Liquid-Liquid Phase Split in Ionic Liquid + Toluene Mixtures Induced by CO_2

Roberto I. Canales and Joan F. Brennecke
Dept. of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556

High pressure carbon dioxide was dissolved in ionic liquid + toluene mixtures to obtain the conditions of pressure and composition where a liquid-liquid phase split occurs at constant temperature. Ionic liquids (ILs) with four different cations paired with the bis(trifluoromethylsulfonyl)imide ($[Tf_2N]^-$) anion were selected: 1-hexyl-3-methylimidazolium ($[hmim]^+$), 1-hexyl-3-methylpyridinium ($[hmpy]^+$), triethyloctylphosphonium ($[P_{2228}]^+$), and tetradecyltrihexylphosphonium ($[P_{66614}]^+$). The solubility of CO_2 was measured in the liquid mixtures at temperatures between 298 and 333 K and at pressures up to 8 MPa, or until the second liquid phase appeared, for initial liquid phase compositions of 0.30, 0.50, and 0.70 mole fraction of IL. Ternary isotherms were compared with the binary solubility of CO_2 in each IL and pure toluene. The lowest pressure for separating toluene in a second liquid phase was achieved by decreasing the temperature of the system, increasing the amount of toluene in the initial liquid mixture and using $[hmim][Tf_2N]$. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 2968–2976, 2015
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Introduction

Ionic liquids (ILs) are salts extensively studied in recent years due to their interesting properties, including very low vapor pressure, high thermal stability, and wide liquid range, many of which include temperatures below 373 K.[1] Additionally, these compounds have adjustable physical and chemical properties. Given the large number of potential combinations of anion and cation,[2] this confers on them great versatility in being applied in a large number of specific processes. The literature describes multiple applications of ILs in separations; for example, in aqueous biphasic systems[3] for extracting conventional salts, amino acids, polymers, metals, or organic compounds from water; in liquid-liquid extractions for obtaining metal ions[4–10] or distributing organic compounds into two immiscible liquid phases[11–14]; for CO_2 capture from industrial gas streams[15,16]; and for separating compounds which form azeotropic mixtures.[17] The attractiveness of ILs in many of these applications coincides with their low volatility; thus, volatile solvents commonly used in separation processes can be replaced, in order to decrease vapor emissions to the environment.

CO_2, a well-known solvent for extraction under supercritical conditions,[18] has been studied in conjunction with ILs. In the first report of this kind, Blanchard et al.[19] mixed naphthalene with $[bmim][PF_6]$ and utilized supercritical CO_2 for extracting the dissolved solid from the liquid phase. After the extraction, no IL was detected in the supercritical phase

and CO_2 could be easily separated from the naphthalene by depressurization, obtaining a solvent-free solute. Moreover, the same procedure has been used for extracting several organic solids and liquids[20] from the IL phase, demonstrating its general applicability. Following the idea of using high pressure CO_2, Scurto et al.[21] proposed a new separation involving CO_2 and ILs applying the method depicted in Figure 1. In that work, an organic compound was mixed with an IL, forming a single liquid phase. Then, high pressure CO_2 was added to the system and solubilized in the liquid mixture until a second liquid phase appeared forming an IL-rich phase and an organic-rich phase, that is, a LV → LLV transition is observed. This is possibly due to the high solubility of CO_2 in ILs[22–25] and the antisolvent activity of this gas in decreasing the organic + IL interactions in the liquid phase.[26] The temperature, pressure, and composition of CO_2 where the phase split occurs, is called the "cloud point." If more CO_2 is added after the cloud point and the pressure of the system is increased, the second liquid phase can disappear, resulting in only two phases, a liquid phase containing the three components and a supercritical phase composed of the CO_2 + organic mixture. The LLV → LV transition that is observed is called the "merging point." This methodology has been applied for extracting water[27] and several organic compounds[26,28] from hydrophobic and hydrophilic ILs, and even for separating organic compounds from surfactants.[29] Also, composition analysis of the three phases for liquid-liquid-vapor equilibrium,[28,30–32] bubble and dew points,[33–35] and the observation of additional phase transitions, by changing the pressure of constant composition and temperature mixtures,[36,37] have been studied for several ILs + organic + CO_2 systems in literature. Most of these ternary systems involve polar organic compounds, opening the opportunity for
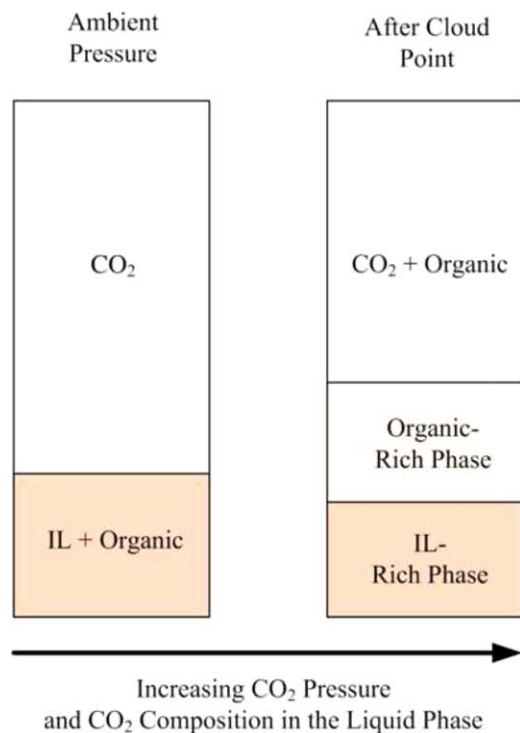
Figure 1. Phase split of an organic + ionic liquid mixture induced by CO₂.

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describing the phase equilibrium of mixtures of CO_2 and ILs with nonpolar aliphatic, aromatic, and cyclic hydrocarbons.

