Tetrabutylphosphonium acetate and its eutectic mixtures with common-cation halides as solvents for carbon dioxide capture

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Abstract

The absorption and desorption isotherms of CO_2 in the ionic liquid tetrabutylphosphonium acetate ($[P_{4\,4\,4\,4}][OAc]$) were experimentally determined at 343.2 K in the pressure range 0-15 bar. Analysed in a mass basis, the CO_2 absorption capacity of $[P_{4\,4\,4\,4}][OAc]$ is particularly competitive among that of phosphonium ionic liquids. A contribution of chemical absorption was evidenced from the shape of the isotherms, and a reaction scheme based on the abstraction of an acidic proton in the cation by the basic acetate anion, with a 1:2 (CO_2 to ionic liquid) overall stoichiometry, was proposed. The investigation of the solid-liquid equilibria of the mixtures of $[P_{4\,4\,4\,4}][OAc]$ with its homologous halides, namely $[P_{4\,4\,4\,4}]Cl$ and $[P_{4\,4\,4\,4}]Br$, led to the identification of eutectic behaviours, with the eutectic compositions having melting temperatures below 308.2 K, remarkably lower than the melting temperature of pure $[P_{4\,4\,4\,4}][OAc]$. The CO_2 absorption capacities of these eutectic compositions were then explored at 308.2 K, and also 343.2 K for comparative purposes. While advantageously

allowing their utilisation as CO_2-capturing solvents at lower temperatures, in comparison to pure $[P_{4\,4\,4\,4}][OAc]$ the eutectic mixtures did not lead to a major loss in CO_2 absorption capacity, with greater physisorption compensating for the reduction in chemisorption.

Keywords: ionic liquid, CO_2, absorption, tetraalkylphosphonium, eutectic.

1. Introduction

Anthropogenic emissions of greenhouse gases are a relevant contributor to the global warming of the surface of the Earth. The volume of emissions of these gases has risen critically over the last decades, surpassing the mark of 15 Gt CO_2-eq/yr in the last report of the Intergovernmental Panel on Climate Change of the United Nations, with CO_2 accounting for 85 % of the total [1]. To mitigate their pernicious effects, new regulations and international agreements have been set up over the last decades, culminating so far in the Paris Agreement (2016) under the United Nations Framework Convention on Climate Change [2]. In this agreement, the objective of holding the increase of the global average temperature to well below 2 ºC above pre-industrial levels was established. To achieve this objective, improved techniques for the reduction of emissions of greenhouse gases of industrial origin are required, such as for example CO_2 capture technologies [1,3].

The most mature technologies for CO_2 capture are gas-liquid absorption-desorption processes. The absorbents commonly used consist of aqueous solutions of amines or amine blends. Unfortunately, these solvents present a series of important drawbacks: chemical degradation which subsequently leads to corrosion of the process units; large emissions due to high volatility and aerosols formation; and the vast

amounts of energy (typically 2-4 GJ per metric ton of CO_2) required to regenerate the solvent in the reboiler (desorption stage) [4,5], in good part as a result of the large latent heat of vaporisation of water. Thus, there is an urgent need for the development of alternative solvents to overcome these problems and render the CO_2-capturing process more sustainable. Among a number of options, generally considering water-lean solvents [6], the use of ionic liquids has arisen as an attractive opportunity.

Ionic liquids [7] are salts with a relatively low melting or glass transition temperature (an arbitrary mark of 100 ºC is usually considered), and thus they can be envisioned as alternative solvents to molecular liquids and electrolyte solutions in industrial processes at typical operation temperature ranges. Due to their integrally ionic character, they present a negligible volatility over the entire span of temperatures in which they are thermally stable, thus preventing both loss of solvent by evaporation and contribution to atmospheric pollution. Moreover, the physical and chemical properties of ionic liquids can be tailored for a specific application to a certain extent by judicious selection and combination of the constitutive ions [7,8]. In the context of CO_2 capture, both physical and chemical absorptions are possible in ionic liquids, and to different extents, depending on the nature of cation and anion. The absorption of CO_2 through an exclusively physical mechanism has been reported in many ionic liquids [9], with the best capacities at a moderate pressure (ca. 15 bar) reaching values of up to ca. 0.50 in CO_2 mole fraction, for example in the case of trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)amide at 293 K [10]. (This is interestingly in contrast to the absorption capacity of gases such as N_2 or O_2, that accompany CO_2-containing flue gases in industrial environments, and which remain barely soluble in ionic liquids in general [11].) It must be noted, however, that the relatively high molar mass of ionic liquids for which these good molar physical absorption capacities are obtained result in

much more moderate absorption capacities if interpreted on a mass basis. On the other hand, the functionalisation with an amino group [12], the selection of an aromatic heterocyclic anion [13,14], or the combination of a basic anion with a cation containing a sufficiently acidic proton (e.g. acetate with a 1,3-dialkylimidazolium cation, where the proton in the C2 position has a certain acidity) [15,16], among other strategies [17], have been found to result in ionic liquids leading to a chemical reaction with CO_2. The 1:1 stoichiometry achieved by ionic liquids containing aromatic heterocyclic anions is superior to that obtained with ionic liquids comprising an amino-functionalised ion, which adheres not unexpectedly to the 1:2 (CO_2-to-absorbent) stoichiometry already known for primary and secondary amines in the benchmark processes. The reaction between CO_2 and 1,3-dialkylimidazolium acetates also corresponds to the 1:2 stoichiometry; but the lower formula weight of these ionic liquids leads, in terms of moles of CO_2 reacted per unit mass of absorbent, to comparable values with ionic liquids with the aromatic heterocyclic anion (which usually contain a bulky tetraalkylphosphonium anion to result in a sufficiently low melting temperature of the salt [18,19], resulting unavoidably in a high formula weight too). Moreover, the acetate may be considered as an affordable and environmentally friendly anion, which would grant it a good acceptance by the industry. Unfortunately, one relevant problem of 1,3-dialkylimidazolium acetates in an absorbing-desorbing process scheme is their relatively limited thermal stability (if thinking of the temperatures that would be needed in the desorbing stage) [20,21]. For example, for the ionic liquid 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]), although regular onset decomposition temperatures in the range 475-500 K were most consistently reported from dynamic thermogravimetric analysis (TGA) [20-22] (and also a more conservative value of 427 K for the 5 % onset decomposition temperature [22]), a decomposition level of 1 %

mass loss after 10 h was found already for a temperature of 375 K via isothermal TGA experiments [20].

