane reactor (MR) system [5]. In our research, we employed a packed-bed MR set-up that operates in a pressure range of 20-30 bar and a temperature range of 200-240 ºC. The reactor contains a high-temperature ceramic membrane (further details about the experimental set-up and conditions utilized can be found elsewhere [5, 6]). A commercial MeS catalyst is placed in between the membrane and the reactor wall (the membrane shell-side) while the IL flows inside the membrane tube. During reactor operation, syngas (CO_2, CO, H_2) is continuously fed into the MR shell-side and in the presence of the catalyst reacts to produce methanol (MeOH).

The role of the flowing IL is as an absorption-medium to remove the MeOH from the reactor and, thus, help overcome equilibrium limitations and to increase the MeOH production rate. Using this reactor concept, carbon conversions significantly higher than equilibrium are attained. In our studies we have also employed a petroleum-derived solvent, namely tetraethylene glycol dimethyl ether (TGDE), as a sweep liquid. In addition to offering greater improvements in conversion over the TGDE, the IL offers other advantages over the petroleum-based solvent relevant to the proposed MR-MeS process that include: (i) its extremely low vapor pressure, which eliminates potential loss of solvent and substantially simplifies downstream separations; (2) its broad operating temperature range, and high decomposition temperature, which permit the operation of the MR for a broader region of MeS conditions.

The global reactions thought to take place during MeS are shown below:

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^o = -90.6 \text{ (kJ/mol)} \qquad \text{(R1)}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^o = -49.5 \text{ (kJ/mol} \qquad \text{(R2)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^o = -41.2 \text{ (kJ/mol)} \qquad \text{(R3)}$$

In choosing [EMIM][BF_4] as the sweep solvent, the initial expectation was that MeOH would have a good solubility in it while other permanent gases like H_2 and CO would not [7]. The main concern with the choice was that CO_2 may also have a high solubility in the IL, and since it serves as a reactant for MeS this would not be a good thing. In fact, the [EMIM][BF_4] was specifically selected

among other ILs because of its (1) relative high decomposition temperature (447 ºC) [8], and (2) its reported relatively lower CO_2 solubility when compared to other imidazolium-based ILs [7].

While CO_2 is a reactant for MeS and high solubility in the IL is not desirable for our reactor, CO_2 is also a key greenhouse gas and ILs have been studied in recent years as absorption media for its capture to reduce its emissions. Extensive research efforts have, therefore, been undertaken in recent years and a good volume of data on CO_2 solubility in ILs at or near ambient temperature and pressure conditions are presently available [7, 9-11]. For the specific IL of interest in this study, [EMIM][BF_4], several studies have appeared on its CO_2 solubility [9, 11-13]. All have, however, been carried out at low temperature (298.15-353.15 K) and pressure conditions, and the only experimental study, we are aware of, performed at high pressure (~15 MPa) was carried out at room temperature [10]. Therefore, past technical literature data are of no direct relevance for the use of [EMIM][BF_4] in the high pressure and temperature MeS reactive application. Such data are presented for the first time in this paper.

In the remainder of the paper, we first describe the experimental set-up and procedures that were followed. We then present the solubility data of CO_2 and MeOH in [EMIM][BF_4] at conditions relevant to the MeS reaction. For the CO_2, we compare our experimental data with the available data from the literature at room temperature. For the IL, we compare MeOH solubility in the [EMIM][BF_4] with solubility data under similar conditions with the petroleum-based TGDE solvent. We also present, here for the first time, experimental data using the Nuclear Magnetic Resonance (NMR) technique that validate the thermochemical stability of the [EMIM][BF_4] during experiments with the MR- MeS set-up.

2. EXPERIMENTAL SECTION

2.1. MATERIALS

Ultra-high purity (UHP) CO_2 (99.999% pure) was purchased from Praxair. UHP 5.0 Grade Nitrogen (N_2) was purchased from the Airgas Company. The [EMIM][BF_4], with a reported purity of ≥98% was purchased from Zhejiang Arts & Crafts Imp. & Exp. Company, China. Upon being received in our Lab, the purity of the IL was confirmed via 400 MHz ^{1}H and 375 MHz ^{19}F NMR analysis (the results can be found in the Supplementary materials section). HPLC-grade MeOH with purity of ≥99.9% was purchased from Sigma Aldrich (a summary of all the chemicals utilized in this study, their supplier, purity, etc. is presented in the Supplementary Materials section).

2.2. EXPERIMENTAL SET-UP

A schematic of the experimental apparatus used in the equilibrium solubility measurements is shown in Figure 1. The main part of the set-up consists of two cells, namely a reference cell and a sample cell. The reference cell, with an inner volume of 250 mL, was purchased from the Anhui Kemi Machinery Technology Co., Ltd., China. Its maximum working temperature and pressure are 300 °C and 200 bar, respectively. A micro-stirred reactor (Series 4590) from the Parr Instrument Company serves as the sample cell (with an inner volume of 50 mL) connected to the reference cell. Its maximum operating temperature and pressure are 275 °C and 345 bar, respectively. Both cells are made of stainless steel, to avoid any potential reaction with corrosive substances. The cells are heated by individual matching metal heating jackets to accurately control the inner temperature for each cell. The pressure in each cell was measured by high accuracy digital pressure gauges (Omega Engineering, DPG4000-1k USA) with data-logging capability. The pressure range of the gauges is 0-1000 psi, with a resolution of 0.1 psi and accuracy of 0.05% full

scale. The sample cell is equipped with a stirrer connected to an overhead agitator controlled by a Parr 4843 controller for the purpose of accelerating the attainment of vapor-liquid phase equilibrium during the measurement of the solubilities.

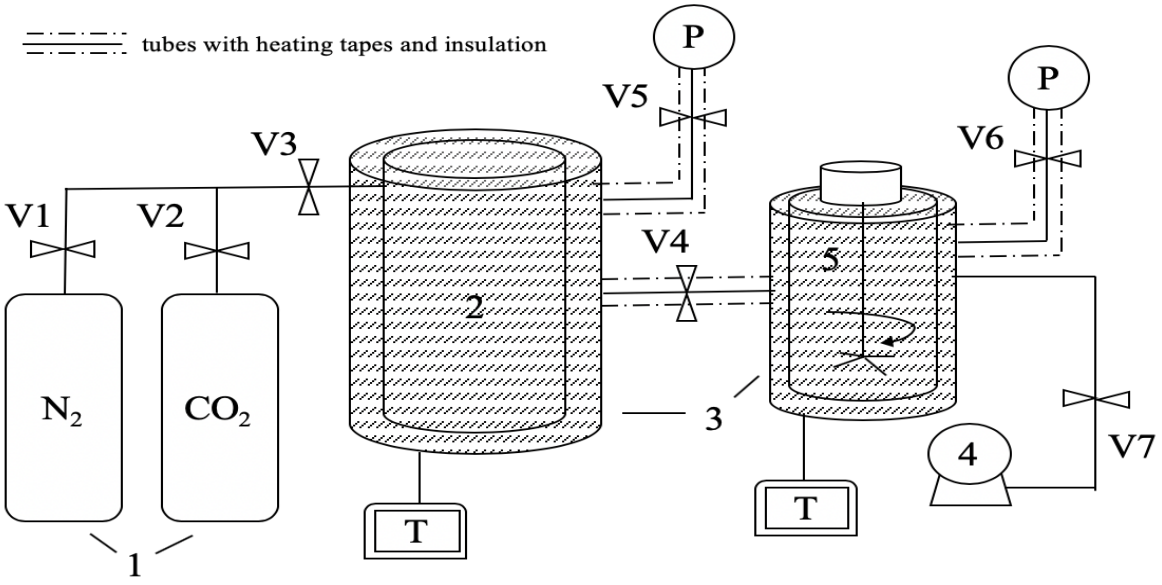

Figure 1. Schematic diagram of the experimental apparatus for measurements of the solubility of carbon dioxide/methanol in ionic liquids: (1) gas cylinder; (2) reference cell; (3) metal heating jacket; (4) vacuum pump; (5) sample cell.