The objective of this work is to measure the solubility of CO_2 in IL + toluene mixtures at 298, 313, and 333 K and up to 8 MPa using three different families of ILs (imidazolium, pyridinium, and phosphonium cation based). Conditions of pressure and temperature at which the cloud point is observed are determined, following the procedure described by Scurto et al.[21] Molar volumes of the mixtures are determined in order to analyze the correlation of volume expansion with CO_2 solubility and the appearance of cloud points. This work provides new phase equilibrium data for CO_2 + IL and CO_2 + toluene + ILs systems that may be useful in designing separation systems for even more complex systems involving hydrocarbons or hydrophobic compounds.

Experimental Methods
Materials

[hmim][Tf₂N] was purchased from Merck. [hmpy][Tf₂N], [P₂₂₂₈][Tf₂N], and [P₆₆₆₁₄][Tf₂N] were synthesized in our laboratory. Structures and purities of ILs used in this work are depicted in Table 1. The purity and full characterization of the synthesized ILs was determined by ^{1}H and ^{13}C NMR spectroscopy and thermogravimetric analysis. [hmpy][Tf₂N] was synthesized by mixing 3-methylpyridine (Sigma-Aldrich, purity ≥ 0.99 mass fraction) with an excess of 1-bromohexane (Sigma-Aldrich, purity ≥ 0.98 mass fraction) in toluene to form 1-hexyl-3-methylpyridinium bromide ([hmpy][Br]). This first product was washed with *n*-hexane and diethyl ether. Then, [hmpy][Br] dissolved in water was mixed with lithium bis(trifluoromethylsulfonyl)imide (LiTf₂N, 3M-Fluorad, purity ≥ 0.995 mass fraction) obtaining

[hmpy][Tf₂N] which is washed with water to remove the lithium bromide. For synthesizing [P₂₂₂₈][Tf₂N], triethylphosphine (Sigma-Aldrich, purity ≥ 0.99 mass fraction) is reacted with octylbromide (Sigma-Aldrich, purity ≥ 0.99 mass fraction) in acetonitrile to form [P₂₂₂₈][Br]. Significant care must be taken in handling triethylphosphine as it is highly flammable, pyrophoric, and corrosive. The product is washed with hexanes. Then, the same procedure of adding LiTf₂N to the bromide is performed to obtain [P₂₂₂₈][Tf₂N]. [P₆₆₆₁₄][Tf₂N] was synthesized following the procedures shown elsewhere.[25] All ILs are placed under vacuum for at least 12 h at 333 K to obtain a water concentration below 0.0006 mass fraction. Water content was measured by Karl Fischer Coulometry (Metrohm 831). The observed [Br]⁻ content in the ILs synthesized in our laboratory is normally below 10 ppm. This concentration is measured by ion chromatography. Toluene (anhydrous, purity > 0.998 mass fraction) was purchased from Acros Organics and CO_2 (purity > 0.998 mass fraction) from Mittler Supply, South Bend, IN.
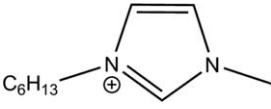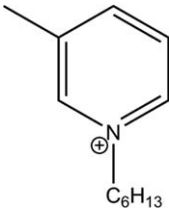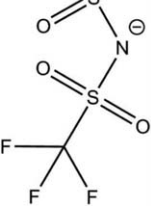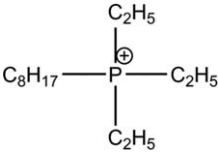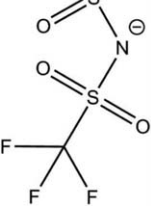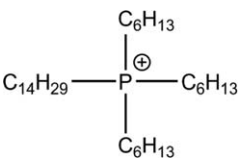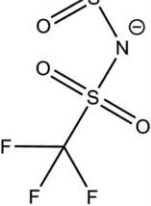
Equipment

A synthetic apparatus with material balance is used for measurements of the solubility of CO_2 in the liquid phase. This device is detailed in previous works.[25,28] The system consists of a thermoregulated air bath containing a high pressure vessel to hold the CO_2 (loading side). The pressure inside the vessel is regulated with a Ruska pump (Model 2200) connected through a line filled with mercury. The temperature is measured with T type thermocouples (±1 K) controlled by a Sargent-Welch ST controller. The pressure is registered with a Heise Bourdon gauge (0–20 MPa with accuracies of ±0.02 MPa). The second side (cell side) is a water bath which controls the temperature of a calibrated volume 10-cm sapphire tube (Saphikon, maximum pressure 20 MPa) where the sample is loaded. A cathetometer (Titan Tool Supply Co., ±0.005 mm) is placed in front of the cell for registering the initial volume and volume change upon addition of CO_2 to the liquid mixture. The water bath is regulated with a quartz heater, controlled with a Sargent-Welch T controller. The temperature is measured with a platinum resistance thermometer (±0.3 K) connected to a Keithley meter (Model 2010, ±0.0001 mV, and ±0.0001 Ω) and the pressure inside the cell is registered with a Heise transducer (0–20 ± 0.01 MPa, Model 901A).

Experimental procedures

For measuring the solubility of CO_2 in the liquid phase (single IL or toluene), the cell is loaded with 1–1.5 g of liquid, placed in a cell holder and connected to the lines. The cell side bath is filled with water, covering completely the cell, and the stirring system is activated to keep the set temperature constant. A small amount of CO_2 is added two or three times to the cell (0.1–0.2 MPa) to purge the remaining air in the lines and cell headspace. CO_2 is released until room pressure is reached. The initial height of the liquid is obtained with the cathetometer to calculate the initial volume with a previous obtained calibration curve (height vs. volume) for the cell. In the loading side, the temperature is kept at approximately 333 K and the pressure at 12.4 MPa. For the first run, a pressure of about 2 MPa of CO_2 is added to the cell and the pressure drop in the loading side is recovered to the initial value with the Ruska pump. The vapor-