In trying to keep the advantage of the acetate anion while improving the thermal stability of the ionic liquid, a phosphonium cation may be considered. For example, from the kinetics of thermal decomposition reported for the ionic liquid tetrabutylphosphonium acetate ([$P_{4\,4\,4\,4}$][OAc]) through TGA isothermal runs [23], it can be estimated that the temperature leading to 1 % mass loss after 10 h would be 411 K – a substantial improvement with respect to [C_2mim][OAc] (see the paragraph above). Although tetraalkylphosphonium cations lack the proton in the C2 position of the imidazolium ring that is key in the mechanism of chemical reaction of 1,3-dialkylimidazolium acetates with CO_2 [16], it has been found that the acidity of protons bound to the carbon in the alpha position of the central phosphorous atom can be also acidic enough for the chemisorption of CO_2 to occur; particularly if the tetraalkylphosphonium cation is paired with a sufficiently basic anion [24-26].

Thus, in this work we have investigated the capacity of [$P_{4\,4\,4\,4}$][OAc] to act as absorbent in CO_2-capture processes. The tetrabutylphosphonium cation, $[P_{4\,4\,4\,4}]^+$, has been selected among other possible tetraalkylphosphoniums because its mid-term thermal stability when paired with the acetate anion is well characterised [23], and its toxicity towards a number of microorganisms is known to be low (as opposed to some of its homologues with longer alkyl substituents) [27,28]. Moreover, $[P_{4\,4\,4\,4}]^+$ has the potential to be cheap and available in the large scale, which in combination with the acetate anion can result in an ionic liquid with a competitive cost at industrial production level [29].

On the downside, [$P_{4\,4\,4\,4}$][OAc] is solid at room temperature, with a reported melting temperature of 329 K at atmospheric pressure [23]. A possible strategy to

achieve liquefaction at lower temperatures is the development of eutectic mixtures; for instance by mixing [P4 4 4 4][OAc] with another ionic liquid, so that the favourable attributes of ionic liquids (such as negligible vapour pressure) are fully preserved. In fact, this is in itself one manner of further tuning the properties of ionic liquids [30]. In this work, a potential eutectic behaviour has been explored for mixtures of [P4 4 4 4][OAc] with tetrabutylphosphonium halides (namely [P4 4 4 4]Cl or [P4 4 4 4]Br), as these halides may be precursors in a possible synthesis route of [P4 4 4 4][OAc] by metathesis with an acetate salt; and the utilisation of the resulting mixtures of ionic liquids would avoid the most tedious stage of such synthesis procedure (i.e. a good completion of the metathesis reaction). The obtained eutectic compositions have been investigated for their CO_2 absorption capacity at near-ambient temperature.

Rigorous experimental data on thermodynamic fundamentals, like the ones reported in this work, are of vital importance for the development of a technology of great interest for the CO_2 capture industry.

2. Experimental

2.1. Materials

Carbon dioxide with purity 99.999 % was purchased from Praxair (Spain), and used as received. The tetrabutylphosphonium halides [P4 4 4 4]Cl (with nominal purity >95 %) and [P4 4 4 4]Br (with nominal purity 98 %) were supplied by Iolitec (Germany) and Sigma-Aldrich (Germany), respectively. Prior to their use, they were purified under high vacuum (absolute pressure <1 Pa) while stirred magnetically and heated at ca. 373-383 K, for elimination of any potential volatile impurities that they might have (in particular water, which is known to critically affect the performance of ionic liquids even in minor amounts [31]).

The ionic liquid [P4 4 4 4][OAc] was synthesised as reported in a previous work [23], via a metathesis reaction between [P4 4 4 4]Cl and potassium acetate (Sigma-Aldrich, Germany, 99 %), following a similar procedure to that described by Mikkola et al. [27]. The solvents ethanol (Scharlau, Spain, >99.9 %) and acetone (Scharlau, Spain, 99.8 %), involved in this synthesis procedure, were used as received. A final purification step under high vacuum for the [P4 4 4 4][OAc] obtained was analogous to that mentioned above for the phosphonium halides, although at a lower temperature (ca. 343 K).

The preservation of the chemical identity of the three phosphonium salts after their purification steps, and absence of major organic impurities, was confirmed by ^{1}H and ^{13}C NMR spectroscopy (in a Varian Mercury 300 spectrometer, using DMSO-*d6* as deuterated solvent). The residual water content was determined by Karl-Fischer titration in a Metrohm 899 coulometer, and it was found to be lower than 0.0003 in mass fraction for all the samples. For [P4 4 4 4][OAc], the residual concentrations of chloride and potassium (the spectator ions in the metathesis reaction) were also measured, by ion chromatography and ICP-OES respectively. They were found to be 0.0014 in mass fraction for chloride (using a Metrohm 861 Advanced Compact IC chromatograph equipped with a Metrosep A Supp5 250/4.0-mm column, and employing a solution of sodium carbonate 3.2 mM and sodium bicarbonate 1.0 mM) and <0.0001 for potassium ion (using a PerkinElmer Optima 4300 DV spectrometer equipped with a 40-MHz RF plasma generator).

2.2. Absorption of carbon dioxide

Absorption isotherms of CO_2 in ionic liquids were determined in a Rubotherm Metal magnetic suspension balance, with a resolution of 10 μg, and equipped with a jacketed chamber thermostated by means of water circulating from a Huber Ministat

230 thermostatic bath that allowed temperature control with an uncertainty of 0.5 K. For each isotherm, ca. 1.0-1.5 g of absorbent was initially loaded into the sample bucket and placed in its position inside the measuring chamber. After vacuuming the chamber and fluxing it with helium gas (Nippon Gases, Spain, 99.999 %) a couple of times, the sample was conditioned under vacuum (absolute pressure lower than 0.05 bar) for a minimum of 6 h at ca. 343 K, ensuring its degasification. The temperature of the chamber was then adjusted to the desired value for the experiment, and upon thermal stabilisation CO_2 was added in a stepwise manner. The additions were planned to adequately describe the isotherms within a pressure range up to ca. 15 bar. After each addition, the system was allowed to equilibrate. The equilibrium criterion was a variation of mass lower than 20 μg over a period of 100 min. Besides the values of temperature and pressure, at the equilibrium stage the mass displayed by the balance (corresponding to the mass of the absorbent, of the CO_2 absorbed, and of the sample bucket and its hook) was recorded, and it was corrected for the buoyancy. For application of this correction, the density of CO_2 at the given conditions of temperature and pressure was obtained from the NIST Chemistry WebBook [32]. The density of the pure liquid absorbent at the specified temperature, needed to calculate its volume, was measured beforehand with an uncertainty of 0.03 kg/m^3 in an Anton Paar DMA 5000 vibrating U-tube density meter equipped with a built-in Peltier effect system for temperature control with a precision of 0.001 K. (The numerical values of density used for the different liquid absorbents in this work at the investigated temperatures are summarised in Table S1 in the Supplementary Material.) The mass and volume of the bucket and hook, also needed for calculation of the buoyancy correction, were determined right before the initiation of the entire set of experiments, in accordance with the manufacturer's instructions, by means of a blank run (with no absorbent) and