2.3 EXPERIMENTAL PROCEDURE

There are a number of methods that are currently being used to measure the solubility of pure gases in ILs [14]. The methods include: (i) the stoichiometric technique [15-18], which involves metering known amounts of gas and liquid into a cell equipped with a viewing window, stirring vigorously for equilibrium to be established at constant temperature, letting the mixture stand and then measuring the level of the liquid with a cathetometer; (ii) the pressure-drop technique [19-21] during which two separate, known-volume cells are used, one referred to as the

reference cell, in which a certain mass of gas is pressurized, and another as the sample cell, in which the IL is placed and which is operating at the start of the tests under vacuum. The cells are connected through a valve which is opened at the beginning of the experiment to allow the gas from the reference cell to fill the sample cell and to dissolve in the IL. When equilibrium is reached, the pressures of the cells are recorded to calculate the solubility of the gas in the IL; (iii) gravimetric methods [22, 23], which use a high-pressure gravimetric microbalance in which a specified mass of IL is loaded and then exposed to the gas while the weight of the IL is being continuously measured until equilibrium is established. In-situ spectroscopic methods such as Fourier Transform Infrared Spectroscopy (FTIR), are also finding use, e.g., to study the chemical interactions of CO_2 molecules with expanded ILs [24, 25]. In our experiments, we employ the pressure-drop technique, which is the simplest among all methods utilized, needing no specialized hardware. A challenge with the pressure-drop technique, but to a certain degree with all other solubility measurement methods, as well, are the long times needed to reach solvation equilibrium, particularly for the less soluble gases. To overcome such a difficulty, in the experiments reported here, we employ a vigorously stirred sample cell.

2.3.1 MEASUREMENT OF CO_2 SOLUBILITY

The CO_2 solubility in the IL was measured using the experimental set-up shown in Figure 1. Prior to initiating the experiments, the system was leak-tested using N_2. For that, the sample and reference cells were pressurized with N_2 at a pressure of 30 bar. Valves V3 and V7 were then closed and the change in the system pressure was monitored over a 24 h period. For the experiments reported here, the pressure drop was less than 0.1 psi during the 24 h period

corresponding to a leak rate of less than 0.046 mmol N_2/h. Since the total quantity of CO_2 that dissolves in the IL during each experiment is at least 0.0014 moles of gas, this leak rate is considered negligible. Though the volumes of both the reference and the sample cells are known accurately, that is not the case for the volumes of the tubing, valves, etc., associated with each cell. The Helium (He) expansion method was, therefore, used to measure the actual volume of the cell (the details of this experimental procedure are explained elsewhere [26]).

After leak-testing the whole set-up, the top of the sample cell was opened and a pre-determined mass of the IL (10 mL) was loaded into the cell. The cell was then closed, and the whole system was leak-tested once more overnight to ensure that it is leak-free. A mechanical vacuum pump was then connected to the system via Valve 7 for two hours to remove any gases present in the cell (including moisture) and/or dissolved in the IL. The temperature controllers were then turned on to control the temperature of both the reference and sample cell at the present value. To carry out the CO_2 solubility experiments, valves V4, V7 are closed. Then, valve V2 connecting the CO_2 cylinder to the reference cell is opened to let the gas flow into the reference cell until a certain pre-determined pressure is reached. When the temperature and pressure in the cell stabilize at their desired values, then valve V3 is closed and valve V4 is opened to let the CO_2 flow into the sample cell and be dissolved into the IL. The overhead agitator in the sample cell was turned on during this time to vigorously mix the IL with the CO_2 to facilitate equilibration. Once the pressure change became negligible, typically, within the first 2 hours, meaning that the dissolution process had been completed, the equilibrium pressure was recorded from the pressure gauges

After the equilibrium pressure was reached, valve V4 was closed again and V3 was opened to allow gas into the reference cell at a higher initial pressure and the above experiment was

repeated once more. By repeating the above procedure a number of times, the equilibrium solubilities corresponding to various pressures were obtained. The experiment was then repeated for another temperature. For each temperature, three different experiments were carried out and the absolute relative percent deviation was calculated to be lower than 2%.

The number of moles present in the reference cell at the beginning of the experiment, and the number of moles in both cells at equilibrium were calculated based on the known volumes of the cells and the measured temperature and pressure by employing the NIST Chemistry WebBook [27]. The number of moles n_i injected into the set-up during each CO_2 charge into the reference cell during the i_{th} pressure increment, i.e., starting from equilibration pressure $P_{i-1,eq}$ (i=1, 2. 3, …n – $P_{0,eq}$ = 0 bar) during the $(i-1)_{th}$ step and ending with initial pressure $P_{i,in}$ for the i_{th} step can be calculated from the following equation:

$$n_i = V_1 * \left(v_i - v_{i-1,eq}\right) \quad (1)$$

where V_1 (cm^3) is the measured volume of the reference cell (including the volume of associated tubing, valve dead volume, etc.), $v_{i-1,eq}$ (mol/cm^3) is the specific volume corresponding to the equilibration pressure $P_{i-1,eq}$, and v_i (mol/cm^3) is the specific volumes corresponding to the initial pressure $P_{i,in}$ for the i_{th} step.

The moles of CO_2, n_{il}, dissolved at equilibrium in the [EMIM][BF_4] at a given temperature T and pressure $P_{i,eq}$ are determined by the following equations:

$$n_{il} = \Sigma n_i - V_g * v_{i,eq} \quad (2)$$

$$V_g + V_l = V_1 + V_2 \quad (3)$$

where V_g (cm^3) is the total gas volume (reference + sample cell) and V_l is the IL volume in the sample cell at equilibrium. V_2 is the volume of the sample cell, with $V_1 + V_2$ being the total set-up volume. In his study of the same IL for a similar region of pressures (<4 MPa), Kang et al. [9] concluded that the volume expansion of the IL due to dissolution of CO_2 was negligible (< 2 % at 25 °C). We have also measured in independent experiments the thermal expansion of IL in the temperature range from 25 °C to 220 °C and found it to be negligible (<1 %). These experiments were carried out using a stainless steel cell equipped with a viewing window and a CMOS camera (C, 1080P, Microsoft, USA) to monitor the change in the liquid level in the cell as the temperature is raised from 25 °C to 220 °C. For the analysis of the CO_2 solubility data, we have, therefore, assumed that the liquid phase volume can be assumed equal to the initial volume of the pure IL.

Finally, the solubility S_C (%) of CO_2 in [EMIM][BF_4] at each pressure is then given by:

$$S_C(\%) = \frac{n_{il}}{n_{IL}} \times 100\% \quad (4)$$

where n_{IL} is the number of moles of the IL.

2.3.2 MEASUREMENT OF METHANOL SOLUBILITY

For the MeOH experiments, we only used the sample cell. To start the experiment, a solution of MeOH in the IL of a pre-determined concentration was loaded into the sample cell. After leak-testing the cell (see above), the temperature of the cell was raised to a pre-set value employing the temperature controller while stirring vigorously the liquid phase to accelerate the equilibration process between the vapor and liquid phases. After a certain period, the pressure in the cell stops from rising, indicative that vapor/liquid phase equilibrium has been reached. The

pressure P would then be recorded and the experiment stopped. A new experiment would then be carried out employing a fresh MeOH in IL solution of different initial composition.

At equilibrium, the liquid-phase volume V_l is described by the following equation

$$V_l = n_{ML} * v_{ML}^o + n_{IL} * v_{IL}^o \quad (5)$$

where n_{ML}, n_{IL} are the number of moles of methanol and [EMIM][BF_4] in the liquid phase, respectively, and v_{ML}^o, v_{IL}^o are their pure state specific volumes. The basic assumption in Eqn. 5 is that volume changes due to mixing can be neglected [28]. In Eqn. 5, v_{ML}^o is obtained from the NIST Chemistry WebBook, while v_{IL}^o was determined by the Rackett equation [28].

$$v_{IL}^o = \frac{RT_c}{p_c} Z_c^{[1+(1-\frac{T}{T_c})^{2/7}]} \quad (6)$$

where T_c, p_c, Z_c are the critical temperature and pressure and the compressibility factor, respectively. The volume of gas phase V_g is given by:

$$V_g = n_{MG} * v(T, p) \quad (7)$$

where n_{MG} is the number of moles of methanol in the gas phase, and $v(T, p)$ is the molar volume of the methanol gas phase, which is obtained from the NIST Chemistry WebBook [17]. V_g and V_l add together to the known volume of the sample cell V.

$$V_g + V_l = V \quad (8)$$

The sum of the number of moles of MeOH in the gas phase n_{MG} and in the liquid phase n_{ML} is equal to the initial number of moles of methanol n_{ML0} dissolved in the IL (equal to the mass of methanol divided by its molecular weight).

