

Low-Pressure Solubility of Carbon Dioxide in Room-Temperature Ionic Liquids Measured with a Quartz Crystal Microbalance

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The solubility of carbon dioxide in a series of imidazolium-based room-temperature ionic liquids has been determined using a quartz crystal microbalance. Henry's constants were obtained for CO₂ in nine different ionic liquids: 1-methyl-3-propylimidazolium bis[trifluoromethylsulfonyl]amide (C₃mimTf₂N), 1-*n*-butyl-3-methylimidazolium bis[trifluoromethylsulfonyl]amide (C₄mimTf₂N), C₄mimTf₂N with polyethylenimine, 1-*n*-hexyl-3-methylimidazolium bis[trifluoromethylsulfonyl]amide (C₆mimTf₂N), 1-methyl-3-*n*-octylimidazolium bis[trifluoromethylsulfonyl]amide (C₈mimTf₂N), 1-methyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-imidazolium bis[trifluoromethylsulfonyl]amide (C₈F₁₃mimTf₂N), 1,4-dibutyl-3-phenylimidazolium bis[trifluoromethylsulfonyl]amide, 1-butyl-3-phenylimidazolium bis[trifluoromethylsulfonyl]amide, and 1-methyl-3-propylimidazolium hexafluorophosphate (C₃mimPF₆). All results were obtained at 25 °C with CO₂ pressures at or less than 1 bar. A comparison of results helps in understanding the role of chemical structure on the separation capabilities of these materials. Notable among the results is a significantly greater measured CO₂ solubility in the ionic liquid having the fluorine-substituted cation as compared to the corresponding ionic liquid with a nonfluorinated cation. CO₂ solubility was found to be lower in the ionic liquid containing PF₆[−] than for the corresponding liquid with Tf₂N[−] anion. Addition of an imine polymer to the ionic liquid did not significantly change CO₂ solubility characteristics. The presence of water had a minor effect on CO₂ solubility for C₈mimTf₂N for environments with a relative humidity of 40% or less. Henry's constant for CO₂ in C₃-mimPF₆ obtained in this study is in good agreement with previously reported Henry's constant values for CO₂ in C₄mimPF₆ that were obtained by other means. This study not only provides some important thermodynamic property information for these unique materials but also illustrates the utility of using a quartz crystal microbalance to obtain this information.

Introduction

Room-temperature ionic liquids are a relatively new class of compounds that have been receiving increased attention in recent years as "green" designer solvents that may potentially replace many conventional volatile organic solvents in reaction and separation processes.^{1–18} These unique compounds are organic salts that are liquid over a wide range of temperatures near and at room temperature. Ionic liquids have no measurable vapor pressure; hence, there has been considerable interest in using them in place of volatile organic solvents that can emit problematic vapors.

The most commonly investigated room-temperature ionic liquids have an alkyl-substituted imidazolium salt as the cation. The imidazolium-based salts are relatively easy to synthesize and have physical properties that make them attractive for many chemical processes. The generally accepted acronym for the alkyl-substituted methylimidazolium cations is C_{*n*}mim, where *n* is the number of carbon atoms on the alkyl side chain. Common anions used in ionic liquids include bis[trifluoro-

methylsulfonyl]amide (Tf₂N[−]), hexafluorophosphate (PF₆[−]), tetrafluoroborate (BF₄[−]), and ethyl sulfate (EtSO₄[−]), although ionic liquids with a variety of other anions have also been synthesized.

There has been considerable interest in the potential of room-temperature ionic liquids for various separation processes. Ionic liquids have shown promise in the liquid/liquid extraction of organics from water,^{1–3} of metal ions from solution,^{4–7} and for separating isomeric organic compounds.⁸ It has been demonstrated that ionic liquid/organic mixtures can be separated by application of CO₂ pressures that induce a phase split, thereby providing a means of recovering ionic liquid from mixtures used in an extraction process.^{9–11} There is also interest in considering ionic liquids for gas separations.^{12–14}

The solution thermodynamics of C₄mimPF₆, C₈mimPF₆, and C₈mimBF₄ in equilibrium with both water vapor and liquid water has been investigated by Anthony et al.¹⁵ Henry's constants for water vapor in these ionic liquids were found to be comparable to those reported for water in ethanol and 2-propanol. Liquid–liquid equilibrium results show significant solubility (1–10 wt %) of water in these ionic liquids and insignificant solubility of the ionic liquids in the water. Seddon et al.¹⁶ measured the water content of a series of C_{*n*}mim ionic liquids. They found that the anion has a primary effect on water solubility, with some ionic liquids showing complete miscibility

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with water while others were completely insoluble. It was also found that the presence of chloride ion had a significant effect on the viscosity and density of C_4mimBF_4 and that mixtures of different solvents with the ionic liquid showed a similar dependence of concentration on viscosity. In a similar study, Huddleston et al.¹⁷ compared the properties of dry ionic liquids and ionic liquids equilibrated with water. Their results showed that ionic liquids with hydrophilic anions have properties that are very sensitive to the water content while the properties of ionic liquids with hydrophobic anions showed considerably less sensitivity to the presence of water.

