



Hydrated carboxylate ionic liquids as chemical CO₂ sorbents of high capacity and moderate enthalpy of absorption

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ABSTRACT

Tetralkylphosphonium carboxylate ionic liquids are herein presented as efficient carbon dioxide chemisorbents in the presence of water. The ionic liquids tetrabutylphosphonium formate and acetate, tributylmethylphosphonium formate and a series of triethylalkylphosphonium formates and acetates, have been prepared by various synthetic procedures either from hydroxide or methylcarbonate precursors, or via multiple steps starting from the parent triethylphosphine. Their physicochemical properties, namely melting or glass transition temperatures, thermal decomposition behaviour, densities and viscosities have been determined. As dry substances, they are viscous liquids or low-melting solids, whereas they show little tendency to solidify in their hydrated forms. They were used mostly as monohydrates in CO₂ solubility measurements, exhibiting highest capacities (3 mol L⁻¹, i.e. $\approx 0.9 \text{ mol}_{\text{CO}_2} \text{ mol}_{\text{IL}}^{-1}$, at 5 bar, 25 °C) at equimolar H₂O/ionic liquid ratios, approaching those of commercial aqueous amine sorbents. Carbon dioxide chemisorption into hydrogencarbonate takes place, as demonstrated by infrared spectroscopy with isotopic labelling. CO₂ absorption isotherms were recorded at various temperatures and the data used to estimate the heat of absorption according to three different thermodynamic models. Enthalpies of CO₂ absorption depended heavily on the model used. Rationalisation of this was done on the grounds of the expected relevance of physical and chemical sorption processes. Average heats of CO₂ absorption lie between -40 and -45 kJ mol⁻¹, in accordance with mild chemical absorption albeit significantly lower than those for typical chemical sorbents such as amines. This reinforces the feasibility of hydrated carboxylate ionic liquids for CO₂ capture technologies of low regeneration energies.

1. Introduction

A large portfolio of well-developed carbon dioxide capture technologies can be currently accessed and implemented [1–3]. Several of them have found way to successful commercial deployment, mostly with the purposes of natural gas sweetening, ammonia production, air purification and distillation or life support systems. Despite the maturity of CO₂ capture, the development of advanced sorbents exhibiting high performance under a variety of conditions and low energetic requirements for regeneration is still intensely sought. This quest is even more urgent for environmental applications related to grand global challenges, namely the need for lowering the costs of flue gas treatment, a key challenge for the deployment of viable and sustainable power generation and manufacturing [4]. Regarding the even more ambitious goal of direct air capture, innovative sorbents that can operate efficiently at ppm-level

concentrations must be designed and tested [5,6]. Under such demanding conditions, chemical absorption holds a more promising position.

The essentially unlimited molecular design possibilities of ionic liquids, that is, salts that remain in the liquid state at or around room temperature, offers a fantastic opportunity for targeting specific applications and end uses [7]. Moreover, ionic liquids are uniquely advantageous for the processing of gaseous streams since they have negligible vapour pressure, and thus, no release in to the treated gas is expected, avoiding unwanted contamination [8]. Therefore, the broad research interest raised around ionic liquids for carbon dioxide capture is not surprising [9–14]. On the one hand, the inherent packing inefficiency of cations and anions needed to avoid solidification (crystallisation) in ionic liquids leads to a significant amount of interstices in their bulk, presumably benefiting the physical absorption of gases [11,15].

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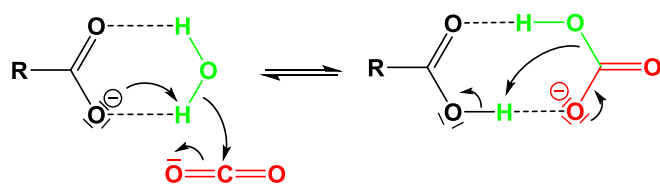
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Moreover, specific interactions of CO₂ with their components, and especially with anions, have been postulated as deciding factors to enhance solubilities and capture performance [15]. A logical way forward to enhance the affinity of ionic liquids for carbon dioxide is their functionalisation with moieties that can enable chemical absorption of the gas [1,10]. The most commonly explored structural modification in this regard is the introduction of amine groups, among which, the use of amino acid anions has proven especially successful in readily reaching equimolar chemisorption of CO₂ [16–24]. To mention a few examples, CO₂ capture capacities reaching 0.93, 1.1 or even 1.2 mol_{CO₂} mol_{IL}^{−1} have been reported for phosphonium salts paired with deprotonated methionine [25], alanine [26] or glycine [17], respectively. The equimolar barrier has been largely surpassed (up to ca. 1.7 mol_{CO₂} mol_{IL}^{−1}) for ionic liquids with multicarboxylate-type amino acid anions [20]. The downside of amino-functionalised ionic liquids, in analogy to the broader family of amine sorbents, is their relatively high enthalpies of absorption (typically > 60 kJ mol^{−1}, absolute values), which in turn imply challenging regeneration [17,27]. Temperatures above 100 °C are generally required to release the carbon dioxide from amines, a process that inevitably leads to thermal degradation of the sorbent to some extent [3,28].