Table 1. Name, Structure, Abbreviation, and Purity of Ionic Liquids Used

Name	Cation	Anion	Abbreviation	Purity
1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide	C_6H_{13}—N⁺⟨imidazolium⟩N—CH_3	(bis(trifluoromethylsulfonyl)imide structure)	[hmim][Tf$_2$N]	Purity > 0.99 mass fraction [H$_2$O] < 0.000326 mass fraction
1-Hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl) imide	(methylpyridinium ring with N⁺—C_6H_{13})		[hmpy][Tf$_2$N]	Purity > 0.99 mass fraction [H$_2$O] < 0.000394 mass fraction
Triethyloctyl phosphonium bis(trifluoromethylsulfonyl) imide	C_8H_{17}—P⁺(—C_2H_5)(—C_2H_5)—C_2H_5		[P$_{2228}$][Tf$_2$N]	Purity > 0.99 mass fraction [H$_2$O] < 0.000601 mass fraction
Tetradecyltrihexyl phosphonium bis(trifluoromethylsulfonyl) imide	$C_{14}H_{29}$—P⁺(—C_6H_{13})(—C_6H_{13})—C_6H_{13}		[P$_{66614}$][Tf$_2$N]	Purity > 0.99 mass fraction [H$_2$O] < 0.000391 mass fraction

liquid equilibrium between CO_2 and the liquid is reached in the cell after stirring the liquid phase (15–30) min and confirmed by the constant pressure of the system. Finally, the new height of the liquid meniscus, the temperature and pressure of the cell, and the lines are recorded for equilibrium conditions. The procedure is repeated by systematically increasing the pressure of CO_2 in increments of 2 MPa until 8 MPa is reached. For calculating the moles of CO_2 in the vessel, lines, and cell headspace, the density of CO_2 is obtained with the Span–Wagner equation,[38] as done previously.[25]

The same procedure is followed to study the solubility of CO_2 in liquid mixtures; the only difference is the preparation of the sample. The cell is loaded with a mixture prepared by weighing the IL and the toluene and mixing them in a closed flask by stirring with a magnetic stir bar. The solubility procedure is analogous to the binary case, but the final pressure is that corresponding to the formation of a second liquid phase, that is, cloud point. The phase split is reached when the mixture becomes cloudy while stirring. An accurate value of the cloud point pressure is obtained by slowly adding CO_2 to the liquid mixture and visually detecting the cloudiness with a boroscope. Calculations are also performed with the Span–Wagner equation, assuming that the gas phase is pure CO_2. In the literature,[39,40] compositions of toluene in the gas phase are no larger than 0.008 mole fraction at 313.15 K and 0.021 mole fraction at 333.15 K within the range of pressures studied. Thus, the density should not be modified significantly with the small amount of toluene dissolved in the CO_2 gas phase.

Propagation of error is obtained analogously as in previous work[25,41] for liquid compositions and molar volumes, with the only difference being the addition of the third component of the ternary system to this analysis. Using this method, the estimated error for the compositions is much smaller than the repeatability of the CO_2 solubility measurements. Therefore, the uncertainties of the compositions are calculated from the repeatability of points with similar pressures. For example, for duplicate or triplicate measurements at pressures that differ by less than 0.12 MPa we estimated the uncertainty in the CO_2 solubility as the standard deviation in the mole fraction for those replicates. After comparing repeatability between our data and reproducibility with literature values of the binary system CO_2 + toluene[39,40,42] and CO_2 + [hmim][Tf$_2$N],[24] we estimate the uncertainty to be ±0.01 mole fraction of CO_2 for pressures over 3 MPa and ±0.02 mole fraction for pressures below 3 MPa for binary and ternary systems. This is true for both binary (IL + CO_2 and toluene + CO_2) and ternary (IL + toluene + CO_2) systems. The uncertainty in the molar volumes was calculated using the CO_2 solubility uncertainty and the uncertainty in reading the cathetometer.

Results and Discussion

Binary mixtures: Toluene + CO_2 and IL + CO_2

The solubility of CO_2 was measured in the liquid phase of toluene at 298, 313, and 333 K in order to compare with literature data. We observed an average error of 1% (a maximum of ±0.02 mole fraction) when comparing our results with values shown in literature.[39,40,42]