The solubility of various gases in C_4mimPF_6 at 10, 25, and 50 °C and pressures up to 13 bar was measured using a gravimetric microbalance by Anthony et al.¹⁸ The gas solubilities were reported as Henry's constants with $H = 53.4$ bar for CO_2 , 173 bar for C_2H_4 , 355 bar for C_2H_6 , and 1690 bar for CH_4 at 25 °C. This same research group reported results from measurements of the high-pressure solubility of CO_2 in six different ionic liquids.¹⁹ Solubilities were determined at CO_2 pressures ranging from 15 to 93 bar and temperatures of 40, 50, and 60 °C. The CO_2 solubility was found to be the greatest in C_4mimPF_6 and in C_8mimPF_6 , with CO_2 mole fractions of 0.729 and 0.755, respectively, at 40 °C and 93 bar of pressure. The solubility of CO_2 in C_8mimBF_4 was about 10% less than in C_8mimPF_6 . The lowest CO_2 solubility was found in $C_2mimEtSO_4$ with a mole fraction of 0.423 at 40 °C and 93 bar of pressure. Measurements of the solubility of the ionic liquid in the CO_2 -rich phase using a dynamic high-pressure extractor showed negligible ionic liquid solubility in CO_2 . Kamps et al.²⁰ also report CO_2 solubility in C_4mimPF_6 at CO_2 pressures ranging from 1 to 97 bar and from 20 to 120 °C. Extrapolation of the data to low pressures yields a Henry constant on a molality scale of 1.20 MPa at 20 °C, corresponding to $H_{CO_2} = 47$ bar on a mole fraction scale. This value is in reasonable agreement with the value of 53.4 bar at 25 °C reported by Anthony et al.¹⁸ However, the high-pressure results of Kamps et al.²⁰ show CO_2 solubilities considerably greater than the values reported by Blanchard et al.¹⁹ The solubility of CO_2 in C_4mimPF_6 was reported by Scovazzo et al.¹⁴ as 0.08 mol/(L atm) at 27.5 °C. Calculating a Henry constant from this value yields $H_{CO_2} = 60$ bar. The solubilities of CO_2 and O_2 in C_4mimBF_4 have been measured by Husson-Borg et al.²¹ using an isochoric saturation method. The reported Henry constants for CO_2 ranged from 60 bar at 30 °C to 86 bar at 70 °C. Oxygen showed considerably lower solubility than CO_2 and increasing solubility with temperature, with $H_{CO_2} = 37$ bar at 40 °C and $H_{CO_2} = 23$ bar at 70 °C.

Bates et al.¹³ synthesized a "task-specific" ionic liquid for CO_2 removal that has an amine covalently tethered to an imidazolium cation. This material fixes the CO_2 as a carbamate, in a manner similar to that of traditional amine scrubbing solutions. The solubility of CO_2 in this liquid was found to be 0.5 mol of CO_2 /mol of ionic liquid, corresponding to an effective Henry constant of 3 bar. Because the amine in this ionic liquid binds the CO_2 , vacuum heating to 80–100 °C is required to regenerate the ionic liquid.

We are interested in examining the potential of ionic liquids for the separation of CO_2 from flue gases emitted from fossil-fuel combustion operations. These gases are typically at atmospheric pressure with CO_2 concentrations of 15–20 mol %.²² A separation system for these gas mixtures will need to operate at low pressures to avoid excessive compression costs. Therefore, solubility data for CO_2 in various ionic liquids at

low pressure are needed. The results presented in this paper provide some of the needed information.

In our experiments, a quartz crystal microbalance (QCM) was used to detect nanogram-sized changes in the mass of a thin film of ionic liquid that result when the ionic liquid is exposed to gas containing CO_2 . The ionic liquid film was coated onto a quartz resonator, and the frequency shift resulting from CO_2 uptake was related to the change in mass of the film using the Sauerbrey equation:

$$\Delta f = -C_1 \Delta m \quad (1)$$

where Δf is the change in frequency of the quartz resulting from a change in mass of the film, Δm .²³ The proportionality factor, C_1 , is related to the properties of the quartz as well as the oscillation circuit. Equation 1 was derived with the assumptions that the film is rigid and that there is no slip between the film and the crystal. Kanazawa and Gordon²⁴ derived a relationship for the frequency shift resulting from the addition of a viscous liquid film to a quartz crystal:

$$\Delta f = -C_2(\rho_f \eta_f)^{1/2} \quad (2)$$

where ρ_f is the fluid density and η_f is the fluid viscosity. Equation 2 was derived for an infinitely thick liquid film; i.e., the thickness of the film is much greater than the decay length of the fluid shear wave into the fluid. Rodahl and Kasemo²⁵ derived a relationship between the thickness, viscosity, and density of a liquid film and the frequency shift resulting from application of the liquid to a resonating quartz crystal. Results from that model show that eq 1 is valid for a liquid film when the film thickness is considerably thinner than the decay length of the fluid shear wave into the fluid.

Experimental Section

All of the ionic liquids were synthesized as described in the literature.^{26–32} For the ionic liquid with the fluorinated cation ($C_8F_{13}mimTf_2N$), our synthesis followed the method reported by Merrigan et al.³² for $C_8F_{13}mimI$. This iodide salt was converted into the bis[trifluoromethylsulfonyl]amide salt by metathesis in water using $LiTf_2N$. Briefly, fluorinated C_8mimI (3.68 g, 6.6 mmol) was dissolved in 40 mL of deionized H_2O at 70 °C. To this solution was added $LiTf_2N$ (1.9 g, 6.6 mmol) in 10 mL of H_2O . The mixture was cooled to room temperature with stirring and then was extracted with dichloromethane (3 × 10 mL). The removal of dichloromethane by rotary evaporation produced fluorinated C_8mimTf_2N as a yellow oil (4.45 g, 6.3 mmol, yield 95%).

A schematic diagram of the QCM system used for CO_2 solubility measurements is shown in Figure 1. This system consisted of an oscillator (ICM model 035360) and a frequency counter (Hewlett-Packard 53131A) that was interfaced with a personal computer for data acquisition. Data acquisition software was used to record the frequency at 1 s intervals. The QCM resonator was a 6 MHz AT-cut quartz crystal (1.36 cm diameter) with gold electrodes (0.68 cm diameter) on each side (International Crystal Manufacturing). Etched crystals with a roughened surface were used to "trap" the ionic liquid film and to minimize viscous effects. To apply a very thin film of ionic liquid to the crystal, a dilute solution ($\sim 10^{-3}$ g/mL) of the ionic liquid was prepared in acetone and 1 μ L of this solution was delivered to the center of the electrode using a gas chromatography syringe. This solution spread to the outer edge of the electrode as the acetone evaporated, leaving a thin film (~ 0.3 – 0.4 μ m) of the ionic liquid. The process was repeated on the

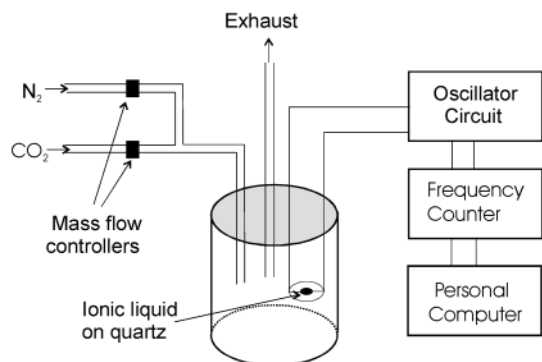


Figure 1. Schematic diagram of the experimental system for QCM measurements of CO₂ uptake into ionic liquid films.

other side of the crystal, yielding an ionic liquid film on both sides of the crystal.

Gas mixtures with varying CO₂ concentration were introduced by mixing CO₂ and N₂ streams. Carbon dioxide with 99.9% purity and nitrogen with 99.5% purity were supplied by Air Liquide. Mixing ratios of the two gas streams were controlled using mass flow controllers (MKS Instruments, Inc.) that were calibrated for each gas. The flow rates of each gas were adjusted so that the volumetric flow rate of gas remained constant.

To begin an experiment, the QCM cell with a clean crystal was purged with dry nitrogen and the frequency of the crystal was recorded once a stable value was achieved. The crystal was removed from the cell, and the ionic liquid solution was applied to the crystal as previously described. The crystal was returned to the cell, and the cell was again purged with dry nitrogen. The frequency of the ionic liquid coated crystal was recorded once a stable frequency was observed (~30 min). A mixture of CO₂ in N₂ was then introduced into the cell by adjusting the settings of the mass flow controllers. Once a steady frequency value was achieved and recorded (~2–3 min), the cell was purged with N₂ and the frequency returned to its original baseline value. CO₂ was again introduced, and the procedure was repeated several times with different CO₂ concentrations. The frequency shifts from the baseline were small (<6 Hz), and frequency fluctuations of 0.1 Hz were observed; therefore, frequency values averaged over 20–25 s were used when frequency shifts from the baseline were determined. Upon completion of one set of experiments, the crystal was removed from the cell and the ionic liquid was removed by rinsing the crystal with acetone. Experiments were also performed to examine the dependence of the frequency response on changing gas concentrations for clean quartz without any ionic liquid.