Among the many ionic liquid design alternatives, the use of weakly basic anions, yet prone to reversibly bind the CO₂ molecule, is a promising strategy to minimise the energy duty of the eventual process. Carboxylate anions are typical in the formulation of ionic liquids and bear a relatively mild basicity, albeit sufficient to interact with carbon dioxide effectively according to a Lewis-type acid-base reactivity [29–35]. In highly ionic media, anhydrous carboxylate anions are capable of deprotonating a range of very weakly acidic hydrogen atoms in both cations and anions, in effect altering their structures. Subsequently, the reacted ionic liquid moieties become strongly nucleophilic and attack the carbon atom in CO₂ to form nascent C-bonded carboxylate moieties [34–39]. Such tight binding to carbon dioxide may be difficult to revert or, on occasions, irreversible. The situation is completely altered in the presence of water. Hydration water molecules are effective hydrogen-bond donors that strongly link the carboxylate anion, disrupt cation–anion interactions and prevent further self-reactivity [37]. Upon interaction with CO₂, water may even hydrolyse the C-bonded carboxylates and promote a different pathway leading to [HCO₃][−] as the trapped species [36]. By employing hydrated carboxylate ionic liquids, the adduct formed between the carboxylate anion and water directly reacts with CO₂ via the hydrogencarbonate route (Scheme 1) [40–48].

The hydrogencarbonate mechanism is readily reversible at moderate temperatures (55–70 °C), as demonstrated by cycling experiments [43,44,48,49]. This opens up possibilities for these class of sorbents to be employed in CO₂ capture processes with low energy requirements for regeneration. In our previous report, the heat of regeneration was determined for a solid-supported tetrabutylphosphonium acetate hydrate between 4.3 and 4.7 kJ g_{CO₂}^{−1}, well within the range of commercial amine sorbents [49]. The main parameter affecting this is the enthalpy of absorption, which has been estimated in a wide range



Scheme 1. A possible concerted reversible CO₂ chemisorption mechanism by carboxylate-water adducts.

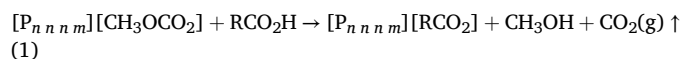
between 30 and 65 kJ mol^{−1} for various hydrated carboxylates by several authors adopting either modelling [46,48] or calorimetry [41]. Considering these figures, the family of carboxylate ionic liquids are proposed as competitive CO₂ capture chemisorbents in the presence of water, with enticing prospects with regards to viability. In this work, a set of tetraalkylphosphonium carboxylate ionic liquids ([P_{*n n n m*}][RCO₂]; *n, m*: number of carbon atoms in the linear alkyl chains; R: H, CH₃), most of them entirely novel, are described and their CO₂ solubilities determined, with the aim of widening the knowledge on such sorbents and defining performance trends. Ultimately, a thorough assessment of modelling methodologies to estimate their enthalpies of carbon dioxide absorption has been undertaken, and the results rationalised in accordance with the expected mechanism. Our broader motivation is to consolidate carboxylate ionic liquids as a family of competitive and viable CO₂ capture materials.