Solving Eqns. (5)-(8) for n_{ML} and n_{MG}, we can finally obtain the solubility (molar basis) $S_M(\%)$ of methanol in [EMIM][BF_4] by:

$$S_M(\%) = \frac{n_{Ml}}{n_{IL}} \times 100\% \tag{11}$$

2.3.3 STABILITY OF THE [EMIM][BF_4] IL DURING THE MR- MeS EXPERIMENTS

Due to the high temperature and pressure conditions employed during the MR-MeS experiments, a key requirement for the sweep liquids chosen is that they remain stable under such conditions. To ensure that this is, indeed, the case for the [EMIM][BF_4], the IL utilized during the MR-MeS experiments is collected, the dissolved products and reactants are removed, and the IL is analyzed via NMR for its structure, which is then compared with that of a pristine IL not used in such experiments. The MR-MeS experimental set-up is shown in Figure 2, and described in greater detail elsewhere [5, 6]. It consists of the syngas delivery system, the MR, the sweep liquid delivery system, and the analysis section using a GC. A mesoporous alumina membrane, whose surface is rendered hydrophobic via grafting of an appropriate modifying agent, is installed in the MR. During operation, the syngas is fed into the shell-side, where it contacts under high pressure and temperature the Cu-ZnO-Al_2O_3 MeS catalyst to convert into MeOH. The sweep liquid (the [EMIM][BF_4] in this case) is pumped through the membrane tube-side to remove the produced MeOH (and the co-product water) to help increase the MeS conversion/yield.

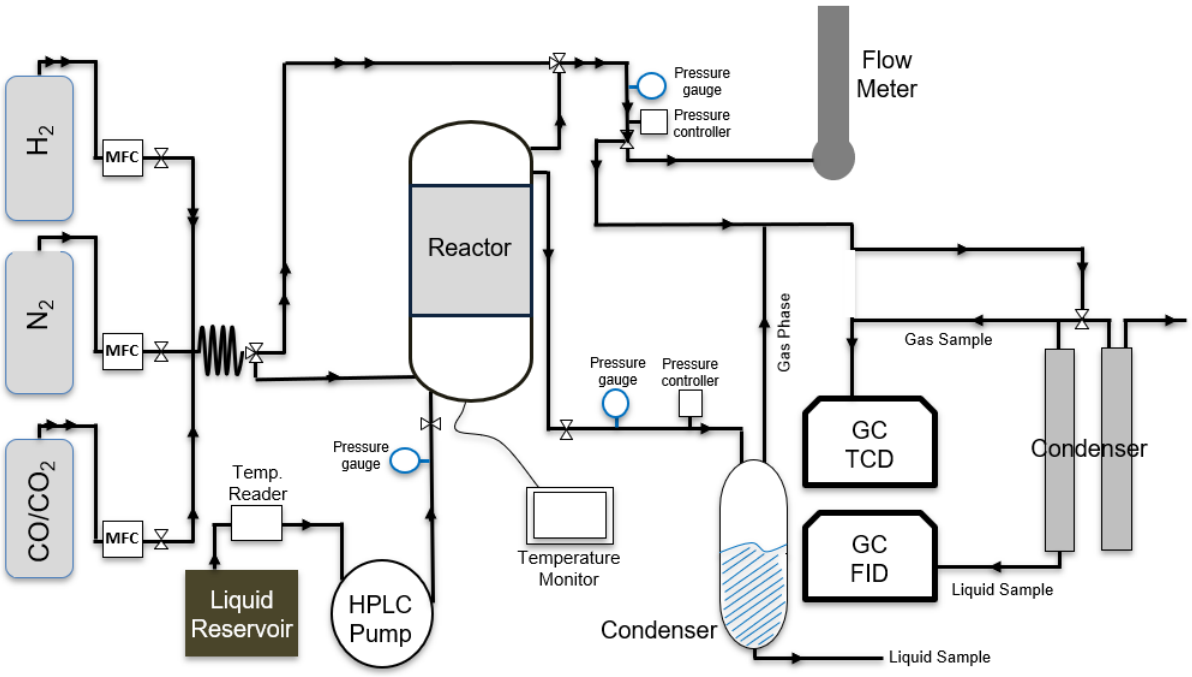

Figure 2. Schematic of the MR-MeS experimental set-up [5]

The IL collected is placed in a closed, magnetically-stirred glass vessel and is heated at 110 ºC in the presence of flowing inert Ar gas to remove any of the MeS components dissolved in it. The IL remaining, free of methanol and water, was then used to prepare samples for NMR analysis and to be compared with those from a pure IL that has not been used in any reactor experiments.

^{1}H and ^{19}F NMR spectra were obtained at room temperature with a Varian 400-MR spectrometer using 5 mm thin-walled NMR sample tubes (provided by Wilmad-LabGlass). All chemical shifts (δ) are reported in parts per million (ppm) relative to residual HDO in D_2O (δ - 4.80, ^{1}H NMR) and C_6F_6 (δ -164.9, ^{19}F NMR). NMR spectra processing was performed with MestReNova 11.0.2.

3. **RESULTS AND DISCUSSION**

3.1 CO_2 SOLUBILITY

When choosing the [EMIM][BF_4] IL as the sweep solvent, the expectation was that MeOH would have a good solubility in it while other permanent gases involved in MeS like H_2 and CO would not [7, 20, 21]. So, by helping to extract the MeOH from the reactor environment, while leaving the reactants like H_2 and CO unaffected, the IL sweep would help enhance the yield and selectivity. CO_2 solubility was, however, a concern since it serves as a reactant for MeS, and ILs including the [EMIM][BF_4] are known to exhibit high CO_2 solubilities [9]. In fact, ILs have been studied in recent years as absorption media for CO_2 capture to reduce its emissions, since CO_2 is considered a key greenhouse gas. Such high CO_2 solubility, if it was to be sustained at the high temperatures and pressure conditions of the MeS reaction would, of course, be detrimental to reactor performance.

Due to the potential use of ILs in CO_2 separation, capture and storage efforts, numerous research efforts were undertaken in recent years and a good volume of data exist on the CO_2 solubility in ILs at or near ambient temperature and pressure conditions [8-11]. For the [EMIM][BF_4], the IL of interest in this study, several studies exist reporting its CO_2 solubility [9-13] at low pressure and /or temperature conditions. In fact, as noted previously, the reason we selected the [EMIM][BF_4] IL for our MR-MeS study was due to its lower solubility toward CO_2 as compared to other better-known Imidazolium-based ILs [13]. Though past low temperature data may have guided the initial selection of the IL, they offer, however, no insight on the potential performance of [EMIM][BF_4] under the high pressure and temperature MeS reactive conditions. Generating such data is, therefore, a key objective of this paper.

Prior to measuring CO_2 solubility in [EMIM][BF_4] under MeS-relevant temperature and pressure conditions, we first generated such data at 25 ºC. These are shown in Figure 3.