These experimental measurements yielded values for the following frequency shifts: (1) the difference in frequency between the ionic liquid coated quartz and the frequency of the clean quartz, both measured in a dry nitrogen environment, Δf_{IL} , (2) the difference between the frequency of the clean quartz in a dry nitrogen environment and the frequency of the clean quartz exposed to CO₂ at a given concentration, $\Delta f_{\text{clean quartz}}$, and (3) the difference between the frequency of the ionic liquid coated quartz in a dry nitrogen environment and the frequency of the ionic liquid coated quartz exposed to CO₂ at the same concentration as used to measure $\Delta f_{\text{clean quartz}}$, Δf_{CO_2} .

Results and Discussion

The frequency response of a quartz crystal coated with C₄-mimTf₂N to changes in CO₂ gas concentration is shown in Figure 2. These results are typical of the response observed with

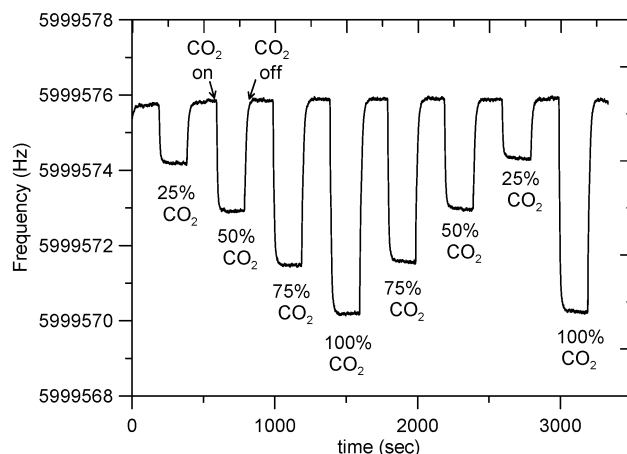


Figure 2. Frequency response for a quartz crystal coated with C₄-mimTf₂N subject to gases with different CO₂ concentrations. The baseline is established with 100% N₂. Measurements were made at 1 bar of total pressure.

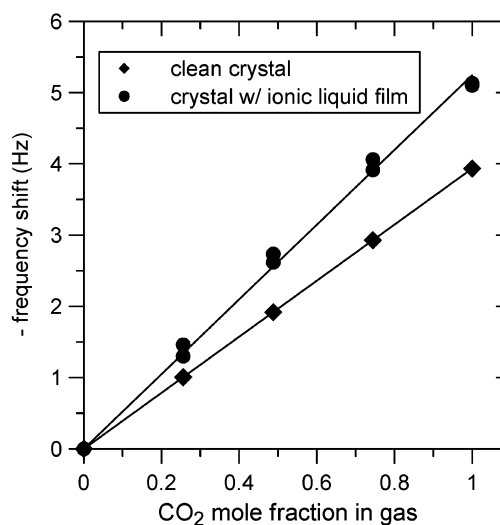


Figure 3. Frequency shift as a function of CO₂ concentration in the gas phase for a clean quartz crystal and for quartz coated with C₄-mimTf₂N. The baseline is established with 100% N₂. Measurements were made at 1 bar of total pressure.

all of the ionic liquids investigated. The baseline frequency was established with a nitrogen environment. When CO₂ was introduced, the frequency of the resonating crystal decreased because of the increased mass resulting from CO₂ uptake by the ionic liquid film. When CO₂ was removed, the frequency returned to its baseline value. Duplicate measurements were made at each CO₂ concentration. In all cases, the magnitude of the frequency shift increased as the CO₂ concentration in the gas was increased. There was no hysteresis observed when low concentration measurements were repeated following exposure to 100% CO₂. Because of the thin liquid films used, the response time to changing gas concentrations was rapid, requiring only several minutes to achieve equilibrium. This rapid response can be compared to the 1–3 h equilibration time reported by Anthony et al.¹⁵ for solution thermodynamic measurements using a gravimetric microbalance.

A plot of the observed frequency shift for a clean (no ionic liquid) quartz film as a function of CO₂ gas concentration is shown in Figure 3. These results show a decrease in frequency that is linearly proportional to the CO₂ concentration in the gas. This response can be attributed to a buoyancy effect resulting from a change in the gas density due to different CO₂/N₂ mole

ratios. The responses for different clean quartz films were similar in magnitude to that shown in Figure 3.