The solubility of CO_2 in [hmim][Tf$_2$N] and [P$_{66614}$][Tf$_2$N] at 298, 313, and 333 K and pressures to 11.56 MPa for [hmim][Tf$_2$N] and 7.31 MPa for [P$_{66614}$][Tf$_2$N] have been measured previously by our research group[24,25] and others.[43–45] However, the solubility of CO_2 in [hmpy][Tf$_2$N] has only been reported at 283, 298, and 323 K and pressures to 1.3 MPa.[46] Therefore, the new binary data measured here
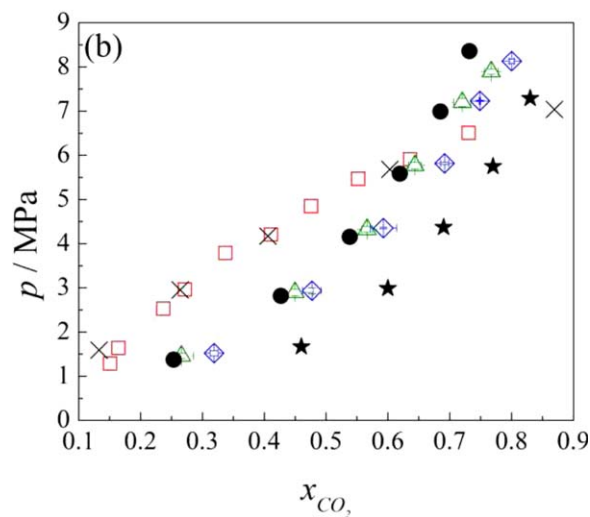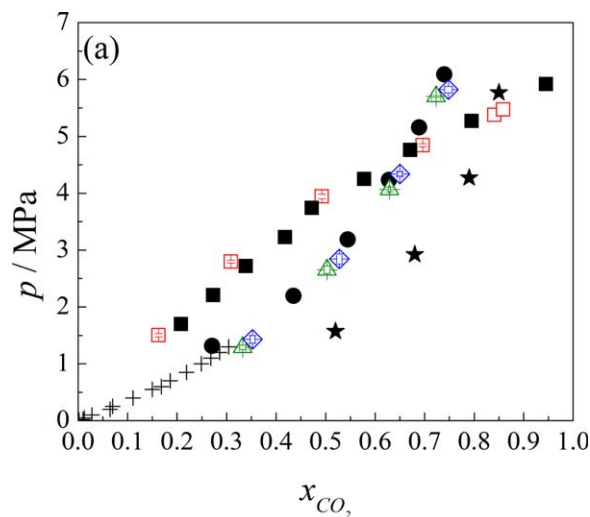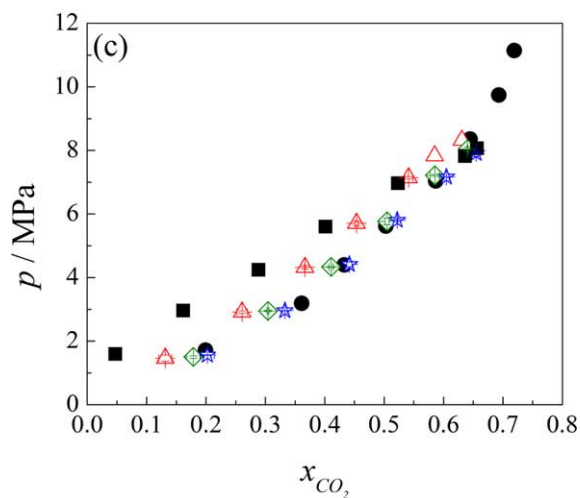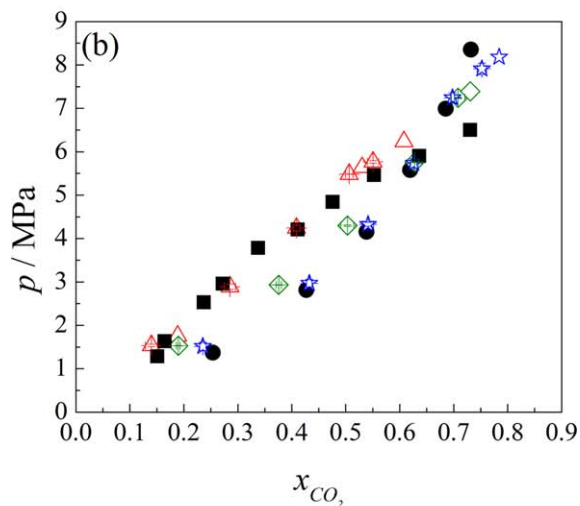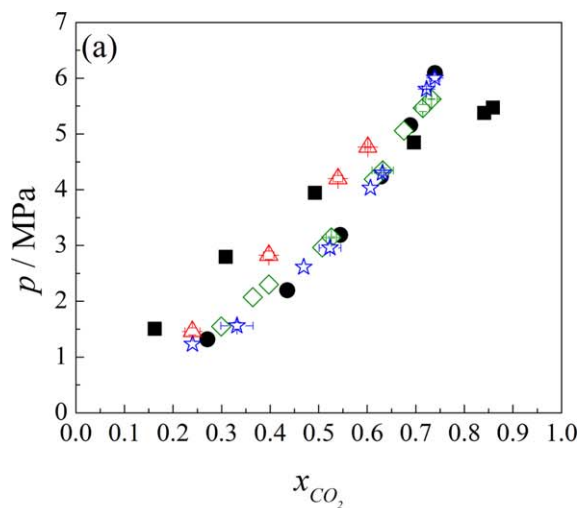
Figure 2. Solubility isotherms of CO_2 in □, Toluene; ■, Toluene,[42] ×, Toluene at 311.26 K,[39] ●, [hmim][Tf$_2$N][24]; △, [hmpy][Tf$_2$N]; +, [hmpy][Tf$_2$N][46]; ◇, [P$_{2228}$][Tf$_2$N]; ★, [P$_{66614}$][Tf$_2$N][25] at (a) 298 K and (b) 313 K.

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includes equilibrium isotherms of CO_2 in [hmpy][Tf$_2$N] and [P$_{2228}$][Tf$_2$N] at 298 and 313 K and pressures to 7.95 and 8.16 MPa, respectively. The new data and the data from the literature for the binary isotherms for all four ILs at 298 and 313 K are compared in Figure 2, along with the toluene/CO_2 binary data. The complete CO_2 solubility data for toluene, [hmpy][Tf$_2$N], and [P$_{2228}$][Tf$_2$N] is shown in Supporting Information Tables S1–S3, respectively.

As is the case for [hmim][Tf$_2$N] and [P$_{66614}$][Tf$_2$N], the solubility of CO_2 in [hmpy][Tf$_2$N] and [P$_{2228}$][Tf$_2$N] is higher at lower temperatures and increases with increasing pressures, as expected. The solubility of CO_2 in toluene is lower than in all the ILs at lower pressures. However, the shape of the toluene isotherm is very different from the ILs and a crossover is observed around 0.7 mole fraction of CO_2. When ILs are compared, [P$_{66614}$][Tf$_2$N] appears to have higher CO_2 solubility at all temperature and pressure conditions than the other ILs. It has been observed

Figure 3. Solubility isotherms of CO_2 in ■, Toluene; △, 0.30 initial mole fraction of [hmim][Tf$_2$N] in the [hmim][Tf$_2$N] + toluene mixture; ◇, 0.50 initial mole fraction of [hmim][Tf$_2$N] in the [hmim][Tf$_2$N] + toluene mixture; ☆, 0.70 initial mole fraction of [hmim][Tf$_2$N] in the [hmim][Tf$_2$N] + toluene mixture; ●, [hmim][Tf$_2$N][24] at (a) 298 K, (b) 313 K and (c) 333 K.