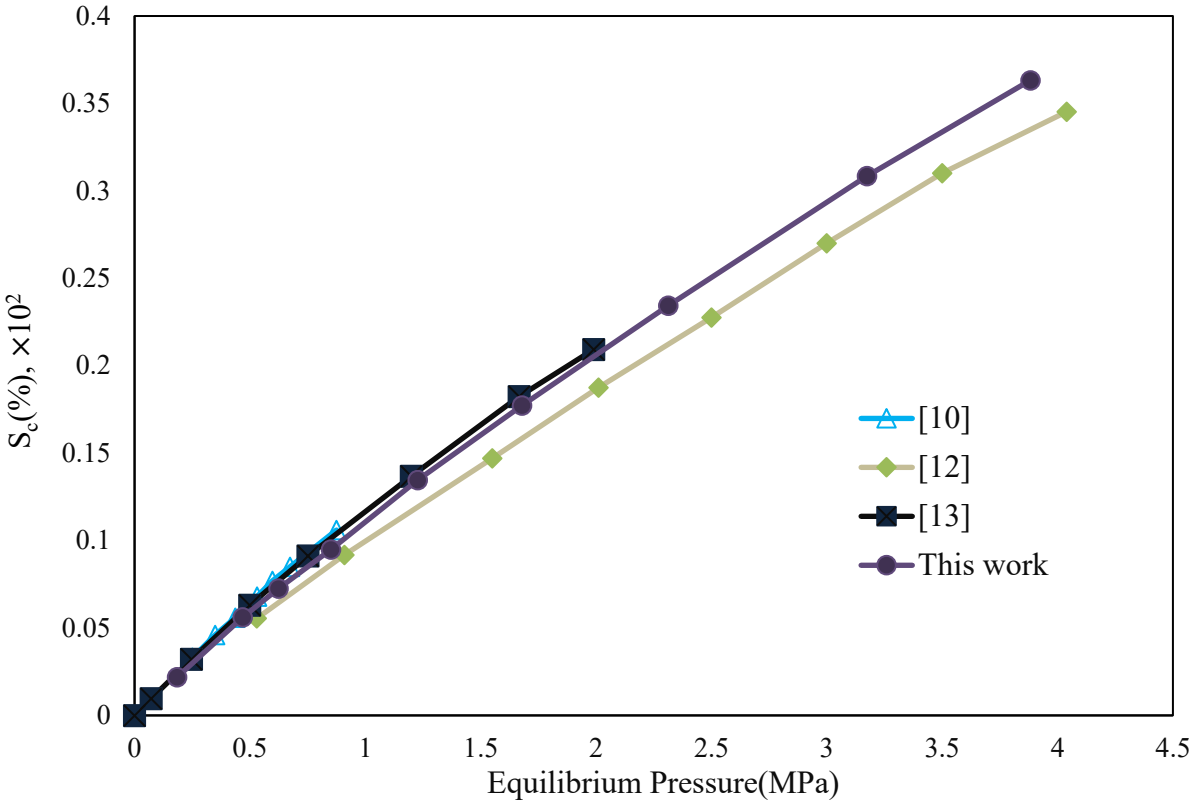

Figure 3. CO_2 solubility, S_c(%), in [EMIM][BF_4] at 25 ºC.

Shown on the same figure are experimental solubility data of CO_2 in the [EMIM][BF_4] at 25 ºC from the technical literature [10, 12, 13]. Our CO_2 solubility data are in good agreement with the prior literature data showing an average of absolute relative percent deviation ($ARD\% = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{X_i - X_i^{ref}}{X_i^{ref}}\right|$) of 5.1% from the data in [12], 1.8% from the data in [12] and 2.3% from the data in [10]. The good agreement with the experimental literature data clearly confirms the ability of our experimental technique to accurately measure the CO_2 solubility in the IL.

Figure 4 compares our experimental data at 25 ºC with solubility data from the technical literature with other well-known Imidazolium-based ILs [13], such as [EMIM][Tf_2N], [BMIM][Tf_2N], [BMIM][BF_4], and [BMIM][PF_6].

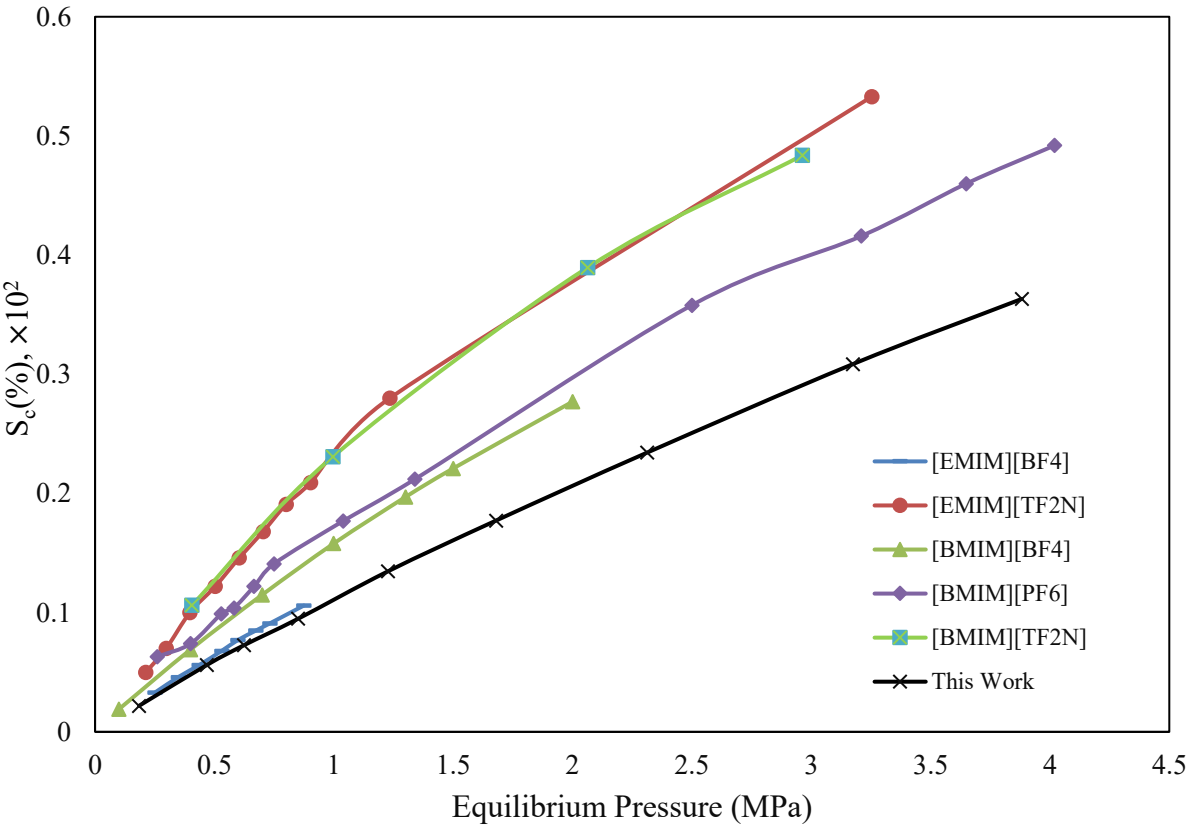

Figure 4. CO_2 solubility, S_c(%), of different imidazolium-based ILs. at 25 ºC [14].

As the data in Figure 4 indicate, the [EMIM][BF_4] has the lowest room temperature CO_2 solubility value among all other ILs. However, its solubility is still high enough, that if it was to be sustained at the MeS reaction temperature conditions, it would render the IL inappropriate for use as a sweep liquid in the MeS-MR system, since it would result in substantial loss of reactant CO_2. This, however, is not the case as Figure 5 shows where we plot our experimental CO_2 solubility measurements in the [EMIM][BF_4] for various temperatures. As one can see from Figure 5, as the temperature increases the CO_2 solubility decreases, and at temperatures relevant to the MeS

reaction (~220 ºC) it is negligible, i.e., $S_c(\%)$= 1% at 3 MPa, compared with a corresponding solubility $S_c(\%)$= 36% at 25 ºC. This is a very positive finding concerning the ability of this particular IL to function as a sweep liquid in the MR-MeS system.