using helium as inert gas. This same procedure was used to estimate the density of the absorbent when in solid state, by loading a known mass of it in the bucket sample. A negligible effect on the buoyancy due the small variation of volume of the sample upon absorption of CO_2 was assumed. The uncertainty in the CO_2 absorbed mole fraction obtained via this procedure has been estimated to be 0.0013.

The recording of ^{31}P NMR spectra was carried out in a Bruker DRX-500 spectrometer (with a resonance frequency of 202.29 MHz for ^{31}P) at 343 K, by placing the neat samples directly in glass NMR tubes and using an inner coaxial capillary tube with D_2O (Aldrich, Germany, 99.9 % atom deuratation degree) as deuterated reference.

2.3. Determination of eutectics

The assessment of a eutectic behaviour in the mixtures of ionic liquids, and the characterisation of the eutectic points, were performed via construction of the corresponding isobaric solid-liquid equilibrium diagrams (temperature-composition diagrams). For each system, samples with a step composition of ca. 0.10 in mole fraction were prepared, covering the entire composition range. The associated weighing was carried out in a Mettler-Toledo XPE205 analytical balance with an uncertainty of 10^{-4} g. Each of these samples was analysed by differential scanning calorimetry (DSC) in a TA Instruments Q2000 differential scanning calorimeter with an RCS 90 cooling system attached. Approximately 5-15 mg of sample was placed in a 40-μL aluminium pan, and sealed hermetically with a lid of the same material. This capsule was then loaded into the measuring chamber with an autosampler. An analogous capsule with no sample was used as reference. A flow of 50 mL/min of nitrogen was used as purge gas. The thermal program consisted of three cycles, each of them comprising a heating ramp at a rate of 5 K/min up to 368 K (for the system $[P_{4\,4\,4\,4}][OAc] + [P_{4\,4\,4\,4}]Cl$) or 393 K (for the system $[P_{4\,4\,4\,4}][OAc] + [P_{4\,4\,4\,4}]Br$), and a cooling ramp at a rate of -5 K/min

down to 183 K, with 10-min isotherms in between ramps. It was ensured that the thermograms of the second and third cycle were essentially coincident, and the thermogram of the heating ramp of the third cycle was used for detailed processing of the thermal events: glass transition temperatures (at the midpoint of the small changes in heat flow) and melting temperatures (at the onset of the endothermic peaks); with an estimated uncertainty of 1 K. Enthalpies of fusion were calculated by integrating the endothermic peaks associated with the melting, with an estimated uncertainty of 0.1 kJ/mol. All the analyses of the thermograms were performed with the software Universal Analysis 2000, version 4.5.0.5, by TA Instruments.

2.4. Thermal stability

A preliminary assessment of the thermal stability of the ionic liquids was carried out by TGA in a dynamic mode. A TA Instruments Q500 thermogravimetric analyser was used, with a weight precision of 0.01 %. For each run, ca. 5-20 mg of sample was placed in an open platinum pan, and loaded into the measuring chamber. Nitrogen (Praxair, 99.999 %) was used as balance purge gas (flow rate of 40 mL/min) and sample pure gas (flow rate of 60 mL/min). The thermal programme consisted of a heating ramp at a rate of 5 K/min from room temperature until a final temperature of 773 K. Analysis of the TGA curves thus obtained was performed with the same software mentioned in Section 2.3. An uncertainty of 1 K was estimated for the recorded decomposition temperatures.

For a more accurate estimation of the stability in the mid-long term of the ionic liquids, isothermal TGA runs with a duration of 24 h were performed at different temperatures, using the same apparatus and analogous settings as above (except for the thermal programme, obviously). Due to the high hygroscopicity of the ionic liquids, these isotherms were preceded by another 60-min isotherm at 383 K to eliminate the

water that the samples could have picked up from the ambient while mounting them on the apparatus.

3. Results and discussion

3.1. Absorption of CO_2 in [$P_{4\,4\,4\,4}$][OAc]

The isotherm of absorption of CO_2 in the ionic liquid [$P_{4\,4\,4\,4}$][OAc] at 343.2 K was determined in the pressure range up to ca. 15 bar. It is shown in Fig. 1, and the corresponding numerical data used for its plotting are presented in Table S2 in the Supplementary Material. The studied temperature was selected as to be sufficiently above the melting temperature of the ionic liquid: 331 K for the purified batch as determined by DSC (which is in acceptably good agreement with the value of 329 K found by ourselves in a previous work with this ionic liquid [23], especially if taking into account not only the uncertainty of the measurements but also the lower water content of the batch used herein). At this temperature, [$P_{4\,4\,4\,4}$][OAc] is also known to be thermally stable in the mid-long term [23]. Starting from sub-atmospheric pressure, the isotherm initially describes a concave shape in the composition-pressure diagram, which can be associated with the predominance of chemical absorption. Indeed, Yeadon et al. have recently provided proof of the chemical reaction that occurs between [$P_{4\,4\,4\,4}$][OAc] and CO_2 [26], via the bubbling of the gas in the ionic liquid at 338 K and atmospheric pressure. At higher pressures (above ca. 5-6 bar), the isotherm describes an approximately proportional increase in the mole fraction absorbed with the increase in pressure, which can be connected with physical absorption as the main sorption mode.

