Impact of water on the $[C_4C_1im][Ac]$ ability for the CO_2/CH_4 separation

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ABSTRACT

The water impact on the CO_2 and CH_4 solubilities and their selectivity in $[C_4C_1im][Ac]$ was evaluated for $[C_4C_1im][Ac]:H_2O$ molar ratios of 5:1, 2:1, 1:1, and 1:2, for temperatures ranging from (293 to 363) K and pressures up to 70 MPa. In addition, density and excess molar volumes of $[C_4C_1im][Ac]$ + water binary systems were measured aiming at understanding the impact of the solvent structure on the gas solubilities. Water is shown to improve the IL capability to solubilize CO_2, with equimolar molar ratios leading to enhanced solubilities for pressures up to 5 MPa, whereas $[C_4C_1im][Ac]:H_2O$ molar ratios of 5:1 and 2:1 present higher CO_2 solubility at higher pressures. The impact of water on the solubility of methane, on the other hand, is small, with only a slight enhancement of methane solubility at high pressures observed. The favorable impact of water, on the carbon dioxide solubility, lead to enhanced CO_2/CH_4 ideal selectivity.

1. Introduction

The CO_2 separation from gaseous effluents is one of the major challenges that researchers have been addressing [1]. Aiming at meet environmental regulations, CO_2 emitting industries worldwide are attempting at developing and implement novel carbon capture technologies [1].

The discovery of pre-salt fields and environmental concerns related to the large amounts of carbon dioxide within the oil and gas reservoirs pose a significant challenge to the natural gas sweetening longstanding and mature technologies [2]. Although the major oil companies involved in the exploration of these fields are committed not to vent the naturally produced CO_2, the high cost, and space and weight requirements of feasible separation units raise striking challenges, prompting the need for groundbreaking developments.

Processes aiming at CO_2 capture based on chemical absorption tend to operate at low pressures and rely on monoethanolamine (MEA) or its commercial derivate (KS-1), developed by Mitsubishi Heavy Industries, being the reference solvent used worldwide, but others, like methyldiethanolamine (MDEA)/piperazine or 2-amino-2-methyl-1-propanol, are also available for this separation [3]. On the other hand, for physical absorption the Selexol process stands among the most used. Although widely and successfully implemented both technologies present important economic and environmental disadvantages that researchers have been addressing [4].

Ionic liquids (ILs), a new class of solvents with outstanding properties, present high CO_2 solubility (in mole basis), high selectivity, low volatility, good thermal stability, and have a very tunable structure that allows the design of compounds that can meet the requirements of a given process. There has been an increasing interest from both academia and industry, and it is widely accepted that ILs are good candidates for CO_2 capture [5]; however, only ILs that present chemical reaction with CO_2 have shown to be solvents with promising capabilities at low temperatures and moderate pressures, to fulfill industrial requirements [6]. Among the continuous growing number of ILs that present chemisorption, the 1-butyl-3-methylimidazolium acetate ($[C_4C_1im][Ac]$) has attracted most interest [7–13]. Shifflett et al [7,9]. have demonstrated the viability of its use at industrial scale. Furthermore, by showing a good sorption capability at high pressures on the physical absorption regime, $[C_4C_1im][Ac]$ presents an interesting advantage when compared with other chemical solvents such as amines.

It is widely accepted that the presence of water, even at very low concentrations, have a negative impact on the carbon dioxide solubility but, few studies have focused on evaluating water real impact on the sorption capability over the entire concentration range. [14–,15,16,17,18,19,20,21,22,23] Baltus et al. [14] showed that water had a minor effect on the physisorption of CO_2 in ILs on environments with a relative humidity of 40% or less. For ILs presenting chemisorption the accepted knowledge was that water would inhibit chemisorption, with authors applying procedures to dry the ILs aiming at enhancing the chemical reaction. However, due to the ILs hygroscopic nature, the ILs water content, despite the drying procedures adopted, is