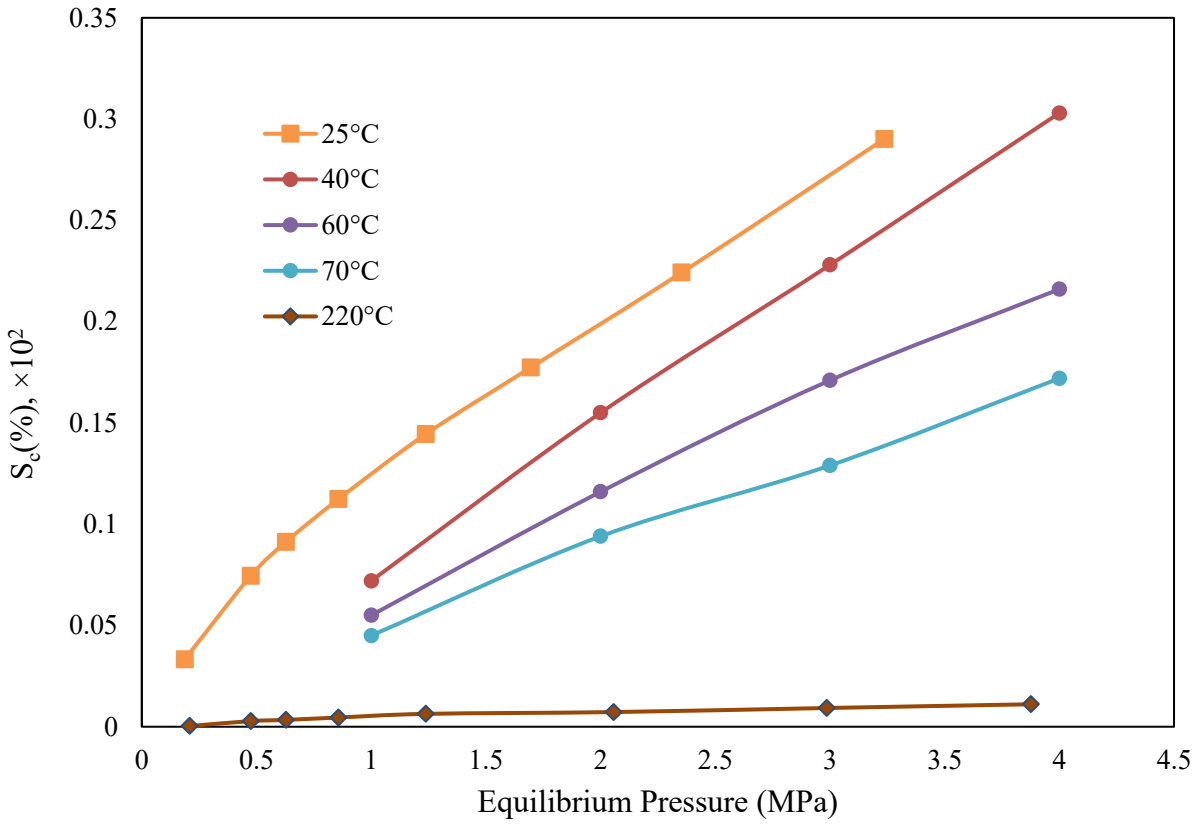

Figure 5. CO_2 solubility, $S_c(\%)$, in [EMIM][BF_4] at high temperatures

3.2 METHANOL SOLUBILITY:

Our experiments indicate that at room temperature (25 ºC) liquid MeOH is completely soluble in the [EMIM][BF_4]. The interest in this study, however, is to determine the MeOH solubility for temperatures of relevance to the MeS reaction, i.e., temperatures in excess of 200 ºC.

Figure 6 shows the MeOH solubility in [EMIM][BF_4] vs. its equilibrium pressure. Shown on the same Figure are the solubility data taken from the technical literature [29] for a petroleum-based organic solvent TGDE that we have also used in our MR-MeS studies (and other Groups have also employed in reactive separation studies of MeS [29]). TGDE is more readily available and affordable than [EMIM][BF_4], but its relatively high vapor pressure (compared to the IL) results in solvent loss during the MR-MeS operation and a more complicated downstream process to separate the MeOH from the TGDE.

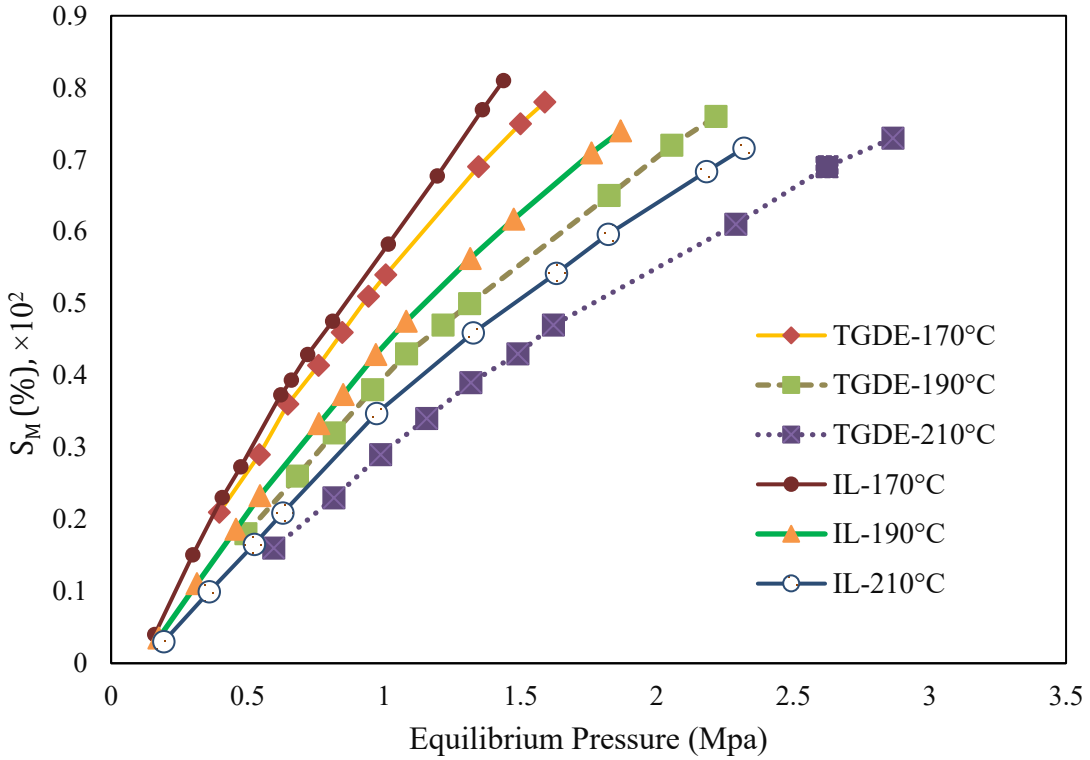

Figure 6. Methanol solubility, S_M (%), in [EMIM][BF4] and TGDE at high temperatures (TGDE data are extracted from reference [29]).

In addition, as detailed in our previous paper [5], the use of the IL as a sweep liquid compared to TGDE results in higher MeOH production rates in the MR-MeS system under otherwise similar

experimental conditions. The reason for the higher conversions becomes obvious from Figure 6, which shows that the MeOH solubility in [EMIM][BF_4] is higher than that in TGDE. In the context of the operation of the MR-MeS system, this means that more MeOH is swept away by the IL rather than by the TGDE, which enhances the MeOH production rates. Figure 7 shows the MeOH solubility at a pressure of 1.0 MPa as a function of temperature for both the [EMIM][BF_4] and TGDE. As the temperature increases the solubility of MeOH in both solvents decreases, but the solubility in the [EMIM][BF_4] remains always higher than that in the TGDE, confirming once more that the increased MeOH productivities in the MR-MeS lab-scale system, when using the IL vs. the TGDE as a sweep solvent, are due to the higher MeOH solubilities in the [EMIM][BF_4]. The high selectivity of MeOH adsorption in the [EMIM][BF_4] as compered to CO_2, presented in this work, is consistent with the experimental findings of our prior MR-MeS studies [5] in which we observed 22.2-51.3% higher methanol conversions than the conventional packed-bed reactor conversions. The solubility measurements and the MR studies validate, in our opinion, the ability of the IL solvent to favorably impact the MeS reaction kinetics.