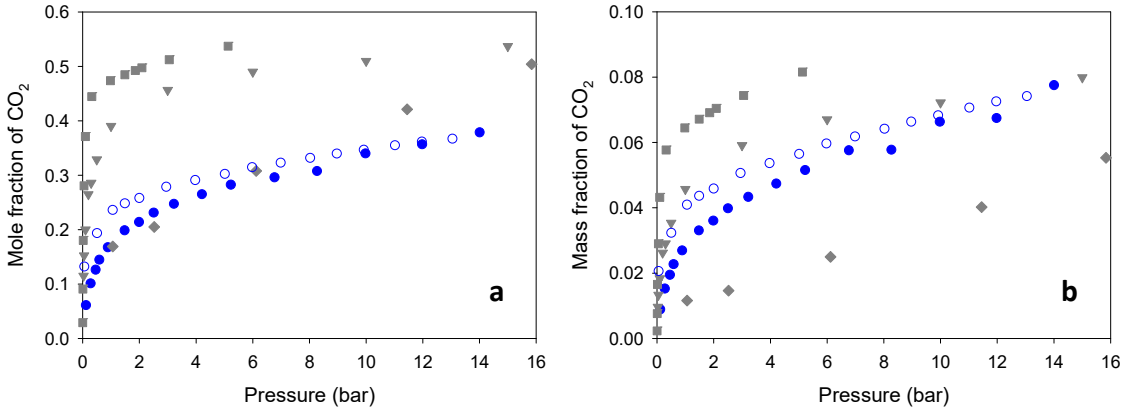

Fig. 1. CO_2 absorption (solid blue circles) and desorption (open blue circles) isotherms in $[P_{4\,4\,4\,4}][OAc]$ at 343.2 K, with the concentration of absorbed CO_2 expressed in: a) mole fraction; b) mass fraction. A comparison is provided with selected CO_2 absorption isotherms in other phosphonium ionic liquids, taken from the literature: $[P_{6\,6\,6\,14}][2\text{-CNpyr}]$ at 295 K (gray squares) [35] and at 329.65 K (gray triangles) [37], and $[P_{6\,6\,6\,14}][NTf_2]$ at 293 K (gray diamonds) [10].

Besides the work by Yeadon et al. [26] studying the kinetics of absorption at 338 K and atmospheric pressure (and reporting an equilibrium CO_2 absorbed mole fraction of 0.22, reasonably consistent with the isotherm reported herein at a somewhat higher temperature), there exist two other studies for the absorption of CO_2 in $[P_{4\,4\,4\,4}][OAc]$ (in liquid state): Shi et al. [33] report an absorption isotherm at 303 K in the pressure range up to ca. 13 bar, and Chen et al. [34] the kinetics of absorption at 313.15 K and atmospheric pressure. Taking into account the melting temperature of 331 K reported above for $[P_{4\,4\,4\,4}][OAc]$, it is probable that the ionic liquid samples used in these two works were actually in a subcooled state or had their melting temperature substantially lowered by the presence of impurities. In any case, it is interesting to note that the shape of the isotherm reported by Shi et al. is also consistent with the existence of chemisorption of CO_2 in $[P_{4\,4\,4\,4}][OAc]$ at sub-ambient pressures [33].

To put the absorption capacity of $[P_{4\,4\,4\,4}][OAc]$ in context, the CO_2 absorption isotherms corresponding to the utilisation of other phosphonium-based ionic liquids as

solvents are included in Fig. 1. In particular, the absorption data for trihexyl(tetradecyl)phosphonium 2-cyanopyrrolide ([$P_{6\,6\,6\,14}$][2-CNpyr]) at 295 K [35] and for trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)amide ([$P_{6\,6\,6\,14}$][NTf_2]) at 293 K [10] were chosen as the best representatives in the literature for chemisorbing and physisorbing ionic liquids of this kind. (Note the difference in temperature with the isotherm reported here with [$P_{4\,4\,4\,4}$][OAc] as absorbent.) [$P_{6\,6\,6\,14}$][2-CNpyr] contains an aromatic heterocyclic anion that reacts in a 1:1 mole ratio with CO_2 molecules, and its absorption capacity approaches the theoretical maximum CO_2 mole fraction of 0.50 due to chemisorption at near-ambient pressure, then increasing slowly with an increase in pressure (Fig. 1a). The molar absorption capacity of [$P_{4\,4\,4\,4}$][OAc] is clearly lower, remaining below a mole fraction of CO_2 absorbed of 0.40 for the entire pressure range studied. Regarding the comparison with [$P_{6\,6\,6\,14}$][NTf_2], the chemical absorption contribution in [$P_{4\,4\,4\,4}$][OAc] allows it to exhibit a higher absorption capacity at low pressures, but at a pressure of ca. 6 bar the mole fraction of absorbed CO_2 is eventually surpassed by that of [$P_{6\,6\,6\,14}$][NTf_2] (Fig. 1a). Nevertheless, these comparisons are substantially affected if a mass basis is taken as a reference for the concentration of CO_2 captured. In Fig. 1b, it can be observed that the mass fraction of CO_2 absorbed by [$P_{4\,4\,4\,4}$][OAc] is clearly greater than that absorbed by [$P_{6\,6\,6\,14}$][NTf_2] at any given pressure in the studied range. On the other hand, although the mass fraction of CO_2 absorbed in [$P_{6\,6\,6\,14}$][2-CNpyr] at 295 K is still greater than that in [$P_{4\,4\,4\,4}$][OAc] at 343.2 K, the difference gets notably reduced if the comparison is made at more similar temperatures (due to the significant reduction of the CO_2 absorption capacity of [$P_{6\,6\,6\,14}$][2-CNpyr] with an increase in temperature [35,36]). Thus, the absorption achieved with [$P_{4\,4\,4\,4}$][OAc] at 343.2 K matches that achieved with [$P_{6\,6\,6\,14}$][2-CNpyr] at 329.65 K [37] at a pressure of ca. 14-15 bar; and this

pressure would be lower if the comparison were possible at the common temperature of 343.2 K. (Unfortunately, data for this exact temperature are not available in the literature for [$P_{6\,6\,6\,14}$][2-CNpyr]).

On the other hand, [$P_{4\,4\,4\,4}$][OAc] is a solid at ambient temperature, which prevents its utilisation as CO_2-capturing solvent at these conditions. An experiment was attempted, though, to determine the CO_2 sorption capacity of [$P_{4\,4\,4\,4}$][OAc] in the solid state; namely at 303.2 K. Unfortunately, it resulted in a very slow and lower sorption capacity (see the obtained isotherm in Fig. S1 in the Supplementary Material), therefore ruling out its potential interest.