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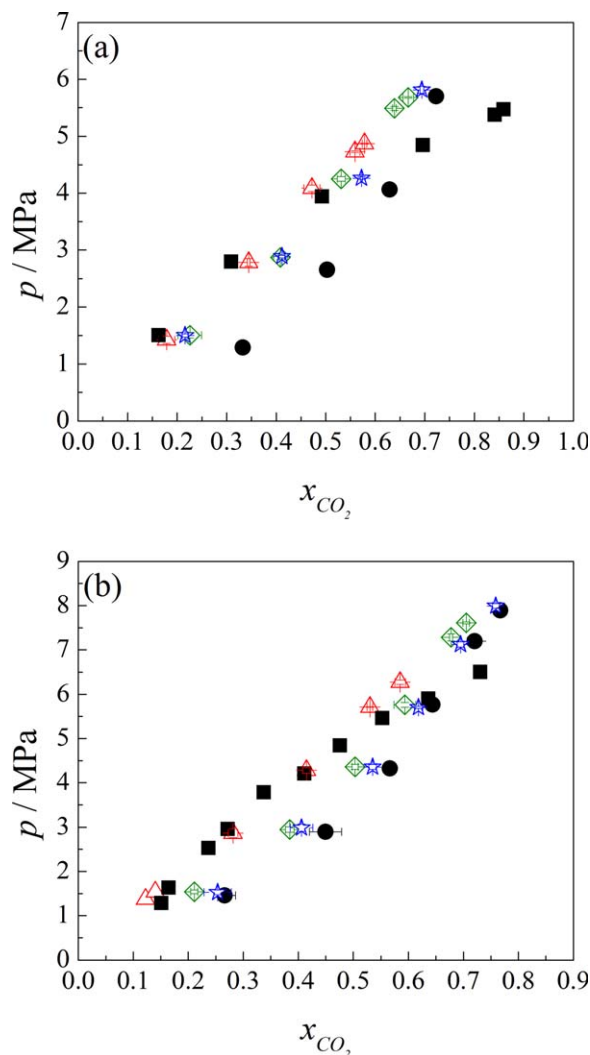
Figure 4. Solubility isotherms of CO₂ in ■, Toluene; △, 0.30 initial mole fraction of [hmpy][Tf₂N] in the [hmpy][Tf₂N] + toluene mixture; ◇, 0.50 initial mole fraction of [hmpy][Tf₂N] in the [hmpy][Tf₂N] + toluene mixture; ☆, 0.70 initial mole fraction of [hmpy][Tf₂N] in the [hmpy][Tf₂N] + toluene mixture; ●, [hmpy][Tf₂N] at (a) 298 K and (b) 313 K.

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previously[25] that this phosphonium-based IL has a remarkably higher capacity for CO_2 than many other ILs with different anion-cation combinations. A reasonable explanation for the high CO_2 solubility is the large free volume available in ILs made from the $[P_{66614}]^+$ phosphonium cation, which contains four long organic chains. [hmim][Tf₂N] and [hmpy][Tf₂N] have very similar CO_2 solubilities; in fact, based on data at pressures below 1.4 MPa, the Henry's law constants and enthalpy and entropy for CO_2 dissolution are virtually identical for the two ILs.[46,47] This is not surprising as the ILs have the same anion and the same length alkyl chains on the cations. Both cations are nitrogen-containing aromatic rings. Only at 313 K and pressures over 7 MPa can one detect slightly higher CO_2 solubility in [hmpy][Tf₂N]. As shown in Figure 2, the high pressure CO_2 solubility data taken here for [hmpy][Tf₂N] is entirely consistent with the

low pressure literature values. For [P₂₂₂₈][Tf₂N], the CO_2 solubilities are comparable to the values for [hmim][Tf₂N] and [hmpy][Tf₂N] at 298 K but are slightly higher at 313 K. The larger molar volume of the $[P_{2228}]^+$ IL and greater flexibility of the alkyl chains of the phosphonium cation at higher temperatures than the more rigid cyclic imidazolium and pyridinium cations may be responsible for the higher solubility of CO_2 at the higher temperature.

Ternary mixtures: IL + Toluene + CO₂

Here, we report three properties of the toluene + IL + CO_2 systems. First, we show how the solubility of CO_2 in the toluene + IL mixtures depends on temperature, pressure, and the relative amounts of toluene and IL in the liquid mixtures. Second, we report the pressures (and corresponding CO_2 solubility) at which the liquid-liquid phase split (or cloud point)
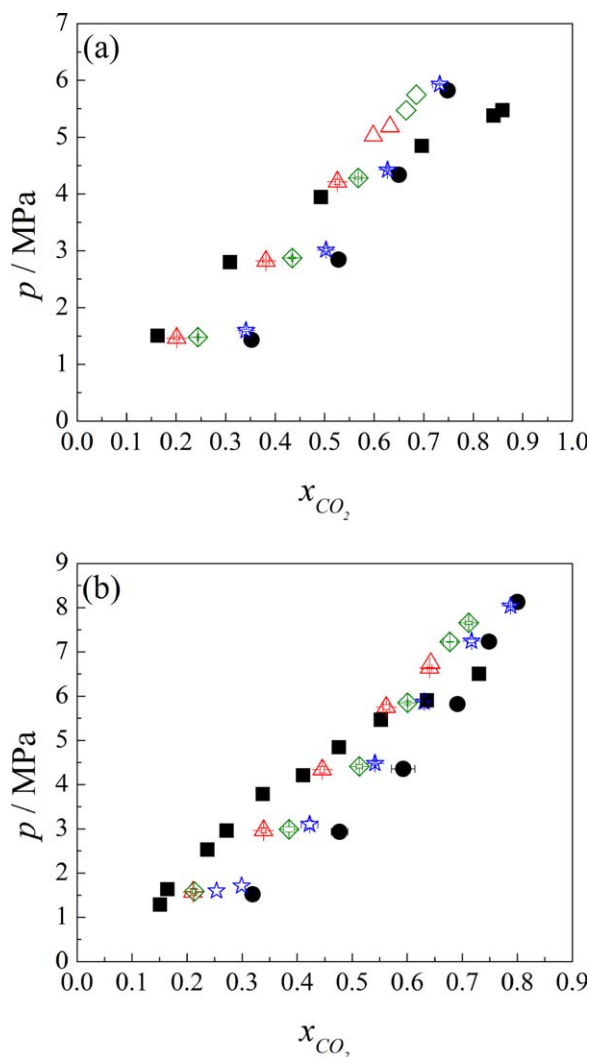
Figure 5. Solubility isotherms of CO₂ in ■, Toluene; △, 0.30 initial mole fraction of [P₂₂₂₈][Tf₂N] in the [P₂₂₂₈][Tf₂N] + toluene mixture; ◇, 0.50 initial mole fraction of [P₂₂₂₈][Tf₂N] in the [P₂₂₂₈][Tf₂N] + toluene mixture; ☆, 0.70 initial mole fraction of [P₂₂₂₈][Tf₂N] in the [P₂₂₂₈][Tf₂N] + toluene mixture; ●, [P₂₂₂₈][Tf₂N] at (a) 298 K and (b) 313 K.