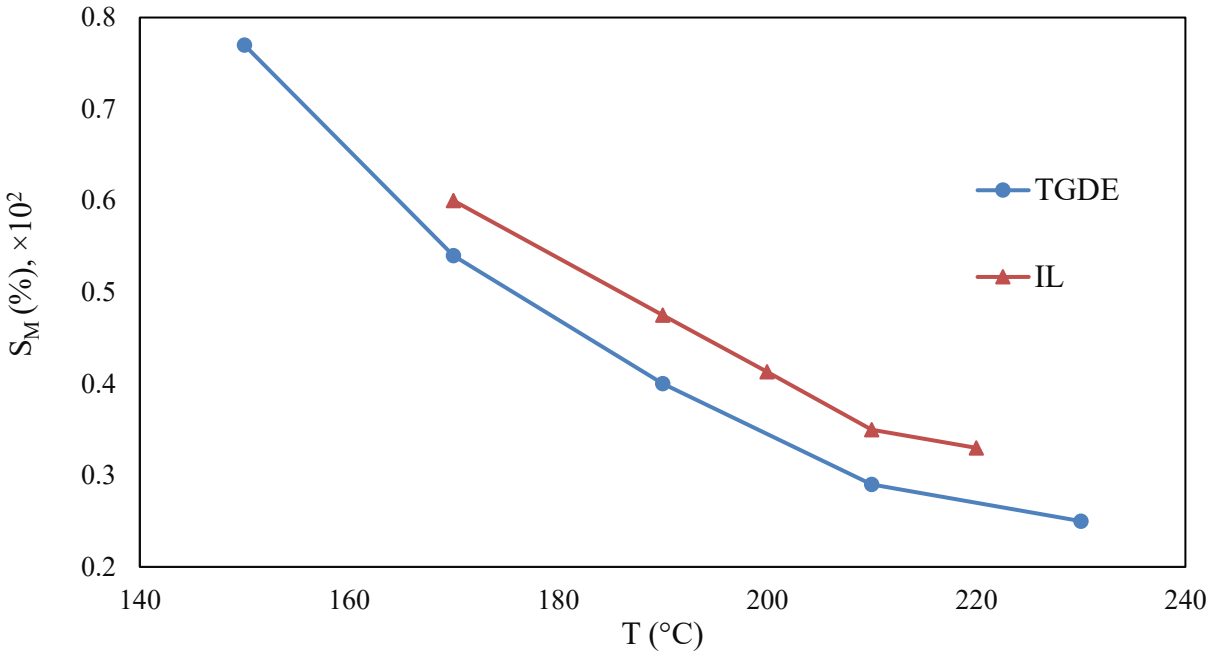

Figure 7. Methanol solubility, S_M (%), in [EMIM][BF4] and TGDE vs. temperature at 1.0 Mpa of pressure (all the TGDE data were extracted from reference [29]).

Water vapor is one of the by-products of the MeS reaction. The concern about water is not with the effect that its dissolution in the IL may have on the reactor conversion (our studies indicate that at room temperature water is completely soluble in the IL), which will in this case be beneficial in terms of enhancing conversion, but on the impact that such dissolution may have on the IL's structural properties. There are a number of past investigations that were done on mixing of water with the imidazolium-based ILs at room temperature showing that the physical and chemical properties (including electrical conductivity, reactivity, viscosity, polarity and solvation characteristics) of the IL may be affected by the presence of water [30-33]. The impact seems to correlate well with the quantity of water present in the IL. Zhang et al. [34], for example, studied solutions of water with 1-ethyl-3-methylimidazolium [(EMI^+) BF_4^-] in the range of water molar fractions of $0.02 \leq x_w \leq 0.90$. By monitoring the stretching vibrations, C_2-H, C_4-H, C_5-H, B-F, as water is being added to [(EMI^+) BF_4^-] they reported no major changes for low water contents of

$0.02 \leq x_w \leq 0.30$ which begin to appear, however, at higher water molar fractions (>0.3). Takamuku et al. [35] investigated the effect of water on the structure of the [EMIM][BF_4]. The absorption enthalpy in the low molar fraction range of $x_w \leq \sim 0.30$ is lower than the enthalpy of vaporization for bulk water; however, the absorption enthalpy overtakes the bulk water enthalpy for $x_w \geq \sim 0.5$. This finding suggests that the water molecules in this lower molar fraction range (<0.5) are weakly interacting with the IL, while they are more strongly interacting with the IL for $x_w \geq \sim 0.50$. During opration of our MR-MeS system the molar fraction water dissolved in the [EMIM][BF_4] will never exceed 0.3,

The aforementioned studies on the impact of water on the stability of the [EMIM][BF_4] IL indicate that if any effect was to be present it would be minimal. These investigations, however, were not conducted under the MR-MeS experimental temperature conditions of our study. A systematic study was, therefore, initiated (following the experimental procedure described in section 2.3.3 above) designed to validate the stability of the [EMIM][BF_4] IL during the MR-MeS system operation. Figure 8 compares the 400 MHz ^{1}H NMR characterization results of the IL, after it had been utilized in such experiments, to that of the pristine IL as received by the manufacturer. The six groups shown on the Figure correspond to the different hydrogen bonding environments that exist in the [EMIM][BF_4] structure. If any decomposition or irreversible bonding with water (and/or MeOH) had happened, the intensity and/or the locations of the peaks for any of these groups in the NMR spectra in the used IL would differ from those of the pristine one. However, as Figure 8 shows, this is clearly not the case here. Therefore, we are confident that the IL solubility properties remain unchanged during the MR-MeS experiments.

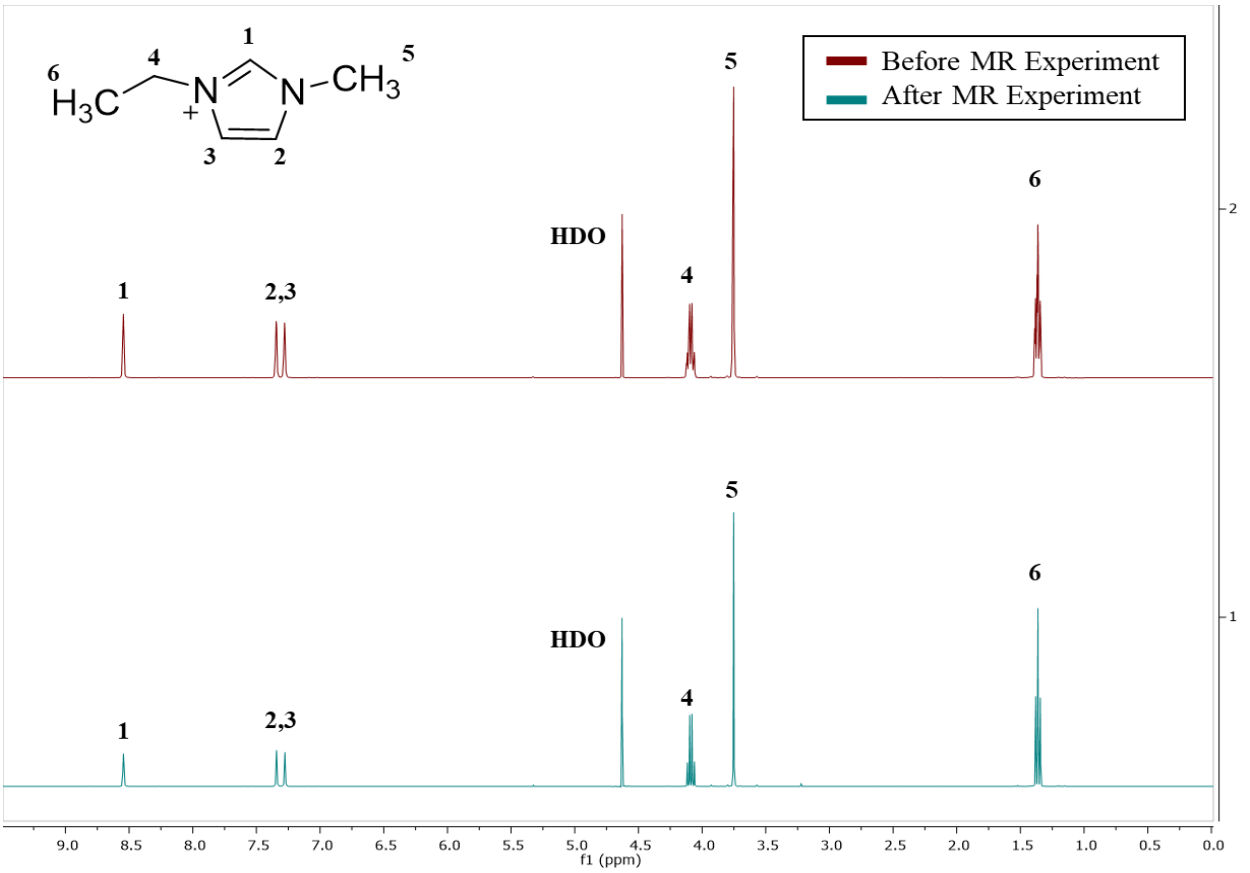

Figure 8. 400 MHz ^{1}H NMR results of the [EMIM][BF_4] IL before and after it was used in the MR-MeS experiments.