The experimentally determined CO_2 desorption isotherm at 343.2 K for [$P_{4\,4\,4\,4}$][OAc] is also plotted in Fig. 1. (The corresponding numerical data can be consulted in Table S2 in the Supplementary Material.) A clear hysteresis phenomenon is observed over the investigated pressure range, more pronouncedly at low pressures. Thus, the concentration of CO_2 absorbed will be higher, for a given pressure, during the desorption stage than during the absorption stage. The preservation of the chemical identity of [$P_{4\,4\,4\,4}$][OAc] after completion of the desorption experiment was evidenced by ^{1}H NMR (Fig. S2 in the Supplementary Material), thus indicating that not only the physical absorption but also the chemical absorption are reversible by reducing the CO_2 pressure of the system.

3.2. Chemisorption of CO_2 in [$P_{4\,4\,4\,4}$][OAc]: proposed reaction scheme

Fig. 2 shows an NMR-based evidence of the formation of a new phosphorous-containing chemical species by reaction of [$P_{4\,4\,4\,4}$][OAc] with CO_2, in line with the spectra that Yeadon et al. have also reported recently [26]. From a mechanistic perspective, they propose the abstraction of one proton bound to a carbon in the α position of the phosphonium cation by the basic acetate anion to give rise to the

corresponding phosphonium ylide, sufficiently stable to act as an intermediate that can be trapped with CO_2 to form the ylide-carboxylate [26]. This is inspired in the mechanism previously proposed by Brennecke and co-workers for the chemisorption of CO_2 by tetraalkylphosphonium ionic liquids with other anions of basic character such as azolides or phenolates [24,25]. In all these cases, the chemical reaction that the respective authors suggested is a 1:1 reaction between CO_2 and the phosphonium ionic liquid, with the volatile acetic acid as a byproduct. However, the absorption-desorption reversibility observed in the present work (Fig. 1 and Fig. S2) seems to be poorly compatible with the presence of a volatile byproduct in the medium. At the same time, the possible extrapolation of the portion of the isotherm with predominant contribution of chemisorption is far from leading to a plateau at $x_{CO2} = 0.50$ (which would be the mole fraction of absorbed CO_2 that would correspond to a complete 1:1 reaction). Instead, the theoretical $x_{CO2} = 0.33$ corresponding to a complete conversion of a 1:2 reaction between CO_2 and the ionic liquid is more in line with what can be inferred from the experimental absorption isotherm. Interestingly, the latter is the stoichiometric ratio that was identified and cyrstallographically proven for the chemisorption of CO_2 in another acetate-based ionic liquid, namely 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) [16], with abstraction of the relatively acidic proton in the C2 position of the imidazolium ring by the acetate anion to yield acetic acid and a carbene intermediate with which the CO_2 reacted to form an imidazolium-carboxylate zwitterion. The acetic acid was stabilised by the acetate anion of another ion pair, creating a complex that would be best described as $H[OAc]_2^-$, and thus resulting in the 1:2 (CO_2 to ionic liquid) stoichiometry [16]. In this vein, we proposed herein the reaction scheme of Fig. 3 for the chemisorption of CO_2 in [$P_{4\,4\,4\,4}$][OAc], with stabilisation of the formed acetic acid by an acetate from a second ion pair of

[$P_{4\,4\,4\,4}$][OAc], which can provide a more facile explanation of the reversibility evidenced by the desorption isotherm, as well as of the "projected chemisorption plateau" at a CO_2 mole fraction of ca. 0.30. It is worth noting that this overall 1:2 stoichiometry is equivalent to the mole ratio for which Brennecke's group observed an unexplained saturation of the reaction with tetraalkylphosphonium phenolates [25]. Also, it may be a scheme providing a better explanation of the mass spectrometry peak found by Yeadon et al. in their work, that was "the result of two $[P_{4\,4\,4\,4}]^+$ cations, one in the ylide form (259.43 and 258.42 *m*/*z*), and CO_2 (44.01 *m*/*z*)" [26].

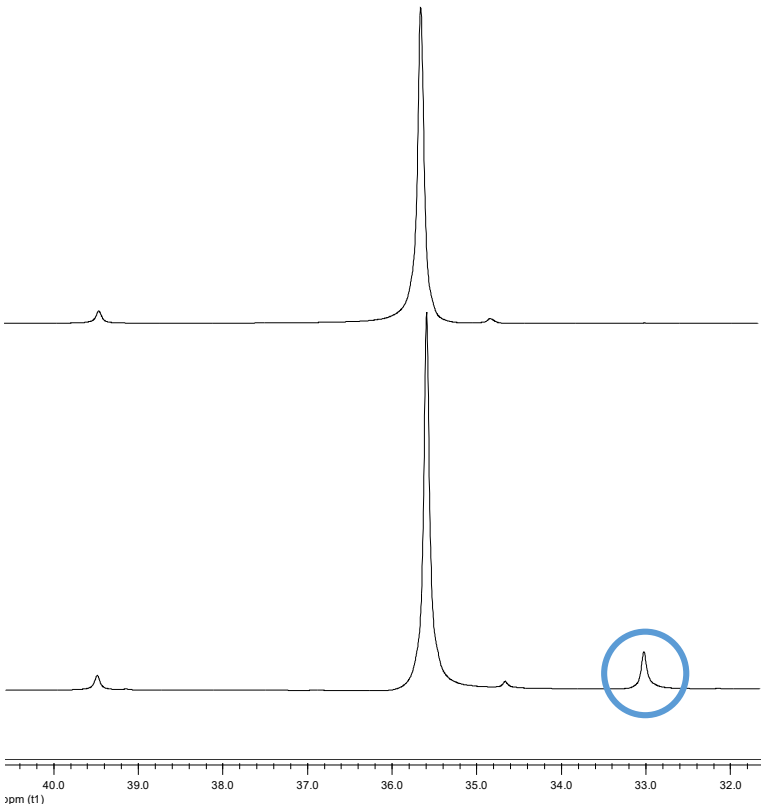

Fig. 2. ^{31}P NMR spectra of pure [$P_{4\,4\,4\,4}$][OAc] (top) and its reacted product with CO_2 (bottom) at atmospheric pressure and 343 K. The peak marked with a circle corresponds to the new species formed upon reaction of the ionic liquid with CO_2.