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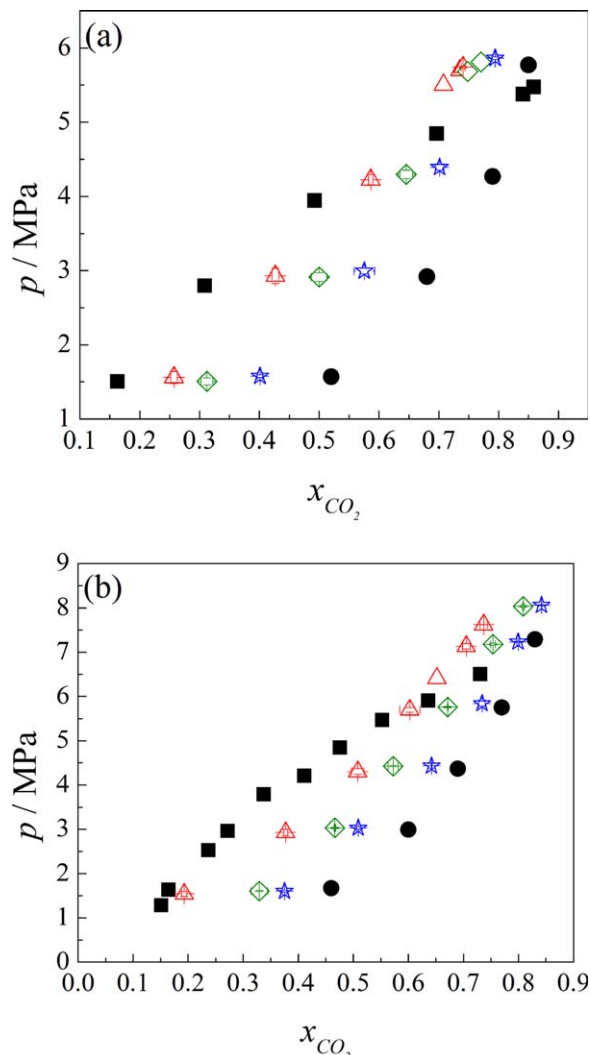
Figure 6. Solubility isotherms of CO_2 in: ■, Toluene; △, 0.30 initial mole fraction of $[P_{66614}][Tf_2N]$ in the $[P_{66614}][Tf_2N]$ + toluene mixture; ◇, 0.50 initial mole fraction of $[P_{66614}][Tf_2N]$ in the $[P_{66614}][Tf_2N]$ + toluene mixture; ☆, 0.70 initial mole fraction of $[P_{66614}][Tf_2N]$ in the $[P_{66614}][Tf_2N]$ + toluene mixture; ●, $[P_{66614}][Tf_2N]$[25] at (a) 298 K and (b) 313 K.

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occurs for each IL as a function of temperature and the relative amounts of toluene and IL in the liquid phase. Finally, we report on the volume expansion that occurs as CO_2 is added to the toluene + IL mixtures and discuss how this influences the pressure (and CO_2 composition) at which the liquid-liquid phase split occurs. The $[hmim][Tf_2N]$ + toluene + CO_2 system was investigated at 298, 313, and 333 K. However, as no liquid-liquid phase split occurred at 333 K with $[hmim][Tf_2N]$ within the pressure range of our apparatus (up to 8 MPa), the $[hmpy][Tf_2N]$, $[P_{2228}][Tf_2N]$, and $[P_{66614}][Tf_2N]$ systems were studied only at 298 and 313 K. In each case, the maximum pressure investigated was either the pressure at which the liquid-liquid phase split was observed, the maximum pressure of the apparatus (8 MPa), or the pressure at which a liquid CO_2 phase is formed. This last situation is only encountered at

298 K, which is below the critical temperature of CO_2. The vapor pressure of pure CO_2 at 298 K is roughly 6.2 MPa.

To determine the range of initial toluene + IL compositions that could be investigated, qualitative measurements of the solubility of toluene in each of the ILs were performed at room temperature. For $[hmim][Tf_2N]$, $[hmpy][Tf_2N]$, and $[P_{2228}][Tf_2N]$, the estimated toluene solubility is between 0.80 and 0.85 mole fraction. Toluene is completely miscible with $[P_{66614}][Tf_2N]$ at room temperature. High solubility of toluene has been measured previously in imidazolium ILs,[48] and this has been attributed to interactions of the highly electrostatic fields of the aromatic rings in both the IL and the toluene, as well as van der Waals interactions of the low polarity toluene with nonpolar chains on the cation of the IL.[49,50] The formation of clathrates by mixing $[hmim][Tf_2N]$ with toluene has been reported, as well.[51] The range of solubilities of toluene in the four ILs investigated here, including complete miscibility with $[P_{66614}][Tf_2N]$, suggests that ILs + toluene exhibit normal liquid-phase dissolution, rather than the formation of any sort of specific stoichiometric complexation that could be characterized as a clathrate. Electrostatic interactions plus van der Waals forces can also account for the high solubility of toluene in $[hmpy][Tf_2N]$, due to the pyridinium cation's similarity with the imidazolium ring. In the case of phosphonium-based ILs, the high solubility of toluene is likely due to van der Waals interactions, which would increase with increasing alkyl chains length.[52] This is consistent with toluene being completely miscible with $[P_{66614}][Tf_2N]$ but only partially miscible with $[P_{2228}][Tf_2N]$. Therefore, the initial compositions of the IL + toluene mixtures studied here were 0.30, 0.50, and 0.70 mole fraction IL. A single liquid phase was observed initially for all the temperatures investigated by using these compositions.