The frequency response to changing CO₂ concentrations for the same quartz film coated with C₄mimTf₂N is also shown in Figure 3. These results show a frequency shift that is larger than that observed with the uncoated quartz and is also linearly proportional to CO₂ concentration.

The Sauerbrey equation (eq 1) predicts a linear response between mass uptake and frequency shift for a rigid film. Anthony et al.¹⁸ report nondetectable solubility of N₂ in C₄mimPF₆. It is reasonable to assume that N₂ is also negligibly soluble in the ionic liquids studied here, enabling us to relate measured frequency shifts to CO₂ uptake using eq 1. The viscosity of the ionic liquids is expected to decrease as CO₂ dissolves in the liquid because the CO₂ can disrupt the ionic bond between anion and cation.^{31,33} If the ionic liquid film coated on the quartz were sufficiently thick that the film behaved as a viscous liquid, eq 2 would predict a positive frequency shift as CO₂ dissolves and viscosity decreases. The fact that our observations show a decrease in frequency that is linearly proportional to CO₂ concentration supports the validity of the Sauerbrey equation for these systems. This argument is supported by measurements performed with considerably thicker films where an increase in frequency was observed when CO₂ was introduced.

By assuming that the buoyancy effect observed with the clean quartz is the same as the buoyancy effect that also influences the response of the coated crystal, the difference between the frequency shift observed with the ionic liquid and the frequency shift observed with the clean quartz can be attributed to the uptake of CO₂ into the ionic liquid. The frequency shift observed when the ionic liquid was applied to the quartz ranged from 300 to 700 Hz. While this frequency shift was easily measured, it was only a small fraction of the resonant frequency of the quartz (6 MHz). Therefore, the mass of the quartz did not change appreciably as a result of the added liquid, and this assumption seems reasonable. Experiments performed using constant-density gas that are described later in this paper also support the validity of this assumption.

The amount of CO₂ in the film is expected to be proportional to the amount of ionic liquid on the quartz, and the frequency shift resulting from the application of the liquid is proportional to the amount of liquid applied. The proportionality constant relating the frequency shift to the mass uptake of CO₂ should be the same as the proportionality constant relating the frequency shift to the mass of applied liquid (i.e., C_1 in eq 1 is the same when Δm is the mass of ionic liquid added to the quartz and when Δm is the mass of CO₂ added to the liquid film). Therefore, the mole fraction of CO₂ in the ionic liquid, x_{CO_2} , can be easily related to the ratio of observed frequency shifts using the molecular weights of CO₂ and the ionic liquid to convert a mass fraction to a mole fraction:

$$x_{\text{CO}_2} = \frac{(\Delta f_{\text{CO}_2} - \Delta f_{\text{clean quartz}})/44}{\Delta f_{\text{IL}}/\text{MW}_{\text{IL}} + (\Delta f_{\text{CO}_2} - \Delta f_{\text{clean quartz}})/44} \quad (3)$$

The solubility of CO₂ in the ionic liquid can be characterized using Henry's constant, H_{CO_2} :

$$H_{\text{CO}_2} \equiv \frac{y_{\text{CO}_2}P}{x_{\text{CO}_2}} \quad (4)$$

which is valid for small x_{CO_2} (low pressure). Henry's constant was calculated from each frequency shift measurement using

TABLE 1: Summary of Henry's Constants for CO₂ in Ionic Liquids^a

ionic liquid	H_{CO_2} (bar)
C ₃ mimTf ₂ N	37 ± 7
C ₃ mimTf ₂ N with constant-density gas	39 ± 1
C ₃ mimPF ₆	52 ± 5
C ₄ mimTf ₂ N	37 ± 3
C ₄ mimTf ₂ N with 2.7 wt % polyethylenimine	38 ± 3
C ₆ mimTf ₂ N	35 ± 5
C ₈ mimTf ₂ N	30 ± 1
C ₈ mimTf ₂ N with 20% relative humidity	30 ± 2
C ₈ mimTf ₂ N with 40% relative humidity	27 ± 4
C ₈ F ₁₃ mimTf ₂ N	4.5 ± 1
58 mol % C ₈ mimTf ₂ N/42 mol % C ₈ F ₁₃ mimTf ₂ N	15 ± 1
1,4-dibutyl-3-phenylimidazolium bis(trifluoromethylsulfonyl)amide	63 ± 7
1-butyl-3-phenylimidazolium bis(trifluoromethylsulfonyl)amide	180 ± 17

^a Uncertainties are the 95% confidence limits.