4. CONCLUSIONS

In this study we investigated the CO_2 and MeOH solubilities in [EMIM][BF_4], to validate its applicability as a sweep solvent in the MR-MeS process currently under study by our Group [5, 6]. The role of the sweep liquid in the MR-MeS process, occurring at high temperatures (200 ºC - 240 ºC) and high pressures (20 MPa - 40 MPa) is to strip in situ the methanol produced in the reactor from the syngas. The sweep liquid is, thus, required to have, under the MR-MeS conditions, a low solubility toward the syngas components and high solubility toward the MeOH. With respect to the syngas components, the IL is known to have very low room temperature solubilities toward

CO, and H_2, and these were no further investigated under the MR-MeS conditions. [EMIM][BF_4] has a relatively high room temperature solubility toward CO_2, and its solubility in the IL under the MR-MeS conditions was further investigated in this research. CO_2 was shown to have negligible solubility in the IL under such conditions, which is a positive finding with respect to the applicability of the selected IL for the MR-MeS process. We also studied the solubility of MeOH in the [EMIM][BF_4] under the MR-MeS conditions and compared it with its solubility in a petroleum-based organic solvent (TGDE) that we and others have previously used in reactive separation processes for MeS. Methanol was shown to have a higher solubility in the IL than in the petroleum solvent, which explains the higher MeOH production rates observed in the MR-MeS system when using the IL solvent.

ACKNOWLEDGEMENT

The support of the US National Science Foundation (Award# CBET-1705180) is gratefully acknowledged.

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ABBREVIATIONS

1; MR, membrane reactor 2; MeS, methanol synthesis 3; IL, ionic liquid 4; PBR, packed-bed reactor 5; FAS, fluoroalkylsilane 6; DI, deionized 7; W/F, catalyst weight/total molar flow rate 8; TEA, technical and economic analysis.

5. REFERENCES

[1] C.P. Fredlake, J.M. Crosthwaite, D.G. Hert, S.N. Aki, J.F. Brennecke, Thermophysical properties of imidazolium-based ionic liquids, Journal of Chemical & Engineering Data 49 (2004) 954-964.

[2] K. Qin, K. Wang, R. Luo, Y. Li, T. Wang, Interfacial tension and wetting properties of 1-ethyl-3-methylimidazolium tetrafluoroborate in carbon dioxide, from atmospheric pressure to supercritical state, The Journal of Supercritical Fluids 116 (2016) 83-89.

[3] L.A. Blanchard, D. Hancu, E.J. Beckman, J.F. Brennecke, Green processing using ionic liquids and CO_2, Nature 399 (1999) 28-29.

[4] R. Hayes, G.G. Warr, R. Atkin, Structure and nanostructure in ionic liquids, Chemical Reviews 115 (2015) 6357-6426.

[5] F.S. Zebarjad, S. Hu, Z. Li, T.T. Tsotsis, Experimental investigation of the application of ionic liquids to methanol synthesis in membrane reactors, Industrial & Engineering Chemistry Research 58 (2019) 11811-11820.

[6] Z. Li, T.T. Tsotsis, Methanol synthesis in a high-pressure membrane reactor with liquid sweep, Journal of Membrane Science 570 (2019) 103-111.

[7] H. Liu, S. Dai, D.E.. Jiang, Molecular dynamics simulation of anion effect on solubility, diffusivity, and permeability of carbon dioxide in ionic liquids, Industrial & Engineering Chemistry Research 53 (2014) 10485-10490.

[8] T. Nishida, Y. Tashiro, M. Yamamoto, Physical and electrochemical properties of 1-alkyl-3-methylimidazolium tetrafluoroborate for electrolyte, Journal of Fluorine Chemistry 120 (2003) 135-141.

[9] K. Qin, K. Wang, Y. Li, F. Kong, T. Wang, High-pressure phase behavior of 1-ethyl-3-methylimidazolium tetrafluoroborate and carbon dioxide system, RSC Advances 5 (2015) 32416-32420.

[10] Z. Lei, J. Yuan, J. Zhu, Solubility of CO_2 in propanone, 1-ethyl-3-methylimidazolium tetrafluoroborate, and their mixtures, Journal of Chemical & Engineering Data 55 (2010) 4190-4194.

[11] Z. Lei, J. Han, B. Zhang, Q. Li, J. Zhu, B. Chen, Solubility of CO_2 in binary mixtures of room-temperature ionic liquids at high pressures, Journal of Chemical & Engineering Data 57 (2012) 2153-2159.

[12] A.H. Jalili, M. Shokouhi, G. Maurer, A.T. Zoghi, J.S. Ahari, K. Forsat, Measuring and modelling the absorption and volumetric properties of CO_2 and H_2S in the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate, The Journal of Chemical Thermodynamics 131 (2019) 544-556.

[13] A. Akbari, M.R. Rahimpour, Prediction of the solubility of carbon dioxide in imidazolium based ionic liquids using the modified scaled particle theory, Journal of Molecular Liquids 255 (2018) 135-147.

[14] M. Koel, Ionic liquids in chemical analysis, CRC press 2008.

[15] M.S. Mittenthal, B.S. Flowers, J.E. Bara, J.W. Whitley, S.K. Spear, J.D. Roveda, D.A. Wallace, M.S. Shannon, R. Holler, R. Martens, Ionic polyimides: Hybrid polymer architectures and composites with ionic liquids for advanced gas separation membranes, Industrial & Engineering Chemistry Research 56 (2017) 5055-5069.

[16] J. Kumełan, A.P.-S. Kamps, D. Tuma, G. Maurer, Solubility of CO_2 in the ionic liquid [hmim][Tf2N], The Journal of Chemical Thermodynamics 38 (2006) 1396-1401.

[17] S.N. Aki, B.R. Mellein, E.M. Saurer, J.F. Brennecke, High-pressure phase behavior of carbon dioxide with imidazolium-based ionic liquids, The Journal of Physical Chemistry B 108 (2004) 20355-20365.

[18] M.J. Muldoon, S.N. Aki, J.L. Anderson, J.K. Dixon, J.F. Brennecke, Improving carbon dioxide solubility in ionic liquids, The Journal of Physical Chemistry B 111 (2007) 9001-9009.

[19] P. Husson-Borg, V. Majer, M.F. Costa Gomes, Solubilities of oxygen and carbon dioxide in butyl methyl imidazolium tetrafluoroborate as a function of temperature and at pressures close to atmospheric pressure, Journal of Chemical & Engineering Data 48 (2003) 480-485.

[20] J. Jacquemin, M.F.C. Gomes, P. Husson, V. Majer, Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283 K and 343 K and at pressures close to atmospheric, The Journal of Chemical Thermodynamics 38 (2006) 490-502.

[21] J. Jacquemin, P. Husson, V. Majer, M.F.C. Gomes, Low-pressure solubilities and thermodynamics of solvation of eight gases in 1-butyl-3-methylimidazolium hexafluorophosphate, Fluid Phase Equilibria 240 (2006) 87-95.

[22] T. Turnaoglu, D.L. Minnick, A.R.C. Morais, D.L. Baek, R.V. Fox, A.M. Scurto, M.B. Shiflett, High-pressure vapor-liquid equilibria of 1-Alkyl-1-Methylpyrrolidinium Bis (trifluoromethylsulfonyl) imide ionic liquids and CO_2, Journal of Chemical & Engineering Data 64 (2019) 4668-4678.

[23] S.H. Barghi, T.T. Tsotsis, M. Sahimi, Solubility and diffusivity of H_2 and CO_2 in the ionic liquid [bmim][PF6], International Journal of Hydrogen Energy 40 (2015) 8713-8720.

[24] T. Seki, J.-D. Grunwaldt, A. Baiker, In situ attenuated total reflection infrared spectroscopy of imidazolium-based room-temperature ionic liquids under "supercritical" CO_2, The Journal of Physical Chemistry B 113 (2009) 114-122.

[25] N. Sakellarios, S. Kazarian, Solute partitioning between an ionic liquid and high-pressure CO_2 studied with in situ FTIR spectroscopy, The Journal of Chemical Thermodynamics 37 (2005) 621-626.

[26] API, Recommended Practices of Core Analysis (2^{nd} ed.), (1998).

[27] N.S.a.T. Databases, Thermophysical properties of fluid systems, (2016).

[28] J.O. Valderrama, R.E. Rojas, Critical properties of ionic liquids. Revisited, Industrial & Engineering Chemistry Research 48 (2009) 6890-6900.

[29] M. Kuczynski, K. Westerterp, Binary vapour-liquid equilibria of methanol with sulfolane. Tetraethylene glycol dimethyl ether and 18-crown-6, Chemical Engineering and Processing: Process Intensification 20 (1986) 60.

[30] J. Wang, Y. Tian, Y. Zhao, K. Zhuo, A volumetric and viscosity study for the mixtures of 1-n-butyl-3-methylimidazolium tetrafluoroborate ionic liquid with acetonitrile, dichloromethane, 2-butanone and N, N–dimethylformamide, Green Chemistry 5 (2003) 618-622.