2. Experimental section

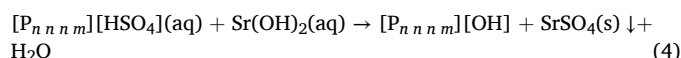
2.1. Synthesis

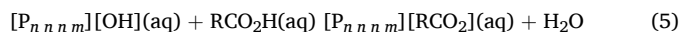
The tetraalkylphosphonium ionic liquids studied in this work were prepared by adapting procedures previously developed by Ferguson *et al.* [50], Adamová *et al.* [51] and Anderson *et al.* [44]. Where available, tetraalkylphosphonium methylcarbonate ([P_{*n n n m*}][CH₃OCO₂]) precursors were used for one-step synthesis with acids to generate the corresponding carboxylate salts according to equation (1) (*Method 1*). Otherwise, synthetic procedures were performed in several stages by two different procedures, both via formation of aqueous hydroxide solutions of the desired cation and final neutralisation with carboxylic acids. One of them (*Method 2*) proceeds via multiple metathesis stages in batch solution mode, involving intermediate precipitation of insoluble strontium sulfate to generate the hydroxide solution. The reason to adopt this rather laborious procedure was the possibility to regenerate all co-products for each of the reactions in a circular overall process [50]. Namely, *Method 2* involves initial quaternisation of trialkylphosphines with chloroalkanes (P_{*n n n*} and C_{*m*}Cl, respectively; equation (2)), reaction with sulfuric acid to generate the hydrogensulfate salts (equation (3)), ion exchange via precipitation using strontium hydroxide (equation (4)), and neutralisation with the desired acid into the final tetraalkylphosphonium carboxylate (equation (5)). A more convenient alternative route entailing only two stages (*Method 3*) has been followed for some of the ionic liquids. In essence, the two reactions involving transformation of the halide salt to the hydroxide in *Method 2* (equations (3) and (4)), are replaced in *Method 3* with one single stage, i.e. an anion-exchange performed by flowing an aqueous solution of a tetraalkylphosphonium halide over a commercial hydroxide resin (equation (6)). In the case of tetrabutylphosphonium ionic liquids, a one-stage neutralisation synthesis was possible from the commercial parent hydroxide (equation (5) starting from aqueous [P_{4 4 4 4}][OH]). Reaction equations are defined below, whereas full details about materials and synthetic procedures can be accessed in the [Supplementary Data](#).

Method 1.

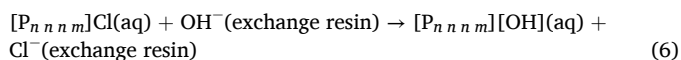


Method 2.





Method 3 (replacing equations (3) and (4) in **Method 2** with the following).



2.2. Characterisation

The expected molecular structures of the prepared ionic liquids were confirmed by 1H , ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectroscopy by measuring samples dissolved in acetone- d_6 at room temperature ($\approx 20^\circ C$) in a Bruker Avance Neo 400 spectrometer. The study of sorption speciation was performed for neat liquid samples by ^{13}C NMR using $dmsd-d_6$ as external standard in a co-axial capillary tube, before and after exposure of the ionic liquid hydrate to an atmosphere of pure CO_2 (1 bar). Basic features of the ionic liquid structures and of the speciation upon CO_2 uptake were also studied by attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy by placing small amounts of samples on the optical window of a Bruker Tensor 27 single reflection diamond ATR instrument.

Phase transitions (namely melting, glass transition or crystallisation points) were determined by the corresponding signals from second heating cycles by differential scanning calorimetry (DSC) traces of samples in aluminium pans with pierced lids (5–10 mg, $5^\circ C \text{ min}^{-1}$ heating/cooling rates) on a TA DSC Q2000 instrument equipped with liquid dinitrogen cryostatic cooling. Thermal decomposition profiles were estimated by thermogravimetric analysis (TGA) traces of samples in platinum pans (5–10 mg, $5^\circ C \text{ min}^{-1}$ heating rate) using a TA TGA Q5000 instrument, under a dinitrogen flow. Densities were measured for ionic liquid hydrate samples (1 cm^3) on an Anton Paar DMA 4500 M oscillating tube density meter. Viscosities were determined using a Bohlin Gemini Rotonetic Drive 2 cone and plate viscometer, equipped with a Bohlin Instruments Peltier circulating heater under a dinitrogen flow, either for fresh ionic liquid hydrate samples or after CO_2 solubility experiments, as described in Section 2.4 below. Water contents were determined using a Cou-Lo Compact (version 08.05) Karl Fischer titrator, and titration solutions from Riedel-de-Haën.