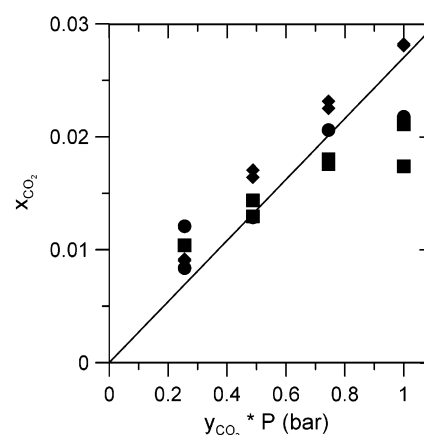


Figure 4. Mole fraction of CO₂ in C₄mimTf₂N as a function of CO₂ partial pressure in the gas phase. Measurements were made at 1 bar of total pressure. Each symbol represents data collected with different ionic liquid films. Henry's law predicts a linear relationship between x_{CO_2} and $y_{\text{CO}_2}P$.

eqs 3 and 4. These H_{CO_2} values were then averaged for each ionic liquid. Henry's constants determined from measurements with nine different ionic liquids are summarized in Table 1. It is helpful to remember that CO₂ solubility increases as H_{CO_2} decreases.

Henry's law predicts a linear relationship between x_{CO_2} and $y_{\text{CO}_2}P$. Deviations from this linearity are expected at higher pressures. The results obtained in this study generally followed the expected Henry's law behavior, as shown in Figure 4 for C₄mimTf₂N. Similar results were obtained with other ionic liquids. However, there does appear to be increased scatter in the data as the CO₂ concentration in the gas increases. A possible explanation for this is a decrease in the liquid viscosity with increasing CO₂ concentration, increasing the effect of viscous dampening. This scatter is accounted for in the reported uncertainties.

To confirm the validity of our assumption that the difference in frequency response to CO₂ between the ionic liquid coated crystal and the clean quartz can be attributed to the addition of CO₂ to the ionic liquid film, an additional experiment was performed with C₃mimTf₂N. In this experiment, mixtures of He, Ar, and CO₂ were prepared with appropriate proportions so that the density (i.e., the molecular weight) of the gas mixture was maintained constant as the CO₂ concentration was changed. The observed frequency shifts for the clean quartz and for the ionic liquid coated quartz are shown in Figure 5. These results

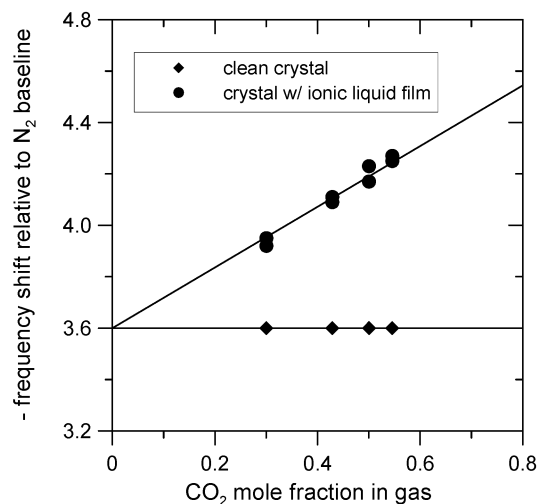


Figure 5. Frequency shift as a function of CO₂ concentration in the gas phase for clean quartz and for quartz coated with C₃mimTf₂N. The baseline is established with 100% N₂. The gas density was kept constant for mixtures with CO₂ by mixing argon, helium, and CO₂ in appropriate proportions. Measurements were made at 1 bar of total pressure.

show no observed change in frequency as the clean crystal was exposed to different CO₂ environments. Therefore, the response to CO₂ of the ionic liquid coated crystal could be attributed solely to the addition of CO₂ to the liquid film if He and Ar can be considered to be negligibly soluble in the ionic liquid. Anthony et al.¹⁸ report a Henry constant of 8000 bar for Ar in C₄mimPF₆, indicating extremely low solubility. There have not been results reported in the literature for the solubility of helium in ionic liquids. However, because helium and argon are both noble gases, it is reasonable to assume that the helium solubility is also negligible in typical ionic liquids. Henry's constant calculated from this experiment is included in Table 1. This value is in excellent agreement with results obtained with the N₂/CO₂ gas mixtures, confirming the approach we have used with our other experiments. The agreement between these values obtained with different gas mixtures provides additional confirmation for our assumption that N₂, Ar, and He are insoluble in the ionic liquids studied here.