Solubility of CO_2 in mixtures of IL + toluene

The solubility of CO_2 in the mixtures of IL + toluene increases with increasing pressure, decreasing temperatures,
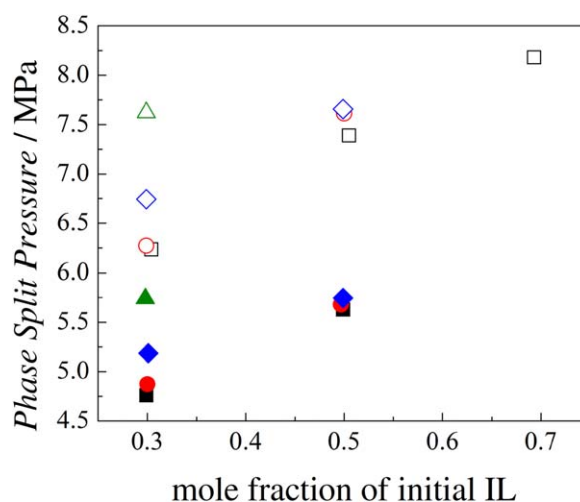
Figure 7. Phase split pressure at a determined initial composition of IL in the toluene + IL mixture for: ■,□, $[hmim][Tf_2N]$; ●,○ $[hmpy][Tf_2N]$; ◆,◇, $[P_{2228}][Tf_2N]$; ▲,△, $[P_{66614}][Tf_2N]$. Filled symbols represent 298 K and open symbols 313 K.
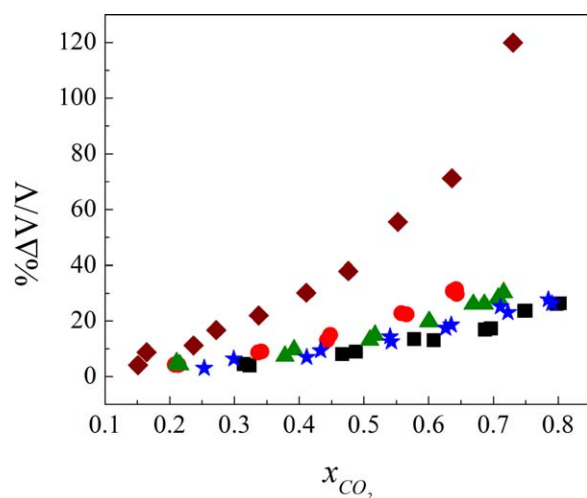
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and increasing amount of IL in the initial mixture. Figures 3–6 show the solubility of CO_2 in mixtures of toluene with [hmim][Tf$_2$N], [hmpy][Tf$_2$N], [P$_{2228}$][Tf$_2$N], and [P$_{66614}$][Tf$_2$N], respectively, at different initial liquid compositions, compared with the binary systems of CO_2 + IL and CO_2 + toluene. Supporting Information Tables S4–S7 show the complete solubility data measured for all these systems. The highest CO_2 solubility reported for each ternary isotherm is the cloud point, except in cases where no phase split had occurred even at the high pressure limit of the experimental apparatus.

Figures with the CO_2 uptake isotherms for the ternary systems can be found in Supporting Information Figures S1–S6. The figures compare the four different ILs at each temperature (298 and 313 K) and each initial IL + toluene composition (0.30, 0.50, and 0.70 mole fraction IL). The solubility of CO_2 in the [P$_{66614}$][Tf$_2$N] + toluene mixture is always higher than in the mixtures with the other three ILs. This is consistent with the binary results, where CO_2 had a higher solubility in pure [P$_{66614}$][Tf$_2$N] at both 298 and 313 K than in the other three pure ILs. For the ternaries, the higher solubility in the [P$_{66614}$][Tf$_2$N] + toluene mixtures is particularly obvious at the higher temperature—313 K. At 298 K, the solubility of CO_2 in the other three pure ILs was virtually identical. This is not the case for the mixtures with toluene. For all three initial IL + toluene compositions at 298 K, the CO_2 solubility is lowest in [hmpy][Tf$_2$N] + toluene and highest in [hmim][Tf$_2$N] + toluene (almost as high as in [P$_{66614}$][Tf$_2$N] + toluene for the 50/50 initial mixtures).
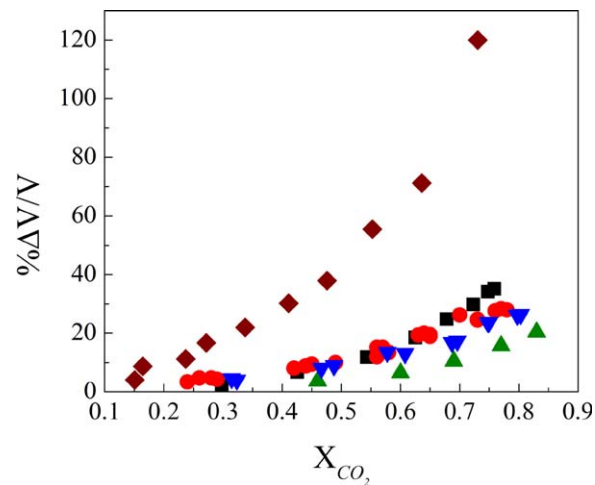
Cloud points

Cloud points (the pressure at which a liquid-liquid phase split occurs) are observed in mixtures of [hmim][Tf$_2$N] + toluene + CO_2 for all the initial liquid compositions at 313 K but only at 0.30 and 0.50 initial mole fraction of IL

Figure 9. Total volume expansion at 313 K of ◆, Toluene; ■, [hmim][Tf$_2$N][24]; ●, [hmpy][Tf$_2$N]; ▼, [P$_{2228}$][Tf$_2$N]; ▲, [P$_{66614}$][Tf$_2$N][25] by adding CO_2.