2.3. CO_2 solubility measurements

The solubility of CO_2 in ionic liquid hydrates was determined by the isochoric method in stainless steel pressure-tight vessels (Parr®) equipped with propeller-stirrers designed to effectively mix the headspace gas with the liquid, outer heating elements and inserted thermocouples to adjust the temperature of the liquid. In a typical procedure, a known amount of an ionic liquid hydrate (ca. 5 mL, based on measured mass and determined density) was placed inside a vessel, then the vessel was attached to the head part and tightly closed, and subsequently the headspace was evacuated under reduced pressure (typically for less than 2 min) down to < 0.01 bar. Then, pure CO_2 was introduced into the vessel while continuously stirring (1000 min^{-1}) up to a final pressure of 5.00 bar at $25.0^\circ C$ after an equilibration time of ca. 15 min, while measuring the volume of gas by means of a calibrated mass flow controller (BROOKS® Smart Massflow). The total molar amount of CO_2 added into the vessel chamber was calculated from the mass flow controller reading, and the amount of gas dissolved into the liquid was determined by subtracting the expected amount of gas in the headspace volume according to the ideal gas law. The method was validated by measuring CO_2 solubility in a widely studied physically-absorbing ionic liquid, i.e. 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_4mim][Tf_2N]$); the Henry's constant determined in our setup upon triplicate measurements at $25^\circ C$ was 33.7 ± 0.3 bar, in good agreement with literature data: 34.3 ± 0.8 bar [52]. In selected cases,

measurements at different pressures and temperatures were performed to produce isotherms. To minimise thermal gradients, the vessel head and gas pipes constituting the headspace were wrapped in heating tape and adjusted to the same temperature as that of the liquid. The possible interference of water vaporisation from the ionic liquid hydrate during experiments at high temperatures has been considered by performing vapour pressure measurements of the ionic liquid hydrates (detailed procedure in [Supplementary Data](#)).

3. Results and discussion

3.1. Preparation and physicochemical properties of carboxylate ionic liquids

The synthesis of carboxylate ionic liquids can be performed by a variety of pathways. Metathetic processes from the parent halides are convenient, given their broad availability and ease of production, although the removal of residual halide in the final ionic liquid is challenging [34,53,54]. A common alternative for a more reliable purity involves neutralisation of hydroxide salt solutions with a carboxylic acid [35,50,55]. To convert halides into hydroxides, a one-step procedure can be followed by using ion-exchange resins, or via a multi-step process encompassing formation of the hydrogensulfate intermediate by reaction with sulfuric acid under reduced pressure, and subsequent reaction with alkaline-earth hydroxides [50]. In this work, the latter multi-step option (**Method 2**, see above) was chosen as the general synthetic route given the prospects of this route regarding recycling of co-products in a circular fashion [50]. Some of the ionic liquids were also prepared by a more convenient, albeit more time-consuming and solvent-intensive, laboratory procedure based on ion-exchange resins (**Method 3**). In both cases, the intermediate aqueous hydroxide solutions were halide-free based on qualitative testing with $AgNO_3$. This implies chloride concentrations below 1000 ppm in the isolated ionic liquid. The presence of lower (trace) amounts of halides is not expected to exert a significant impact on the performance for CO_2 absorption. In the case of $[P_{4441}][HCO_2]$, a simplified procedure from the methylcarbonate precursor salt was employed (**Method 1**) given the availability of the precursor.

The versatility of **Method 2** allowed to generate a family of $[P_{222m}][RCO_2]$ ionic liquids starting from triethylphosphine (P_{222}) via quaternisation with chloroalkanes of varying chain length. Quaternisation can be also performed by employing bromoalkanes, benefiting from their enhanced readiness for nucleophilic substitution owing to the better leaving group character of bromine as compared to chlorine [56]. However, chloroalkanes were employed instead in view of the easier removal of the more volatile HCl as compared to HBr during $[P_{222m}][HSO_4]$ production (equation (3)). The subsequent reactions to generate the $[P_{222m}][OH]$ in aqueous media were performed using strontium hydroxide, which combines acceptable solubility in water and insolubility of the $SrSO_4$ by-product [50]. The hydroxide solution was neutralised with either formic or acetic acid to produce the final $[P_{222m}][HCO_2]$ and $[P_{222m}][CH_3CO_2]$, respectively. Tetrabutylphosphonium analogues were synthesised from commercially available aqueous hydroxide solutions via the latter step. All carboxylate ionic liquids were dried under high vacuum to water contents below 600 ppm. Structural characterisation of the final carboxylate ionic liquids and/or their hydrates was performed by NMR; an example is shown in [Figure S1](#).