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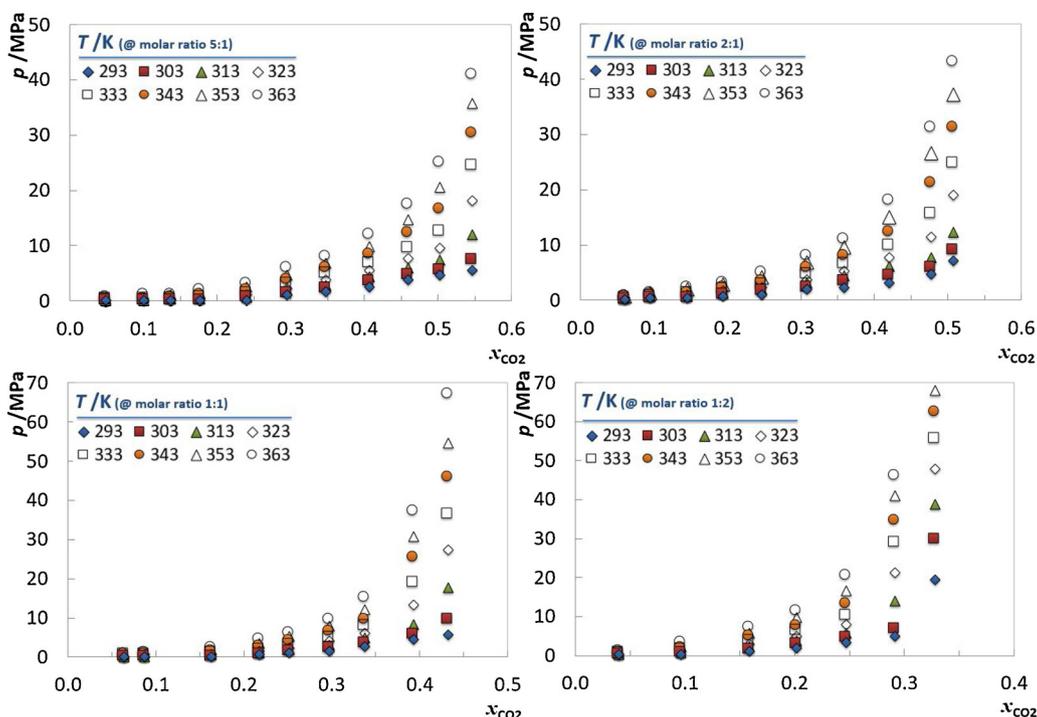
Fig. 1. *pTx* diagrams for the systems CO_2 + $[C_4C_1im][Ac]$ + H_2O at different IL:H_2O molar ratios.
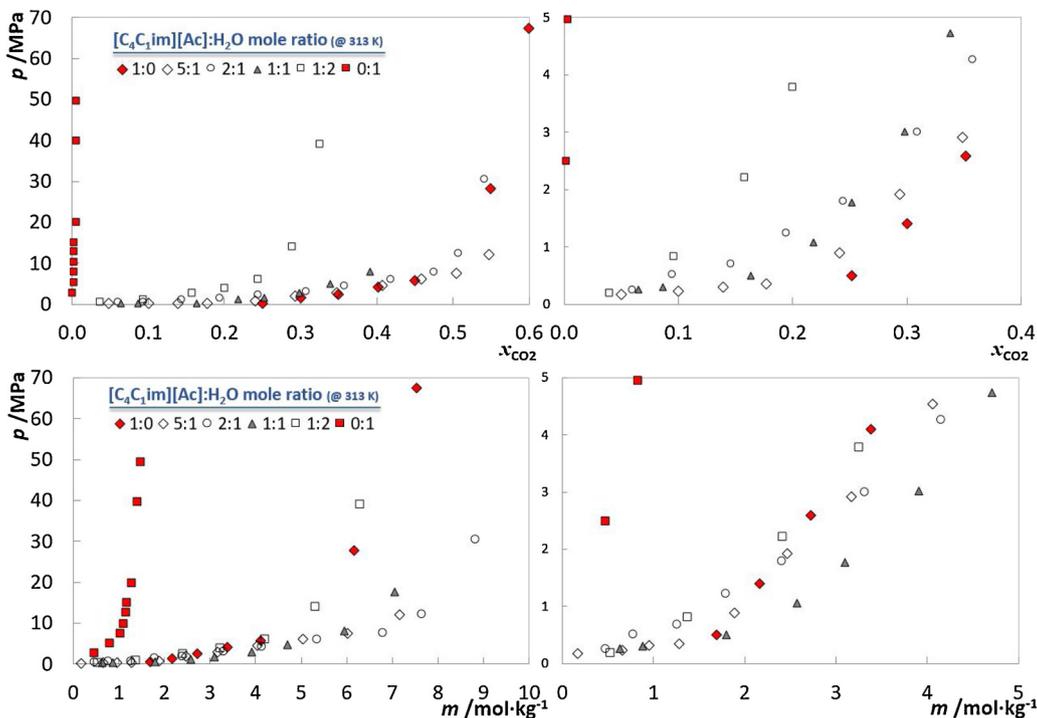
Fig. 2. *pTx* (top) and *pTm* (bottom) diagrams for the systems CO_2 + $[C_4C_1im][Ac]$ + H_2O, at 313 K. CO_2 + $[C_4C_1im][Ac]$ and CO_2 + H_2O data from literature (low concentration zoom on the right) [8,34].

always significant and therefore, at industrial operations the systems may not be strictly binary but to a large extent a ternary system of CO_2 + IL + water.[7] In fact several authors suggested that water may have a favorable contribution to the chemical reaction between ionic liquids and CO_2. In previous works [18–,19,20,21] we have shown that water plays a vital role on promoting the chemical reaction between the species for the system $[C_4C_1im][Ac]$ + CO_2. In the presence of water, $[C_4C_1im][Ac]$ and CO_2 react forming 1-butyl-3-methylimidazolium-2-