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at 298 K. No cloud points were obtained for this IL at 333 K at pressures below 8 MPa, so this temperature was not studied for the other IL mixtures. Cloud points are observed for initial IL + toluene mixtures containing both 0.30 and 0.50 mole fraction of IL with [hmpy][Tf$_2$N] and [P$_{2228}$][Tf$_2$N] but only for an initial IL + toluene mixture containing 0.30 mole fraction of IL with [P$_{66614}$][Tf$_2$N]. This is true for both 298 and 313 K. Recall that at 313 K the highest pressure investigated was the pressure limit of the apparatus—8.2 MPa. However, at 298 K the highest pressure investigated was the pressure at which a liquid CO_2 phase appears—about 6 MPa. As shown in Figure 7, cloud point pressures are lower at lower temperature and lower initial mole fractions of IL in the IL + toluene liquid mixtures. It is observed that at the same initial composition of IL and different temperature, the same composition of CO_2 in the liquid mixture is required to induce a phase split for that IL. This behavior agrees with qualitative[53,54] and quantitative[37] ternary data for CO_2 + IL + methanol and CO_2 + IL + water systems shown by several authors. They show pressure-temperature diagrams at defined ternary system compositions, where the phase split pressure increases with increasing temperature until a tricritical point appears, that is, the high pressure and temperature point where the three phases coexist. Furthermore, previous work[21,26–28] has shown that cloud points are not observed when the initial composition of the polar organic compound is low in the IL phase. The same situation occurred with toluene mixed with the ILs studied here; a higher pressure is required to induce the second liquid phase when the amount of organic in the IL is small. Note that in all cases there is more than sufficient vapor phase volume (more than 50% of the volume in the cell) to allow the system to phase split if that were the thermodynamic equilibrium state.

In summary, one can most easily separate toluene from an IL using CO_2 to induce the formation of a second liquid phase, when the temperature is low (298 K) and there is a large amount of the organic dissolved in the IL. This scenario provides the lowest phase split pressures.

Figure 8. Total volume expansion at 313 K of ◆, Toluene; ●, 0.30 mole fraction of initial [P$_{2228}$][Tf$_2$N] in the [P$_{2228}$][Tf$_2$N] + toluene mixture; ▲, 0.50 mole fraction of [P$_{2228}$][Tf$_2$N] in the [P$_{2228}$][Tf$_2$N] + toluene mixture; ★, 0.70 mole fraction of [P$_{2228}$][Tf$_2$N] in the [P$_{2228}$][Tf$_2$N] + toluene mixture; ■, [P$_{2228}$][Tf$_2$N] by adding CO_2.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Volume expansion

The liquid-liquid phase split occurs because the concentration of CO_2 in the liquid mixtures increases at a higher pressure, which increases the volume of the liquid phase. This expansion decreases the ability of the toluene and the IL to solvate each other, resulting in the phase split.

Total volume expansion[55] is calculated with Eq. 1, where V_L is the actual volume of the mixture when CO_2 is added and V_2 is the initial volume of the IL or the IL + toluene mixture

$$\frac{\Delta V}{V}\,(\%) = \frac{V_L(T,P,x_1) - V_2(T,P_0)}{V_2(T,P_0)} \cdot 100 \qquad (1)$$

The total volume expansion of toluene when adding CO_2 to the liquid phase is very high compared with ILs. This situation can be observed in Figure 8, where 0.70 mole fraction of CO_2 in toluene expands the solution to 100% more than its initial volume, while $[P_{2228}][Tf_2N]$ at the same condition expands only 17%. The small expansion of IL + CO_2 systems can be attributed to the strong Coulombic forces that exert a large free energy penalty for separation of the cations and anions. Separation into two liquid phases, one rich in IL and the other rich in toluene, minimizes the free energy. Volume expansion depends mainly on the concentration of CO_2 in the liquid phase and it has a very small dependence on temperature.

From Figure 8, it is clear that mixtures with larger initial concentrations of toluene have higher volume expansions and these are the same mixtures that have lower cloud point pressures. Therefore, larger volume expansion of the ternary liquid mixture can be associated with milder conditions for obtaining a liquid-liquid phase split. This tendency is also observed in the other three ILs. Note that in the binary systems, larger volume expansion is observed for $[hmim][Tf_2N]$ and a smaller volume expansion is observed for $[P_{66614}][Tf_2N]$ (Figure 9). This is consistent with the phase split pressure being lower for $[hmim][Tf_2N]$ than $[P_{66614}][Tf_2N]$.

Conclusions

Binary solubility isotherms of CO_2 were measured in toluene and two ILs for high pressure phase equilibrium, $[hmpy][Tf_2N]$ and $[P_{2228}][Tf_2N]$. These data were contrasted with ternary solubility isotherms of CO_2 in mixtures of toluene and four ILs, $[hmim][Tf_2N]$, $[hmpy][Tf_2N]$, $[P_{66614}]$ $[Tf_2N]$, and $[P_{2228}][Tf_2N]$, obtaining cloud points at determined conditions for all systems.

Solubility of CO_2 in liquid phases measured in this work increases with decreasing temperature and is enhanced by increasing the pressure of the system. The observation of cloud points in ternary systems is favorable when the concentration of toluene in the IL is high and when the temperature is low, because they are produced at lower pressures. This condition also coincides with a larger volume expansion of the liquid. Toluene can be separated from all the ILs studied in this work. A lower cloud point pressure is obtained when toluene is separated from $[hmim][Tf_2N]$, followed closely by $[hmpy][Tf_2N]$. $[P_{2228}][Tf_2N]$ has the same behavior as $[hmim][Tf_2N]$ and $[hmpy][Tf_2N]$ at 313 K but induces the phase split at higher pressure at 298 K. $[P_{66614}][Tf_2N]$ only showed a cloud point at higher compositions of toluene in the initial mixture with IL and high pressures were required to induce a second liquid phase with this compound.

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