Examination of the results in Table 1 shows a number of trends. Comparison of results for Tf₂N⁻ ionic liquids with different hydrocarbon alkyl groups on the imidazolium ring shows that Henry's constant decreases slightly (i.e., CO₂ solubility increases) as the length of the carbon chain on the imidazolium ring increases. As the length of the carbon chain increases, steric constraints will decrease the strength of the ionic interaction between the imidazolium cation and the Tf₂N⁻ anion. The weaker cation–anion interactions can strengthen the interaction between the cation and CO₂, leading to an increased CO₂ solubility. A trend opposite this was reported by Anthony et al.¹⁵ where water was found to be slightly less soluble in C₈mimPF₆ than in C₄mimPF₆. Given the different nature of CO₂ when compared to water, these different trends are not surprising.

A comparison of the CO₂ solubility in C₈mimTf₂N and C₈F₁₃mimTf₂N shows a significant increase in solubility with the addition of fluorine atoms to the octyl side chain. Fluorine has about twice the electronegativity of hydrogen. This increase in electronegativity apparently counters the steric constraints introduced with the larger fluorine atoms and increases the strength of the interaction between the ionic liquid and CO₂, leading to the observed increase in solubility.

The significant CO₂ solubility in C₈F₁₃mimTf₂N makes this

ionic liquid attractive for a CO₂ separation process. However, this liquid was observed to have a viscosity considerably greater than that of the corresponding ionic liquid having a nonfluorinated cation. This large viscosity could lead to slow rates of mass transfer. To take advantage of the thermodynamic characteristics of the ionic liquid with a fluorinated cation and the lower viscosity of the ionic liquid with a nonfluorinated cation, a mixture of 58 mol % C₈F₁₃mimTf₂N/42 mol % C₈mimTf₂N was prepared. The measured Henry's constant value of 15 bar for this mixture is in excellent agreement with the value predicted from the weighted average of the *H*_{CO₂} values measured for the individual liquids in this mixture, which is also 15 bar. Knowledge of the viscosity of these materials would enable one to optimize the composition needed to prepare a mixture suitable for a CO₂ separation process.

The effect of the ionic liquid anion can be assessed by comparing Henry's constants for C₃mimTf₂N and C₃mimPF₆. This comparison shows higher CO₂ solubility in the ionic liquid with a Tf₂N⁻ anion compared to the solubility in the ionic liquid with a PF₆⁻ anion. This increase in solubility can again be attributed to steric constraints. The larger Tf₂N⁻ leads to weaker cation–anion interactions when compared to PF₆⁻, increasing the interactions between the ionic liquid and CO₂. C₃mimPF₆ was also noticeably more viscous than C₃mimTf₂N, which would lead to lower mass-transfer rates in a separation process.

A comparison of Henry's constant for C₄mimTf₂N to that observed with C₄mimTf₂N with 2.7 wt % polyethylenimine shows that the addition of the imine polymer has no influence on CO₂ solubility. Apparently, additional amine groups in solution with added polymer are not sufficient to increase the CO₂ solubility compared to that of a pure ionic liquid.

A comparison of the two liquids with phenyl groups on the imidazolium ring shows significantly greater solubility of CO₂ in 1,4-dibutyl-3-phenylimidazolium bis[trifluoromethylsulfonyl]amide when compared to CO₂ solubility in 1-butyl-3-phenylimidazolium bis[trifluoromethylsulfonyl]amide. These observations can be explained using steric arguments, with the additional butyl side chain yielding weaker cation–anion interactions. However, a comparison of Henry's constant measured with 1-butyl-3-phenylimidazolium bis[trifluoromethylsulfonyl]amide with Henry's constant for C₄mimTf₂N shows a trend opposite this with considerably lower CO₂ solubility measured with the bulkier phenyl-substituted cation. An explanation for these observations is not clear but is likely due to differences in electronegativity and hydrophobicity between the two cations.

It is recognized that the presence of water can have an impact on the properties of some ionic liquids.¹⁶ For most of our measurements, the ionic liquid films were equilibrated with dry nitrogen. However, two solubility measurements were performed with C₈mimTf₂N that was equilibrated with humid nitrogen, and Henry's constants determined from these measurements are included in Table 1. These results show a slight decrease in Henry's constant as humidity is increased. Because this QCM approach measures mass uptake in the film without differentiation between water and CO₂, it is unclear whether this apparent increase in CO₂ solubility is real or whether there may be an increase in water solubility resulting from CO₂ uptake into the ionic liquid film. It should be noted that measurements of CO₂ solubility using other gravimetric techniques would also be limited by their inability to distinguish between water and CO₂ uptake. CO₂ solubility measurements using dry nitrogen were repeated following exposure of the ionic liquid to humid gas. Results showed *H*_{CO₂} values that were consistent with those measured with dry nitrogen prior to exposure to water. This

comparison indicates that the characteristics of these ionic liquids are not changed in any permanent manner by contact with water vapor.