carboxylate, involving also the isomerization process and the formation of a "transient" CO_2−carbene complex, and acetic acid [18,19]. Moreover, the formation of bicarbonates (HCO_3^-) was also observed and their concentration increases with the water content increase, not affecting the carboxylate formation. [20,21] However, the water impact at moderate to high pressures, out of the chemisorption region, remains unclear and worth exploring. The current literature remains contradictory on this subject. Stevanovic et al. [22] reported a decrease of
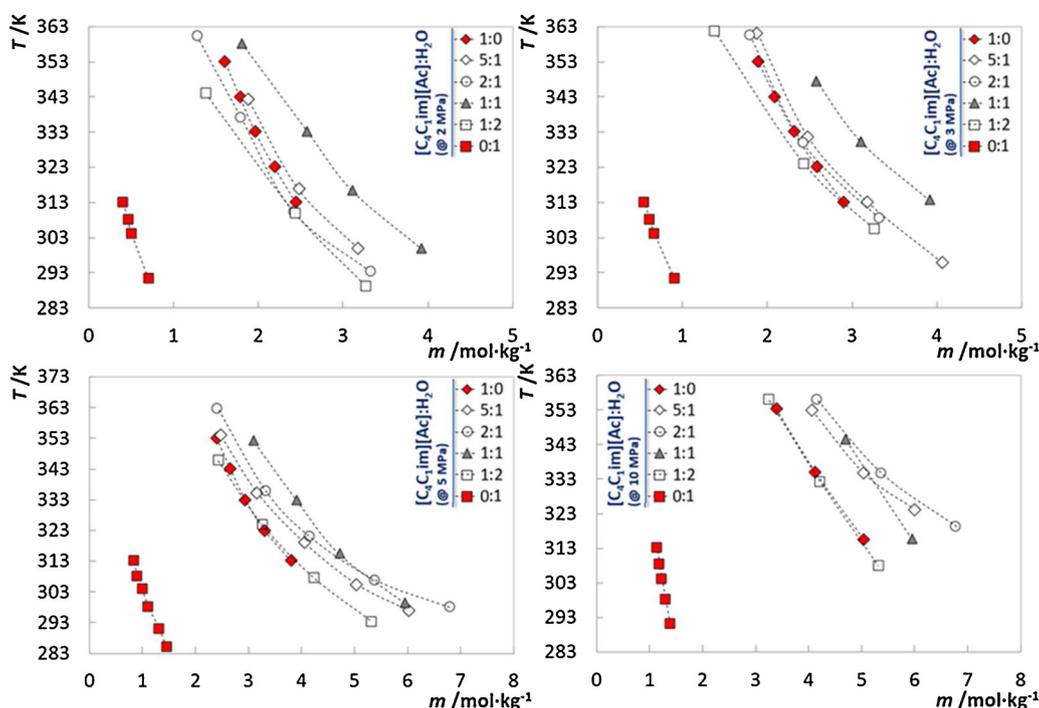
Fig. 3. pTm diagrams for the systems CO_2 + $[C_4C_1im][Ac]$ + H_2O, at 2, 3, 5 and 10 MPa. The lines are guides to the eyes. CO_2 + $[C_4C_1im][Ac]$ and CO_2 + H_2O data was taken from literature [8,34].
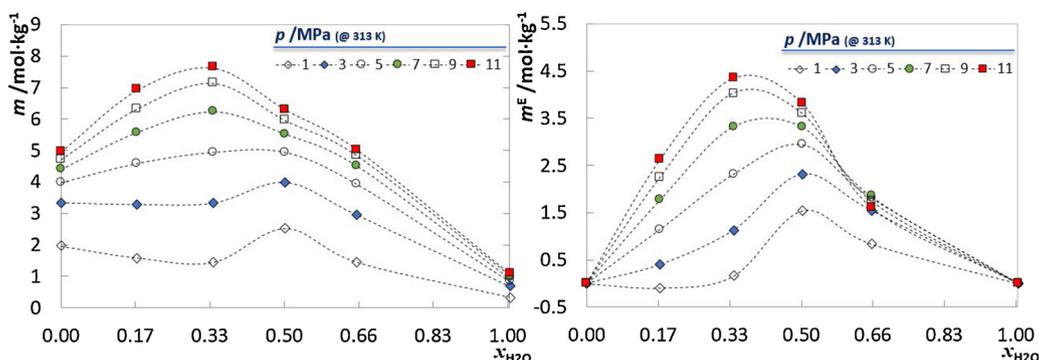
Fig. 4. CO_2 molality and excess molality (m^E) in $[C_4C_1im][Ac]$ + H_2O system as a function of the water mole fraction, at 313 K. Lines are guides for the eyes.

83% in CO₂ absorption for 1-butyl-3-methylimidazolium acetate $[C_4C_1im][Ac]$ with 0.6 mol fraction of water at 303 K. Furthermore, the authors state that "*water not only renders the chemical reaction between the gas and the ionic liquid less favorable but also lowers the (physical) solubility of the gas as it competes by the same solvation sites of the ionic liquid*". Later, Lei and coworkers [5] reviewed the water influence on gas solubility in ILs in three distinct scenarios: *i*) degradation, where water reacts with the IL; *ii*) dilution; with water diluting the ILs and inhibiting the CO₂ dissolution *iii*) enhancement; where the presence of water promotes the CO₂ chemical absorption.

It was only recently that Anderson *et al* [23]. developed a new acid gas stripping solvent for removal of carbon dioxide from natural gas sources based on ionic liquids with carboxylate anions where the water content was carefully controlled at near equimolar amounts. As positively identified by the authors [23], the ionic liquid/water mixtures showed enhanced carbon dioxide solubility relative to both anhydrous and aqueous IL solutions. Anderson *et al* [23]. also studied the impact of large molar contents of water on the solubility of CO₂ in acetate-based ILs, concluding that H_2CO_3 formation improves the CO₂ solubility at equimolar proportions, attributing to water an important role in CO₂ absorption. The industrial relevance of the results obtained by adding water to acetate-based ILs led the authors to patent the use of aqueous

solutions of ionic liquids to capture CO₂.[24] In these acetate-based IL + water mixtures, equimolar proportions are ensured to be the best conditions, whereas a previous patent on the $[C_4C_1im][Ac]$ + water use as absorbent for CO₂ showed interesting results with a water content of 14 wt.% (water mole fraction of 0.66). [25] Recently, Gómez-Coma et al. [26] evaluated a hybrid solvent, composed of $[C_2C_1im][Ac]$ and water, on a hollow fiber contactor for a continuous CO₂ capture (from a 15% CO₂ + 85% N₂ stream) reporting that a mixture of 30 vol % of water allows to achieve a 72.5% CO₂ capture efficiency. Although, the authors [26] come to the conclusion that is the water impact on the viscosity, on top of the reversible chemisorption, that allows achieving the high capture efficiency reported and place the proposed separation unit competitive against traditional processes based on power stations and alkanolamines.