[31] U. Domańska, A. Marciniak, Liquid phase behaviour of 1-hexyloxymethyl-3-methyl-imidazolium-based ionic liquids with hydrocarbons: The influence of anion, The Journal of Chemical Thermodynamics 37 (2005) 577-585.

[32] R.A. Brown, P. Pollet, E. McKoon, C.A. Eckert, C.L. Liotta, P.G. Jessop, Asymmetric hydrogenation and catalyst recycling using ionic liquid and supercritical carbon dioxide, Journal of the American Chemical Society 123 (2001) 1254-1255.

[33] V. Najdanovic-Visak, J.M. Esperanca, L.P. Rebelo, M. Nunes da Ponte, H.J. Guedes, K.R. Seddon, H.C. de Sousa, J. Szydlowski, Pressure, isotope, and water co-solvent effects in liquid− liquid equilibria of (ionic liquid+ alcohol) systems, The Journal of Physical Chemistry B 107 (2003) 12797-12807.

[34] L. Zhang, Z. Xu, Y. Wang, H. Li, Prediction of the solvation and structural properties of ionic liquids in water by two-dimensional correlation spectroscopy, The Journal of Physical Chemistry B 112 (2008) 6411-6419.

[35] T. Takamuku, Y. Kyoshoin, T. Shimomura, S. Kittaka, T. Yamaguchi, Effect of water on structure of hydrophilic imidazolium-based ionic liquid, The Journal of Physical Chemistry B 113 (2009) 10817-10824.

Supplementary Information

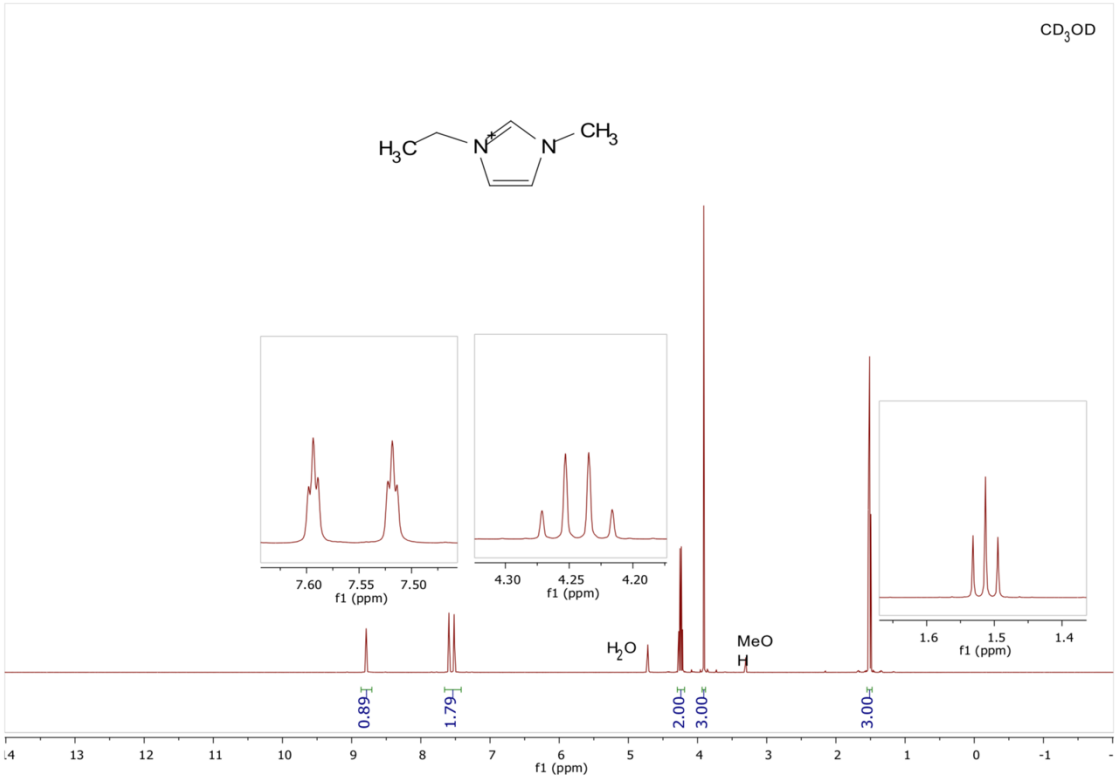

Figure (a). 400 MHz ^{1}H Nuclear Magnetic Resonance (NMR) results of the [EMIM][BF4] IL.

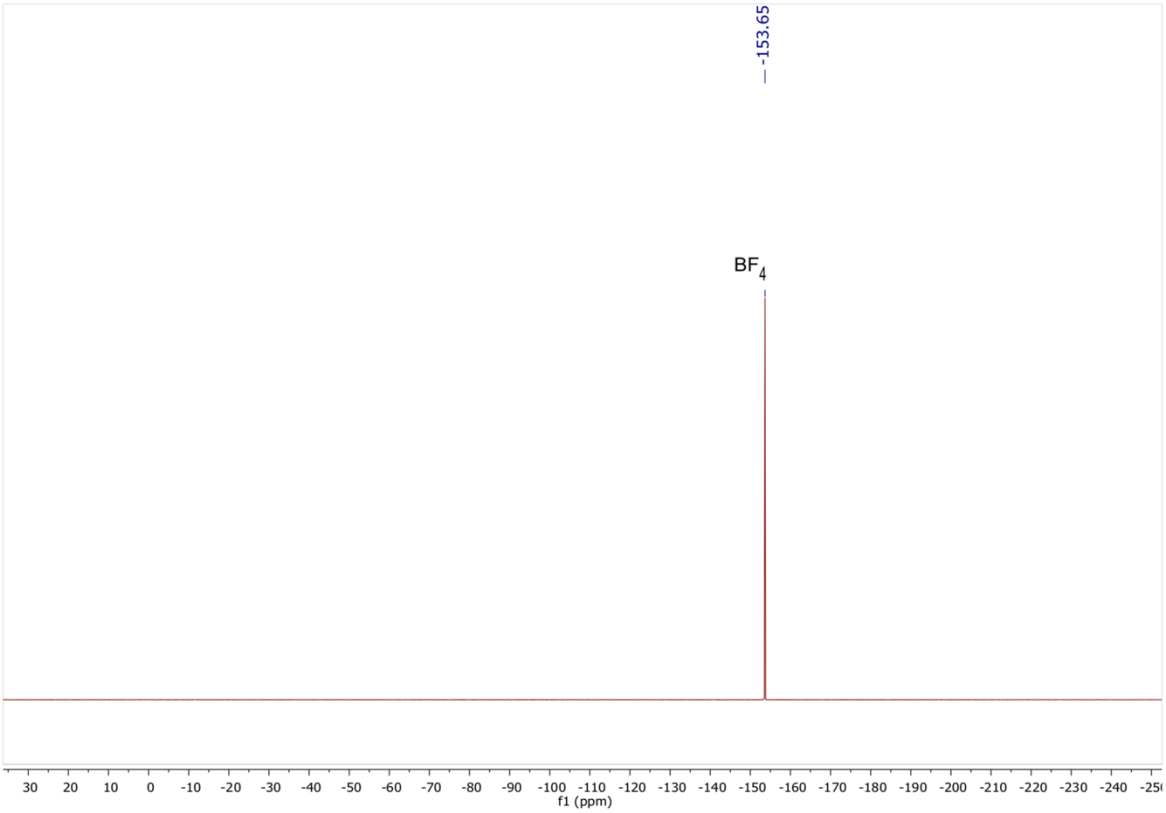

Figure (b). 376 MHz ^{19}F Nuclear Magnetic Resonance (NMR) results of the [EMIM][BF_4] IL.

Table 1. Data of materials utilized

Chemical Name	**Molecular Formula**	**CAS Registry Number**	**Mass Fraction Purity**	**Source**
Carbon dioxide	CO_2	[124-38-9]	99.999%	Praxair, Inc.
Methanol	CH_3OH	[67-56-1]	>99.9%	Sigma-Aldrich Corporation
Nitrogen	N_2	[7727-37-9]	99.999%	Airgas Company
1-Ethyl-3-methylimidazolium([Emim][BF4])	C6H11BF4N2	[143314-16-3]	>98%	Zhejiang Arts & Crafts Imp. & Exp. Company