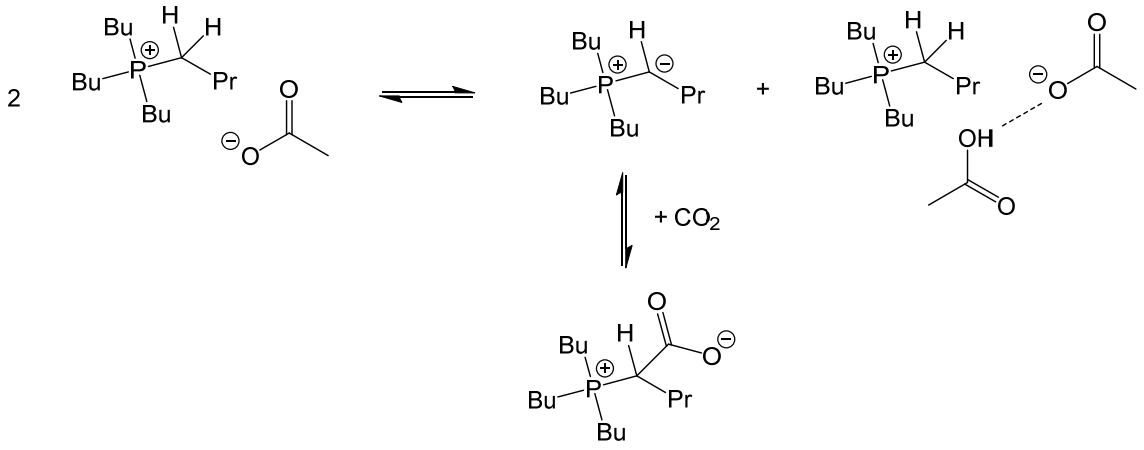

Fig. 3. Scheme of the proposed 1:2 chemical reaction between CO_2 and $[P_{4\,4\,4\,4}][OAc]$. For the sake of clarity, resonance forms have not been displayed.

3.3. Eutectic mixtures and their CO_2 absorption capacity

A limitation of $[P_{4\,4\,4\,4}][OAc]$ is its relatively high melting point (331 K), which prevents its application at near-ambient and lower temperatures, or in processes in which it might be subjected to these temperatures at certain stages, posing a risk of undesired solidification. One possibility to overcome this issue, while fully keeping the advantage of lack of volatility associated with the use of an ionic liquid as absorbent, is the utilisation of a eutectic mixture of $[P_{4\,4\,4\,4}][OAc]$ with a second ionic liquid. Since one of the routes of synthesis of $[P_{4\,4\,4\,4}][OAc]$ (particularly the one used in this work) consists of a metathesis reaction of a halide of the cation with potassium acetate, it could make sense to select either $[P_{4\,4\,4\,4}]Cl$ or $[P_{4\,4\,4\,4}]Br$ as second ionic liquid candidates. The utilisation of a combination of $[P_{4\,4\,4\,4}][OAc]$ and the analogous halide would avoid the most costly part of the process of preparation of $[P_{4\,4\,4\,4}][OAc]$ by the aforementioned metathetic route, namely the complete exchange of anions in the desired product.

The systems $[P_{4\,4\,4\,4}][OAc]$ + $[P_{4\,4\,4\,4}]Cl$ and $[P_{4\,4\,4\,4}][OAc]$ + $[P_{4\,4\,4\,4}]Br$ were therefore investigated by DSC to develop a knowledge on their solid-liquid equilibrium.

The corresponding phase diagrams are shown in Fig. 4 in temperature-composition plots. (The DSC thermograms used in the construction of these diagrams are compiled in Fig. S3 in the Supplementary Material.) As observed, these systems exhibit a eutectic behaviour with miscibility of the compounds in the liquid phase and immiscibility in the solid phase (no solid solution). The eutectic temperatures obtained were 297 K for $[P_{4\,4\,4\,4}][OAc]$ + $[P_{4\,4\,4\,4}]Cl$ at a nearly equimolar composition, and 305 K for $[P_{4\,4\,4\,4}][OAc]$ + $[P_{4\,4\,4\,4}]Br$, with a $[P_{4\,4\,4\,4}][OAc]$ mole fraction of ca. 0.70. These represent a substantial depression of the melting temperature from the parent compounds – not just from $[P_{4\,4\,4\,4}][OAc]$, but also from the halides: melting temperatures of 361 K for $[P_{4\,4\,4\,4}]Cl$ and of 374 K for $[P_{4\,4\,4\,4}]Br$. (In the literature, Adamová et al. [38] have reported a melting temperature of 70.6 ºC (344 K) for $[P_{4\,4\,4\,4}]Cl$; significantly lower than the value reported herein. This difference may be due, at least in part, to the higher water content of their sample: 0.0006 in mass fraction, which is double than ours, rendering it difficult to establish a fair comparison with our value.)

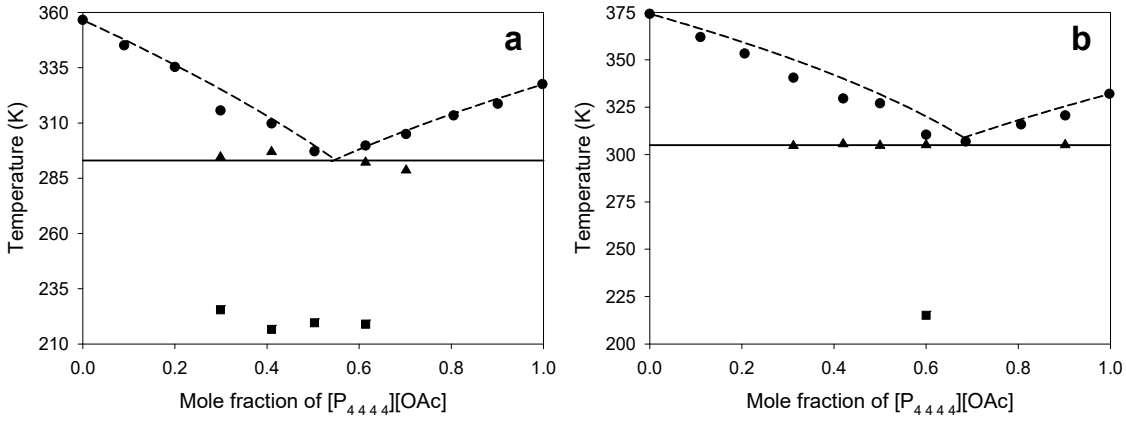

Fig. 4. Temperature-composition diagrams for the solid-liquid equilibrium of the systems $[P_{4\,4\,4\,4}][OAc]$ + $[P_{4\,4\,4\,4}]Cl$ (a) and $[P_{4\,4\,4\,4}][OAc]$ + $[P_{4\,4\,4\,4}]Br$ (b). Legend: ▲, melting of the eutectic composition; ●, melting of the excess compound; ■, glass transition. The horizontal solid lines represents the eutectic lines (calculated as the

average of the eutectic melting temperatures observed). The dashed lines correspond to the Schröder-van Laar model (eq. 1).