The impact of water in the solubility and on the solvent selectivity at high pressures stands as extremely relevant, especially if one considers that most potential streams to be treated have some water in their composition. The concept of water as an enhancer of the absorption rather than an impurity stands as a paradigm shift capable of changing ways of thinking and contributing to the development of new methods for CO₂ capture. Although the water impact in the CH₄ solubility and ultimately on the separation efficiency and CO₂/CH₄ selectivity stands
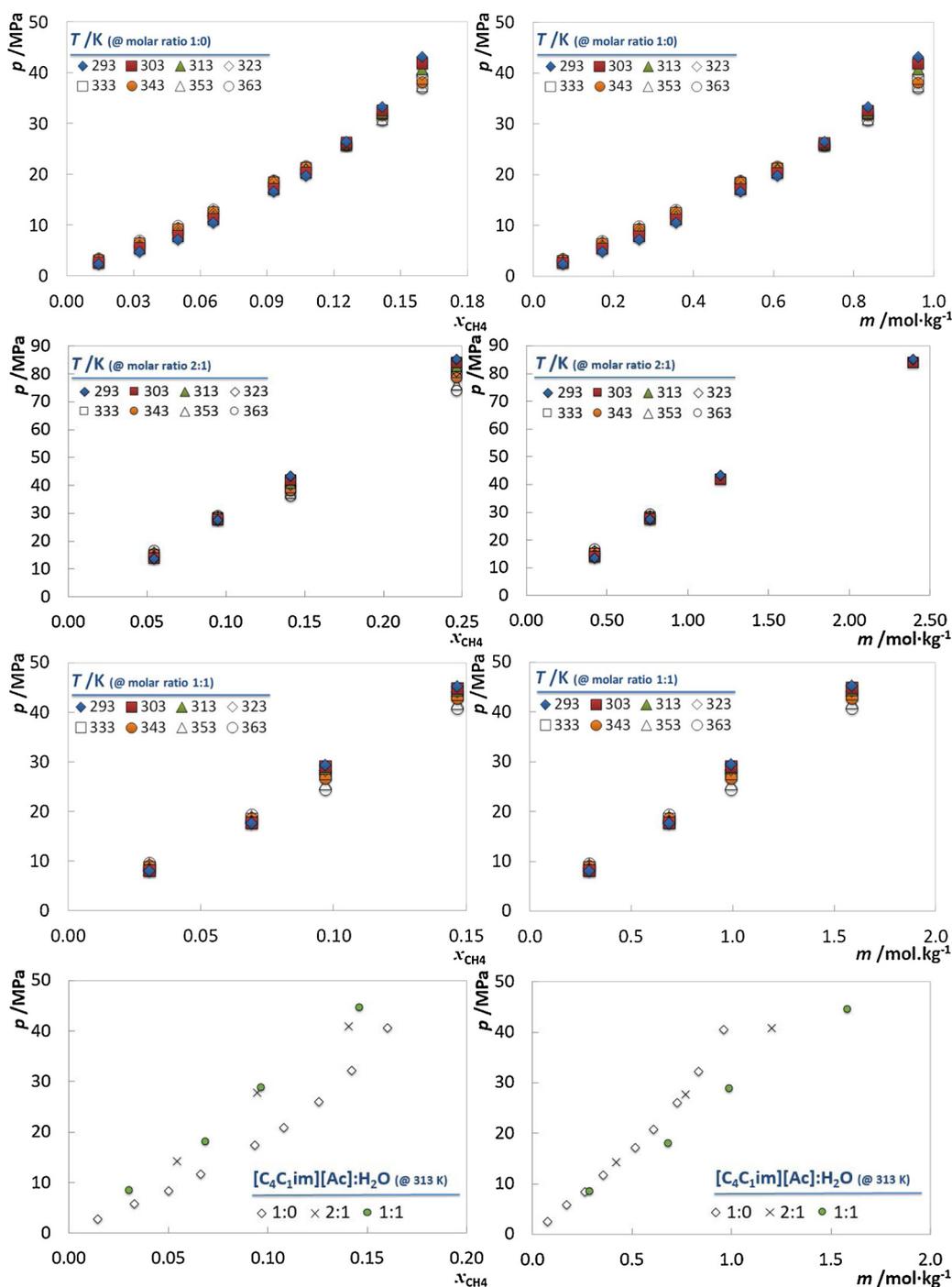
Fig. 5. pTx and pTm diagrams for the systems CH_4 + $[C_4C_1im][Ac]$ + H_2O.

highly relevant if one aims at developing a capture/separation unit to operate at medium to high pressures, it real impact has never been addressed.

In this work the impact of water on CO_2 and CH_4 solubilities and selectivity in the $[C_4C_1im][Ac]$ IL is evaluated. $[C_4C_1im][Ac]$:H_2O molar ratios of 5:1, 2:1, 1:1, and 1:2 were experimentally investigated for temperatures ranging from (293.2 to 363.2) K and pressures up to 70 MPa. In addition, density data of $[C_4C_1im][Ac]$ + water binary systems were measured to further analyze the excess molar volumes in the ranges of (283.2 to 363.2) K and (0.1 to 95) MPa aiming at evaluate the impact of the volume variations on the gas solubility.

2. Experimental section

2.1. Materials

The 1-butyl-3-methylimidazolium acetate, $[C_4C_1im][Ac]$, was acquired from Iolitec GmbH with a mass purity greater than 99%. Prior to its use, the IL was further purified through vacuum (1 Pa), moderate temperature (303 K) and continuous stirring for a period greater than 48 h. The procedure adopted aims at reducing to negligible values both the water and other volatile compounds. The water content measured by Karl-Fischer titration, after purification, was found to be lower than 100 ppm. ¹H and ¹³C NMR were used to confirm the purity of the IL before and after the experimental measurements.
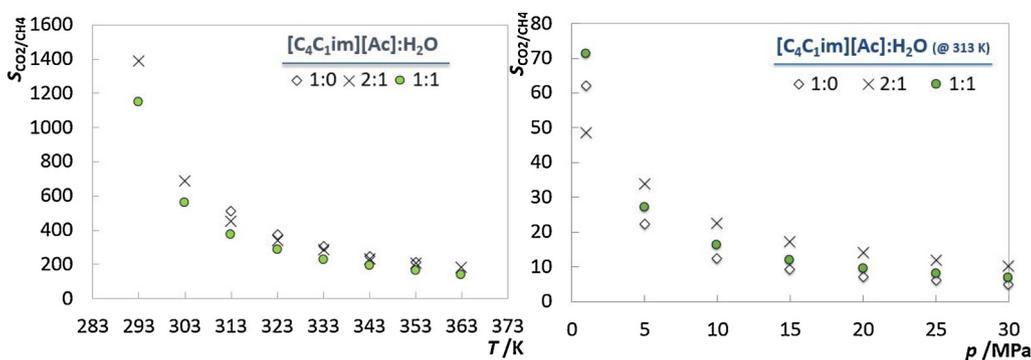
Fig. 6. Ideal CO$_2$/CH$_4$ selectivity ($S_{CO2/CH4}$) for the studied systems calculated in molality basis.
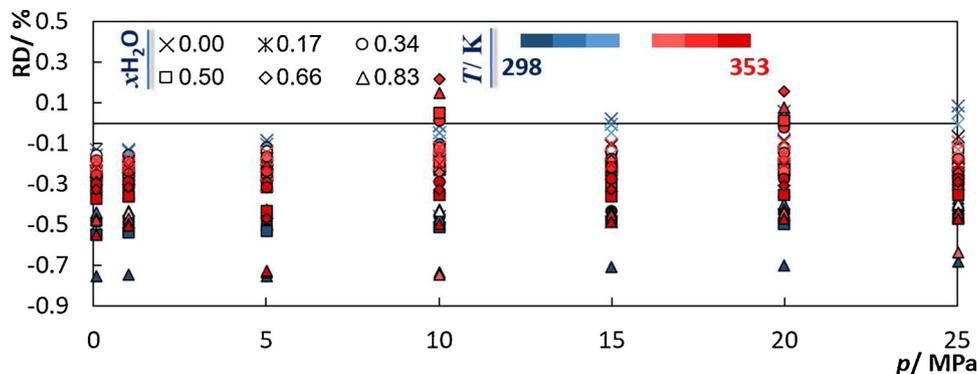