All prepared formates and acetates were viscous liquids or low-melting solids. To ascertain their liquid range of operation, calorimetric (DSC) and gravimetric (TGA) measurements were performed. The melting or glass transition temperatures, defining their low temperature liquid limits, and dynamic decomposition temperatures of alkyltriethylphosphonium ionic liquids are listed in [Table 1](#). The symmetrical tetraethylphosphonium salts studied are solids at room temperature that melt below $100^\circ C$. Asymmetry introduced by longer alkyl chains depresses melting temperatures to around or below room

Table 1Thermal behaviour of pure $[P_{2.2.2.m}]^+$ carboxylate ionic liquids.

ionic liquid	$T_g/^\circ\text{C}^a$	$T_m/^\circ\text{C}^a$	$T_{dec}/^\circ\text{C}^b$
$[P_{2.2.2.2}]\text{Cl}$	—	60	320
$[P_{2.2.2.2}][\text{HCO}_2]$	—	40	160
$[P_{2.2.2.6}][\text{HCO}_2]$	−69	26	230
$[P_{2.2.2.8}][\text{HCO}_2]$	—	—	220
$[P_{2.2.2.10}][\text{HCO}_2]$	—	23	220
$[P_{2.2.2.2}][\text{CH}_3\text{CO}_2]$	—	93	270
$[P_{2.2.2.6}][\text{CH}_3\text{CO}_2]$	−64	18	250
$[P_{2.2.2.8}][\text{CH}_3\text{CO}_2]$	−73	9	240
$[P_{2.2.2.10}][\text{CH}_3\text{CO}_2]$	—	31	250

^a Glass transition (T_g) and melting or clearing (T_m) temperatures recorded during the second heating cycles in DSC traces (−80 to 150 °C for symmetric $[P_{2.2.2.2}]^+$ salts; −80 to 50 °C for asymmetric $[P_{2.2.2.m}]^+$ salts; 5 °C min^{−1}).

^b Decomposition temperatures (T_{dec}) taken as the onset of weight loss in dynamic TGA traces (5 °C min^{−1}, N₂ atmosphere).

temperature, with the notable exception of $[P_{2.2.2.8}][\text{HCO}_2]$, which shows no sign of solidification down to −80 °C. Some ionic liquids show low-temperature glass transitions and a sequence of crystallisation and melting events upon heating ($[P_{2.2.2.6}][\text{HCO}_2]$, $[P_{2.2.2.8}][\text{CH}_3\text{CO}_2]$ and $[P_{2.2.2.8}][\text{CH}_3\text{CO}_2]$), as shown in Figure S2.

Regarding decomposition temperatures, the data listed in Table 1 are determined as onset points in dynamic TGA curves. All such mass losses events were observed around or above 200 °C. According to these data, acetate ionic liquids are expected to be more thermally stable than formate counterparts. This trend is most clearly apparent for $[P_{2.2.2.2}][\text{HCO}_2]$, which starts to decompose gradually at significantly lower temperatures than any other of the studied ionic liquids. However, real decomposition temperatures may be considerably lower upon long-term thermal treatment. This was clearly seen by undertaking static TGA measurements for one of the ionic liquids at 100 and 150 °C (Fig. 1). The ionic liquid $[P_{2.2.2.6}][\text{CH}_3\text{COO}]$ seems stable at 100 °C after one day, since the minor weight loss recorded (<1%) could be due to water release. Nevertheless, a significant weight loss is observed at 150 °C, i.e. 13 % after 20 min and then slower but steady decrease up to a total time of 24 h. Therefore, $[P_{2.2.2.6}][\text{CH}_3\text{COO}]$, and most likely any tetraalkyl-phosphonium carboxylate ionic liquid, might decompose rapidly at 150 °C, whereas it should be stable at operating temperatures up to 100 °C. Possible decomposition mechanisms encompass decarboxylation of the anion, probably accompanied or followed by β -elimination of the cation alkyl chains.

For the purpose of studying the CO₂ solubility in hydrated form, the pure ionic liquids were mixed with water at various ratios. All of them were studied at equimolar H₂O/IL (IL: $[P_{n.n.n.m}][\text{RCO}_2]$) ratio, on the grounds of evidence from our own experience and from literature

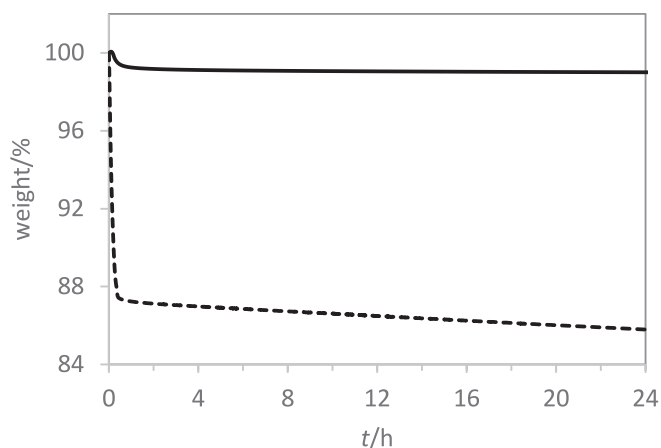


Fig. 1. Static TGA curves for $[P_{2.2.2.6}][\text{CH}_3\text{CO}_2]$ at 100 (solid trace) and 150 °C (dashed trace) during 24 h.