Fig. 4 also shows that, interestingly, the melting curves of the two systems (especially in the case of the [P4 4 4 4][OAc] + [P4 4 4 4]Cl mixture) are very well described by the simplified version of the Schröder-van Laar model:

$$T_m = \left(\frac{1}{T_{m,i}} - \frac{\ln x_i}{\Delta H_{m,i}/R} \right)^{-1} \quad (1)$$

where T_m is the observed melting temperature; x_i, $\Delta H_{m,i}$, and $T_{m,i}$ are respectively the mole fraction, molar enthalpy of fusion, and melting temperature of the excess component in the evaluated melting curve; and R is the universal gas constant [39]. (The numerical values for $\Delta H_{m,i}$, as obtained from integration of the endothermic melting peaks in the corresponding DSC thermograms, were: 14.1 kJ/mol for [P4 4 4 4][OAc], 10.9 kJ/mol for [P4 4 4 4]Cl, and 16.8 kJ/mol for [P4 4 4 4]Br.) Besides other simplifications (see, for instance, the analysis by Martins et al. [40]), this equation assumes that an ideal liquid solution (activity coefficients equal to the unity) is in equilibrium with pure solid phase [39]. The good description that it provides of the solid-liquid equilibria of the eutectic systems investigated, as assessed in Fig. 4, can be taken as an indicator of the quite ideal mixing of [P4 4 4 4][OAc] and [P4 4 4 4]Cl, and of [P4 4 4 4][OAc] and [P4 4 4 4]Br, with values of the activity coefficients close to the unity. This should not be unexpected, since each pair of ionic liquids has same bulky cation in common, and the two anions involved are notably smaller, thus accommodating well and without much difference in the void spaces left by the network of the bulky cations in its three-dimensional arrangement.

It can be added that the participation of [P4 4 4 4]Cl or [P4 4 4 4]Br in lowering the melting temperature of [P4 4 4 4][OAc] does not compromise the thermal stability of the

resulting absorbent. A dynamic TGA analysis yielded 5 % onset decomposition temperatures ($T_{d,5\%onset}$) of 590 K for [P4 4 4 4]Cl and 609 K for [P4 4 4 4]Br. Following a similar procedure to what we did in a previous work to ascertain the thermal stability of [P4 4 4 4][OAc] in the mid-long term [23], and taking as reference the values of $T_{d,5\%onset}$ mentioned, 24-hour isothermal TGA runs were performed for [P4 4 4 4]Cl and for [P4 4 4 4]Br at different temperatures. The corresponding isothermal thermograms are shown in the temperature-time plots of Fig. 5, revealing for example less than 1 % decomposition after 24 h at temperatures as high as 473.2 K for [P4 4 4 4]Cl or 493.2 K for [P4 4 4 4]Br. The sets of isothermal TGA thermograms were used to model the kinetics of thermal decomposition of the ionic liquids with the Arrhenius equation, following an analogous procedure to that reported previously for [P4 4 4 4][OAc] [23]. The details can be found in the Supplementary Material (including Fig. S4 and Tables S5 and S6). By extrapolation of the model, it could be estimated that, at a temperature of 343.2 K, even after one year the fraction thermally decomposed would be negligible (lower than 0.01 %) in any of these ionic liquids.

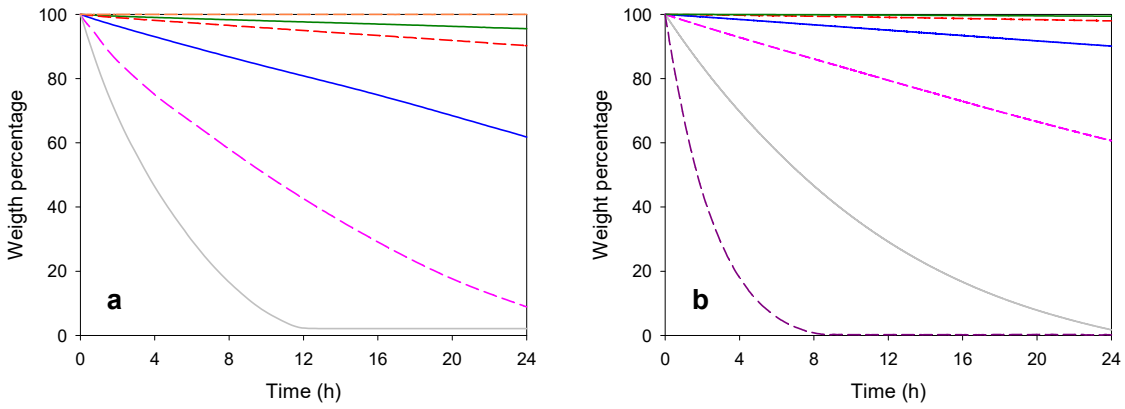

Fig. 5. TGA isotherms for [P4 4 4 4]Cl (a) and [P4 4 4 4]Br (b) at different temperatures. From top to bottom: 473.2 K (orange dashed line, only in the plot for [P4 4 4 4]Cl), 493.2 K (green solid line), 513.2 K (red dashed line), 533.2 K (blue solid line), 553.2 K

(pink dashed line), 573.2 K (gray solid line), and 593.2 K (purple dashed line, only in the plot for [$P_{4\,4\,4\,4}$]Br).

In view of the phase behaviour for the eutectic systems investigated, it was decided to test the CO_2 absorption capacity of their corresponding eutectic compositions at 308.2 K (a temperature just above the melting temperature of either eutectic temperature); and also at 343.2 K, for direct comparison with the isotherm for pure [$P_{4\,4\,4\,4}$][OAc], and for a concomitant assessment of the effect of temperature on their absorption capacity. The four absorption isotherms for the eutectic mixtures (a 50:50 mol/mol mixture of [$P_{4\,4\,4\,4}$][OAc] and [$P_{4\,4\,4\,4}$]Cl, and a 70:30 mol/mol mixture of [$P_{4\,4\,4\,4}$][OAc] and [$P_{4\,4\,4\,4}$]Br) are plotted in Fig. 6 (and the corresponding numerical data are listed in Tables S3 and S4 in the Supplementary Material), together with the isotherm for [$P_{4\,4\,4\,4}$][OAc] at 343.2 K for comparative purposes. (Since the formula weight of [$P_{4\,4\,4\,4}$][OAc], [$P_{4\,4\,4\,4}$]Cl, and [$P_{4\,4\,4\,4}$]Br are relatively similar, there is no strong difference in carrying out the plotting of the CO_2 concentration in a mole basis or in a mass basis. Thus, only the mole fraction plot is displayed herein. The equivalent plot with the mass fractions can be found in the Supplementary Material as Fig. S5.) For these two eutectic mixture, a lower contribution of the chemical absorption is noticeable in the low pressure range (ca. <3 bar) when compared to pure [$P_{4\,4\,4\,4}$][OAc], as it would be expected from the assumption that only the [$P_{4\,4\,4\,4}$][OAc] is able to react chemically with CO_2. With an increase in pressure, physical absorption becomes clearly predominant. The isotherms at 308.2 K and 343.2 K are approximately coincident in the pressure range where chemical absorption prevails (indicating little influence of temperature on the equilibrium thermodynamics of the reaction of [$P_{4\,4\,4\,4}$][OAc] and CO_2); whereas at higher pressures a superior absorption capacity is