Fig. 7. Relative deviation in percentage (RD /%) between experimental and literature density data [22].

Ultra-pure water (double distilled, passed through a reverse osmosis unit, and further treated with a Mili-Q plus 185 water purification apparatus) with a resistivity of 18.2 MΩ·cm, a total organic carbon lower than 5 μg·L^{-1}, and particles smaller than 0.22 μm was used to prepare the aqueous mixtures. Carbon dioxide and methane were acquired from Air Liquide with a mass purity of ≥ 99.999% and ≥ 99.998%, respectively.

2.2. Solubility measurements

Both the apparatus and the methodology used in this work were fully described in previous publications [8,27,28] and shown to adequately and accurately measure gas–liquid equilibrium for a wide range of fluids, pressures and temperatures. The high pressure equilibrium cell is based on the synthetic method and consists of a horizontal hollow stainless-steel cylinder, closed at one end with a movable piston and at the other end with a sapphire window, from which the operator follows the behavior of the sample with pressure and temperature. An exact mass of IL, determined using a high weight/high precision balance (Sartorius LA200 P) with an accuracy of 1 mg, was introduced in the cell followed by an exhaustive *in situ* drying procedure (1 Pa, 303 K and stirring) to ensure the removal of any atmospheric gas and water that may have been absorbed during the IL manipulation. For the aqueous mixtures preparation, water was added to the cell after the IL, with the system still under vacuum, through a flexible pressure capillary and its mass measured with the mentioned high weight/high precision balance. The gas was introduced under pressure, from an ultra-lightweight composite cylinder, by means of a flexible pressure capillary and its mass measured also with the high weight/high precision balance.

Once the mixture with known composition is prepared and the desired measurement temperature achieved, the pressure is increased until the system becomes monophasic. The pressure is then slowly decreased until a phase change is observed and then slowly increased until the last bubble disappears. The methodology is repeated by measuring

at each step equilibrium pressures lower than those measured in the previous attempts. The lowest pressure, at which all the gas absorbs into the liquid phase represents the equilibrium pressure, at that fixed temperature and composition. The pressure was measured by a piezoresistive silicon pressure transducer (Kulite HEM 375) fixed directly inside the cell, to reduce dead volumes, with an accuracy better than 0.2%.

2.3. Density measurements

Densities were measured using an Anton Paar high pressure density meter DMA-HPD equipment coupled to a mPDS 5 unit with a standard uncertainty in the density of 5·10^{-4} g·cm^{-3} in the (283–363 K) temperature and (0.1–95 MPa) pressure ranges. A Julabo MC bath was used for the thermostatization of the measuring cell with a temperature stability of 0.01 K and an uncertainty of 0.1 K. The pressure was measured using a Kulite HEM 375 transducer with accuracy better than 0.2% and placed directly in a ¼ in. stainless steel line, between the measuring cell and the movable piston to minimize dead volumes. More details regarding this equipment, calibration, viscosity corrections and methodology can be found in previous publications [29,30].