An important aspect of our solubility measurements using the QCM is the thin film of ionic liquid that was applied to the quartz crystal. The application of a thin film of liquid (with thickness less than the decay length of the fluid shear wave into the fluid) enabled us to assume that the liquid behaves as a rigid film and to interpret frequency shifts resulting from CO₂ uptake by the ionic liquid using eq 1. The thickness of the liquid films was $\sim 0.3\text{--}0.4\text{ }\mu\text{m}$. The decay length, δ , can be calculated using $\delta = \eta/(\pi f_0 \rho_f)^{1/2}$,²⁵ where f_0 is the resonant frequency of the quartz (6 MHz for our measurements). Assuming an ionic liquid density for C₄mimTf₂N of 1.4 g/cm³ and a viscosity of 50 cP,²⁸ the decay length of the wave into this liquid can be estimated to be 1.4 μm , over 3 times larger than the film thickness. The other ionic liquids studied here were noticeably more viscous than C₄mimTf₂N, giving decay lengths in these liquids larger than this estimate for C₄mimTf₂N.

Another concern with this approach was whether the thickness of the liquid films was sufficient to ensure that bulk properties were being measured. With an ionic liquid density of 1.4 g/cm³,²⁸ the molecular diameter of C₄mimTf₂N can be estimated to be $10^{-3}\text{ }\mu\text{m}$ (10 Å). Therefore, a film with a thickness of 0.3 μm is equivalent to ~ 300 molecular diameters. This is a reasonably thick film and should not lead to significant errors due to film surface effects.

Additional support for the validity of the Henry's constant values measured with the QCM comes from comparing values reported in this paper to gas solubility values measured using other techniques. In an earlier study of gas solubilities measured using a gravimetric microbalance, Anthony et al.¹⁸ report a Henry constant for CO₂ in C₄mimPF₆ of 53.4 bar at 25 °C. Solubility data for CO₂ in C₄mimPF₆ reported by Kamps et al.²⁰ yield a Henry constant of 47 bar at 20 °C. Calculating a Henry constant from solubility data reported by Scovazzo et al.^{14,21} for CO₂ in C₄mimPF₆ yields $H_{\text{CO}_2} = 60$ bar at 27.5 °C. Calculation of the temperature correction for H_{CO_2} using the enthalpy of absorption reported by Anthony et al.¹⁸ for this mixture (-16.1 kJ/mol) shows little difference in H_{CO_2} between 20 and 27.5 °C. In our measurements, H_{CO_2} for C₃mimPF₆ was 52 bar and essentially no difference was observed between H_{CO_2} in C₃mimTf₂N and H_{CO_2} measured in C₄mimTf₂N. Therefore, little difference is expected between CO₂ solubility in C₃mimPF₆ and that in C₄mimPF₆. Our value for H_{CO_2} for C₃mimPF₆ is within the range of values reported by others for C₄mimPF₆, confirming the validity of the values determined using the QCM measurements. The range of values reported in these different studies with the same ionic liquid may be due to different water contents in the ionic liquid samples because it is recognized that ionic liquids with PF₆[−] anion are particularly sensitive to water.¹⁶

Conclusions

The solubility of carbon dioxide in a series of imidazolium-based room-temperature ionic liquids has been determined using a quartz crystal microbalance. The results from this study demonstrate that a quartz crystal microbalance provides a convenient tool to measure gas solubilities in these nonvolatile liquids in a relatively short time period. By applying sufficiently thin liquid films, frequency shifts can be interpreted in a straightforward manner by assuming the liquid films behave as rigid solids.

Measurements of the solubility of CO₂ in a number of different ionic liquids illustrate the important role played by

the structure of the ionic liquid in determining solubility. CO₂ solubility was found to increase as the length of the alkyl side chain on the imidazolium ring increased but was lower in ionic liquids with phenyl groups when compared to alkyl groups on the imidazolium ring. CO₂ solubility was greater in ionic liquids with Tf₂N[−] anions when compared to ionic liquids with PF₆[−] anions. Amine groups added to the ionic liquid with polyethylenimine did not change the solubility of CO₂ in C₄mimTf₂N. The most encouraging result is the significant increase in CO₂ solubility measured for an imidazolium-based ionic liquid with a fluorine-substituted C₈ side chain relative to the corresponding ionic liquid having a nonfluorinated C₈ side chain. Solubility measurements with a mixture of the fluorinated and nonfluorinated ionic liquids show that it should be possible to counter the relatively large viscosity of the fluorinated ionic liquid without losing all of the thermodynamic advantages of this material by mixing with a lower viscosity ionic liquid. Humidity had a small effect on CO₂ solubility for C₈mimTf₂N in environments up to 40% relative humidity.

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