evidenced at 308.2 K, due to greater physical absorption than at the higher temperature. At pressures above 10 bar, the mole fraction of CO_2 absorbed in the eutectic mixtures at 308.2 K is comparable to that in the pure $[P_{4\,4\,4\,4}][OAc]$ at 343.2 K. It can be additionally said that the $[P_{4\,4\,4\,4}][OAc]$ + $[P_{4\,4\,4\,4}]Br$ eutectic mixture exhibits a slightly better CO_2 absorption capacity than the $[P_{4\,4\,4\,4}][OAc]$ + $[P_{4\,4\,4\,4}]Cl$ eutectic mixture at 343.2 K, but the difference becomes negligible at 308.2 K.

The isotherms in Fig. 6 show, therefore, that the investigated eutectic mixtures can be used as absorbents for CO_2 capture at near-ambient temperatures, at which pure $[P_{4\,4\,4\,4}][OAc]$ cannot be efficiently used due to its solid condition (see Section 3.1). In comparison to pure $[P_{4\,4\,4\,4}][OAc]$ in the liquid state, the lower contribution of chemical absorption in the CO_2-capturing process by the eutectic mixtures (due to the introduction of an only-physisorbing ionic liquid in the formulation of the absorbent) is partially compensated by a greater physical absorption capacity.

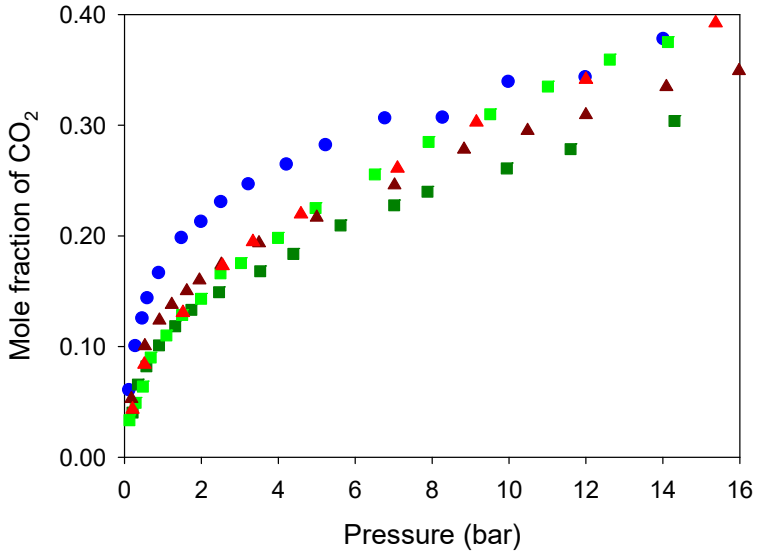

Fig. 6. CO_2 absorption isotherms in the eutectic mixtures of $[P_{4\,4\,4\,4}][OAc]$ + $[P_{4\,4\,4\,4}]Cl$ (green squares) and of $[P_{4\,4\,4\,4}][OAc]$ + $[P_{4\,4\,4\,4}]Br$ (red triangules), at temperatures of 308.2 K (light-coloured symbols) and 343.2 K (dark-coloured symbols). The isotherm in pure $[P_{4\,4\,4\,4}][OAc]$ at 343.2 K (blue circles) is added for comparison purposes.

The desorption process in both eutectic mixtures was also investigated. At the two temperatures explored, a similar hysteresis behaviour to that already reported for pure [$P_{4\,4\,4\,4}$][OAc] (see Section 3.1) was observed. The experimentally determined desorption isotherms are plotted along with the corresponding absorption isotherms in Fig. S6 in the Supplementary Material, for direct visual assessment of the hysteresis loop. (The corresponding numerical data are included in Tables S3 and S4 in the Supplementary Material.)

4. Conclusions

The absorption isotherm of CO_2 in the ionic liquid [$P_{4\,4\,4\,4}$][OAc] was experimentally determined at 343.2 K, exhibiting characteristics of chemical absorption. The postulated reaction (with incorporation of CO_2 as a carboxylate substitute in one of the carbons in α position in the phosphonium cation) involves a stoichiometric relation of two moles of ionic liquid per mole of CO_2 absorbed. At pressures higher than ca. 5-6 bar, however, the CO_2 absorption capacity of [$P_{4\,4\,4\,4}$][OAc] in a mass basis is comparable to that of other ionic liquids that have been reported in the literature to react in a 1:1 mole ratio with CO_2. Along with a low toxicity and a potentially affordable production at industrial scale, [$P_{4\,4\,4\,4}$][OAc] is thus showing promise as the solvent of choice in the development of CO_2 capture technology based on ionic liquids. For its utilisation as CO_2-capturing absorbent at lower temperatures (its melting temperature is 331 K, and attempts to use it in the solid state resulted in reduced capacity with extremely poor kinetics), it is possible to combine [$P_{4\,4\,4\,4}$][OAc] with [$P_{4\,4\,4\,4}$]Cl or [$P_{4\,4\,4\,4}$]Br, resulting in eutectic systems very well described by the simplified Schröder-

van Laar model, and for which the eutectic compositions have melting temperatures of 297 K and 305 K, respectively. The CO_2 absorption isotherms for these eutectic compositions at 308.2 K present a lower chemical absorption contribution, which in turn is partially compensated by a greater physical absorption, as compared to pure $[P_{4\,4\,4\,4}][OAc]$ at 343.2 K. All the absorbents tested in this work exhibited hysteresis in the absorption-desorption loop, with the concentration of CO_2 absorbed being higher for the desorption stage than for the absorption stage at a given pressure.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://.....

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