3. Results and discussion

3.1. Carbon dioxide solubility

The carbon dioxide solubility in [C$_4$C$_1$im][Ac] + water mixtures has been the focus of a large number of studies during the last years [18–26,31]. Two main mechanisms of solvation have been identified: chemisorption and physisorption. For physisorption, the CO$_2$ sorption mechanism is well established and widely accepted. However, the chemisorption mechanism, while well described for the neat IL here studied, [18–,19,20,21,23], is not fully understood in presence of solvents and seems to be dependent on the solvent chemical nature and
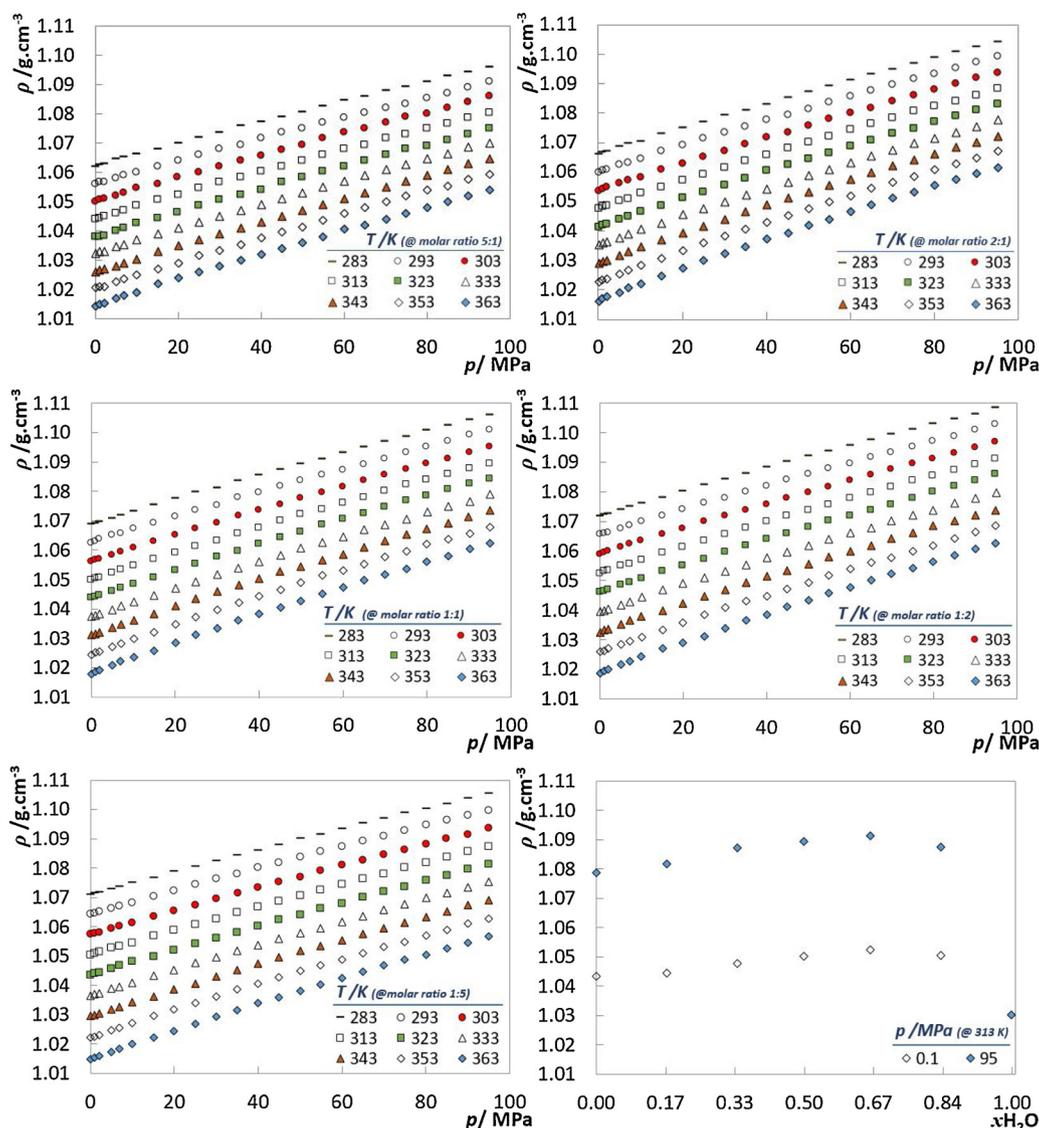
Fig. 8. Density as a function of pressure at different temperature and [C$_4$C$_1$im][Ac]:H$_2$O molar ratios.

solute-solvent interaction [32,33].

The impact of water on the CO$_2$ solubility in [C$_4$C$_1$im][Ac] is here studied in the concentration range from $x_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O} + n_{IL}} = 0.05$ to 0.55, temperature range from (293.2 to 363.2) K, pressures up to 70 MPa, and IL:H$_2$O molar ratios ($\frac{n_{IL}}{n_{H_2O}}$) of 5:1, 2:1, 1:1, and 1:2, as depicted in Fig. 1 and reported in detail in supporting information (Tables S1 to S4).

As shown in Fig. 1, the increasing water content does not inhibit the chemical reaction between [C$_4$C$_1$im][Ac] and CO$_2$; the four mixtures evaluated present an initial region with low pressure sorption, typical of chemisorption, followed by physical sorption leading to the well-known exponential increase of the equilibrium pressure with the CO$_2$ content. However, as depicted in Fig. 2, the equilibrium pressures, at 313.2 K, clearly reveal that the water has an important impact on the gas solubility in the IL.

As depicted in Fig. 2, if the CO$_2$ solubility is evaluated in mole fraction, the presence of even smaller amounts of water leads to higher equilibrium pressures than those determined for the neat IL. However, if the analysis is made in molality basis, *i.e.* moles of CO$_2$ per kilogram of solvent, removing the molecular weight effect on the solubility, the solubility actually increases due to presence of water. Three different solubility regions can be identified: up to 2 mol·kg^{-1}, from 2 to

5 mol·kg^{-1}, and above 5 mol·kg^{-1}. Up to 2 mol·kg^{-1}, water has, independently of its content, a negligible effect upon the system with equilibrium pressures similar, within the uncertainty of the experimental data, to those reported for the neat IL. For concentrations from 2 to 5 mol·kg^{-1}, water has an important effect on the solubility. In this region, while water mole ratios of 5:1, 2:1 and 1:2 present similar solubilities to the neat IL, the 1:1 mol ratio presents higher solubilities, thus lower equilibrium pressures, than the neat IL. For concentrations above 5 mol·kg^{-1}, the 1:1 mol ratio starts to present higher equilibrium pressures than the 5:1 and 2:1 mixtures, but still lower than those of the neat IL. The 1:2 ratio, on the opposite, present solubilities similar to those of the neat, with the equilibrium pressure showing the known exponential increase.

As depicted in Fig. 3, the 1:1 mixture shows the higher solubility, in molality, independently of the temperature and for pressures up to 5 MPa. The 1:2 mol ratio presents equilibrium pressures similar to those of the neat IL, in all ranges of temperature and pressure, whereas the remaining mixtures present solubility that range between those reported for the neat IL and the 1:1 mol ratio. The solubility enhancement, observed for the 1:1 mol ratio, disappears for pressures above 5 MPa and molalities higher than 5 mol·kg^{-1}.

Fig. 4 shows the CO$_2$ molality and excess molality dependence on the water molar fraction in the solvent, at 313 K. The molality and
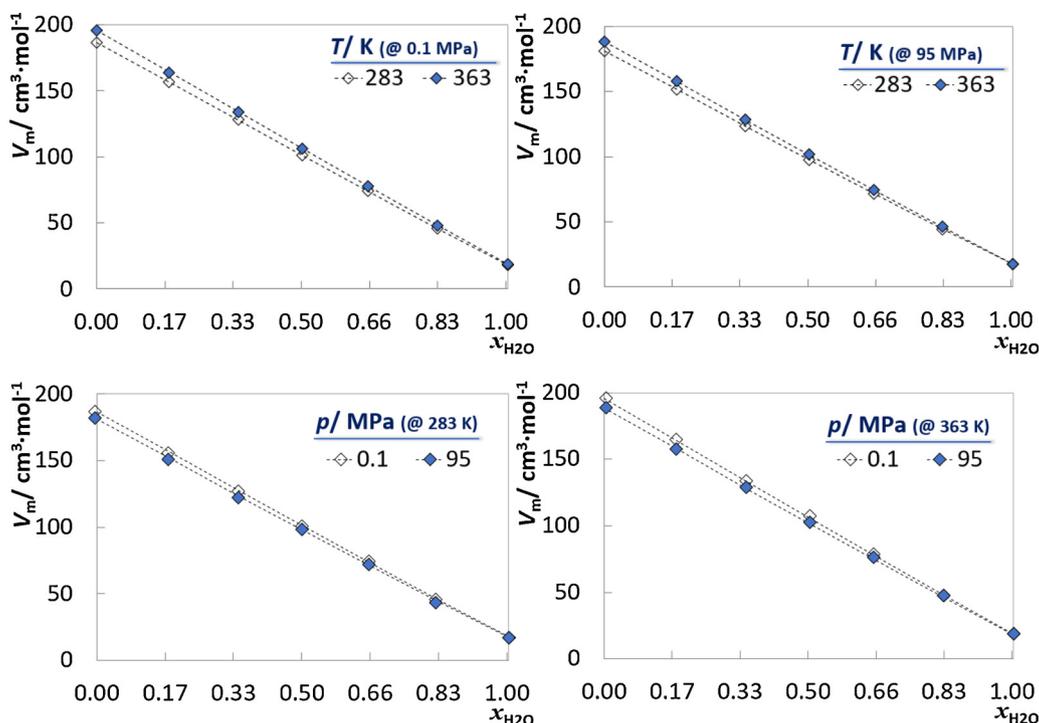
Fig. 9. Molar volumes as a function of water mole fraction for the $[C_4C_1im][Ac]$ + H_2O binary mixture, at different pressures and temperatures. The data of the pure compounds were taken from literature [44,45].
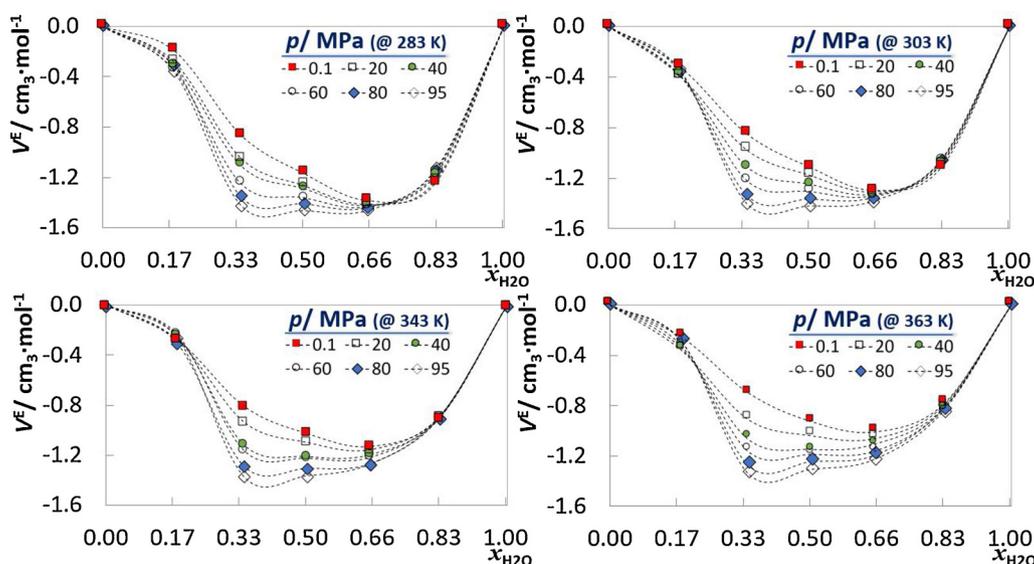

Fig. 10. Excess molar volumes for $[C_4C_1im][Ac]$ + H_2O binary mixtures as a function of water mole fraction, temperature and pressure. Lines are guides to the eyes.

excess molality show a maximum with water that changes from equimolar proportions, at pressures below 5 MPa, to IL: H_2O ratio of 2:1 (water mole fraction of 0.34). If one aims to design a process to capture CO_2 at low or moderate pressures, the equimolar IL:H_2O ratio stands out as the target condition (with an enhancement in molality, compared to the pure IL, of around 38%), while for processes operating at higher pressures the carbon dioxide capture is enhanced when using a IL:H_2O molar ratio of 2:1 (with an enhancement in molality of around 40% and 16% compared to the pure and the 1:1 molar ratio, respectively). At low to moderate pressures the carbon dioxide solubility presents a maximum at equimolar proportions, due to the formation of hydrated complex anions of the general formula $[anion… H−O−H… anion]^{2-}$ as reported previously by Anderson et al.[23]. However, the shift on the solubility maximum observed at the 2:1 mol ratio (water mole fraction

of 0.34) with increasing pressure denotes that pressure not only do not prevent the complex formation, but may impose an important entropic effect on the resulting mixture of IL cation, H_2O, hydrogencarbonate anion and carboxylic acid that allows the solvation of more carbon dioxide.

3.2. CH₄ solubility and CO₂/CH₄ selectivity

Experimental CH_4 solubilities in the neat IL and in the binary solvent for $[C_4C_1im][Ac]$:H_2O molar proportions of 2:1 and 1:1 were determined to evaluate the water impact on the CH_4 adsorption and are reported in detail in Tables S5 to S7.

As depicted in Fig. 5, water has a small impact on the methane solubility. Furthermore, if analyzed in a molality scale, the presence of

water slightly enhances the methane absorption at higher pressures, when compared to the neat IL. Although the formation of CH_4 + H_2O hydrates could enhance the gas absorption, [35,36] no hydrates were observed during the VLE mainly due to the presence of the IL, known to mitigate the hydrates formation [37–40]. Thus, the methane uptake increase must be related to the structure of the aqueous solution of the IL that seems to be favorable to the solvation of methane. Furthermore, temperature has a negative impact at low methane concentrations but a positive impact as the methane concentration increases. The cross-over point is located at methane mole fractions around 0.12 and 0.08 for the neat IL and the binary solvent at equimolar proportions, respectively.

Using CO_2 and CH_4 experimental solubility data it is possible to estimate the ideal CO_2/CH_4 selectivity ($S_{CO2/CH4}$), in molality, as depicted in Fig. 6. At low CO_2 molalities, up to $2\,mol\cdot kg^{-1}$, the solubility in the chemisorption regime, and the presence of water presents a low impact on the ideal selectivity, as depicted in Fig. 6. However, if the selectivity on the physisorption regime is evaluated, looking at the selectivity as function of pressure, the presence of water becomes more significant with a stronger impact on the ideal selectivity. In fact, the increased methane absorption is compensated by the higher CO_2 uptake at similar pressure conditions, leading thus to higher selectivities and denoting the CO_2 capture enhancement at higher pressures. This observation highlights the $[C_4C_1im][Ac]$:H_2O molar ratio of 2:1 the best solvent in terms of both capability and selectivity. Even comparing against other approaches based on composite materials, with CO_2/CH_4 selectivities around 50 at low pressures near 0.1 MPa, [41–43] the selectivities reported here are higher even for high pressure, standing the suitability of the $[C_4C_1im][Ac]$ and water mixture.

3.3. Pressure – density – temperature (pρT) for the $[C_4C_1im][Ac]$ + H_2O binary mixtures

Densities of the $[C_4C_1im][Ac]$ + H_2O system, at molar ratios of 5:1, 2:1, 1:1, 1:2 and 1:5, were determined in the 283–363 K temperature and 0.1–95 MPa pressure ranges. Stevanovic et al. [22] reported densities for the same system up to 25 MPa in the whole range of the mixture composition. In Fig. 7, the relative deviations between new and literature data is depicted as function of composition, pressure, and temperature. As seen, a good agreement between the two data collections is observed with a percentage average relative deviation ($\%ARD = \frac{100}{n}\sum_{i=1}^{n}|\rho_{exp} - \rho_{lit}|$) of 0.27%. The new experimental pρT data is depicted in Fig. 8 and the values are detailed in Tables S8 to S13 in the Supporting Information.

As seen in Fig. 8, an increase in the water content hardly changes the density values, with an almost identical behavior with pressure and temperature for all cases studied. In order to understand the water effect, molar volumes for the $[C_4C_1im][Ac]$ + H_2O binary system were calculated as a function of temperature and pressure (Fig. 9). The excess molar volumes for the studied mixtures are reported in Table S10 in the Supporting Information. The pρT data of the pure compounds were taken from literature and regressed to independent polynomial expansions as function of temperature and pressure. [44,45] It is clear that the molar volumes show a linear dependence on water mole fraction in the pressure and temperature ranges studied in this work. However, the slope of this linear dependence changes when temperature or pressure increases due to a higher impact of both variables in the property.

Fig. 10 shows the excess molar volumes for the $[C_4C_1im][Ac]$ + H_2O binary systems as a function of IL:H_2O molar ratios at different temperatures and pressures. Fig. 10 allows inferring on the intermolecular interaction between the neat compounds (negative excess molar volumes) or changes in the molecular size (positive excess molar volumes). Hydrogen bonded complexes between water and the IL are known to occur in symmetric 2:1 type complexes: [anion… H−O−H… anion]$^{2-}$ allowing one to expect a minimum on the excess molar volumes at the corresponding concentration. [23] However, the negative excess molar volumes reported present a minimum at a molar ratio of

1:2 ([IL:H_2O]; x_{H2O} = 0.66), indicating that on top of the IL−H_2O−IL complexes formed, water continuous promoting intermolecular interactions through hydrogen-bonded clusters. The observed excess molar volume minimum shifts towards lower water mole fractions while becoming less pronounced with the pressure increase. This is an indication that pressure promotes IL−H_2O−IL interactions, improving the interaction between the neat compounds at lower water contents. On the other hand, the temperature lowers the excess molar volumes of the $[C_4C_1im][Ac]$ + H_2O binary mixture at all pressures, indicating that temperature seems to mitigate the IL–H_2O interaction.

This pressure interaction-promoting phenomena stands more relevant if one pictures pressure stabilizing the species formed by the CO_2 reaction (carboxylation reaction), supporting thus the CO_2 enhanced physisorption observed with increasing pressure. [20]

4. Conclusions

The impact of water in the $[C_4C_1im][Ac]$ ability to selectively separate CO_2 from CH_4 was investigated. Water has shown to improve the IL capability to solubilize CO_2 with IL + H_2O mixtures, with water mole fraction ranging between 0.17 to 0.66, showing better performance than the neat $[C_4C_1im][Ac]$. Equimolar ratios have shown to allow enhanced solubilities at pressures up to 5 MPa, whereas $[C_4C_1im]$ $[Ac]$:H_2O proportions of 5:1 and 2:1 have shown higher CO_2 solubility at higher pressures. The enhanced impact of water in the CO_2 solubility and on the CO_2/CH_4 selectivity stands as extremely relevant especially considering that water is present on the streams to treat and therefore, can be considered an advantage rather than an impurity.

Furthermore, the CO_2/CH_4 selectivity has shown not to deteriorate by the presence of water. In fact, water enhances the selectivities at moderate to high pressure conditions. On the other hand, the presence of water is known to further improve the solvent thermophysical properties, like viscosity, and thus enhancing the mass transfer and consequently the sorption kinetics. [26,31,46] Overall, $[C_4C_1im]$ $[Ac]$:water molar proportion of 2:1 stands as the most potential solvent to separate CO_2 from CH_4 at moderate-high pressures.

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