reports regarding highest CO₂ uptake at 1:1 ratios [43,44,46,53]. Isotopic and spectroscopic studies demonstrated that small amounts of water (up to ca. 2:1 H₂O/IL ratios) effectively breaks ion pairs by hydrogen-bonding the carboxylate anion while maintaining its relatively strong basicity, whilst an excess of hydration weakens its hydrogen-acceptor ability—and most likely, by extension, its Lewis basicity [37]. It is worth noting that all hydrated carboxylate ionic liquids used in this work ($[P_{n.n.n.m}][\text{RCO}_2] \cdot x\text{H}_2\text{O}$) show widened liquid ranges due to the suppression of crystallisation events. For example, pure $[P_{4.4.4.4}][\text{CH}_3\text{CO}_2]$ is a solid at room temperature with a melting point at 56–58 °C, whereas its monohydrate ($[P_{4.4.4.4}][\text{CH}_3\text{CO}_2] \cdot \text{H}_2\text{O}$) does not show any sign of solidification down to its glass transition temperature at −72 °C.

Density and viscosity measurements have been performed as a function of temperature for selected carboxylate ionic liquids (Tables S1 and S2). Densities of $[P_{n.n.n.m}][\text{RCO}_2]$ decrease with increasing chain lengths, as expected by the growing influence of less dense aliphatic domains. On the other hand, formates are marginally denser than acetates for a given cation. The temperature dependence is shown in Fig. 2 for some $[P_{2.2.2.m}][\text{RCO}_2] \cdot \text{H}_2\text{O}$ ionic liquid hydrates, clearly evidencing the expected linear relationship. In addition, the densities of all ionic liquids have been measured at the temperatures and at the different hydration degrees of CO₂ solubility experiments. As shown below (Table 2), addition of water generally results in slight density increases.

Viscosities of carboxylate ionic liquids are greatly diminished upon hydration, as shown in literature reports [53,57], and confirmed herein for $[P_{2.2.2.8}][\text{HCO}_2]$ (Fig. 3). At room temperature, the highly viscous pure ionic liquid becomes almost three times as fluid after blending with one equivalent of water. As viscosities decrease at higher temperatures, differences become narrower. Moreover, the acetates are more viscous than the formates (Table S2 and Figure S3), with the exception of $[P_{2.2.2.8}][\text{HCO}_2]$, showing the highest viscosity of the family. Temperature increases invariably lead to lower viscosities, as widely reported for pure ionic liquids.

3.2. Solubility of CO₂ as a function of hydration degree, anion and alkyl chain lengths

Carbon dioxide solubility measurements have been performed by an isochoric methodology under varying pressure and temperature conditions in a range of $[P_{n.n.n.m}][\text{RCO}_2] \cdot x\text{H}_2\text{O}$ liquids to gain insight into the sorption process. The effects of alkyl chain lengths, anion basicity and degree of hydration have been studied. The main results at a fixed partial pressure of CO₂ (5 bar) and temperature (25 °C) are listed in Table 2. The solubility of CO₂, expressed as molar concentration, is clearly dependent on the degree of hydration. This is clearly seen from the set of data for $[P_{4.4.4.4}][\text{HCO}_2]$: maximum solubility ($C_{\text{CO}_2,l} = 2.16 \text{ mol L}^{-1}$, equivalent to $0.73 \text{ mol}_{\text{CO}_2} \text{ mol}_{\text{H}_2\text{O}}^{-1}$) was achieved for the equimolar H₂O/IL mixture. The trend entailing lower CO₂ uptake for compositions departing from such 1:1 ratio is confirmed for other hydrated ionic liquids, e.g. $[P_{4.4.4.4}][\text{CH}_3\text{CO}_2]$, $[P_{2.2.2.8}][\text{HCO}_2]$ or $[P_{2.2.2.8}][\text{CH}_3\text{CO}_2]$. Previous knowledge about such behaviour whereby both carboxylate anion and water, and especially their molar ratio, severely impact the ability to absorb CO₂ [44,46], is herein confirmed. To further investigate about the role of the carboxylate hydrate complexes, an inorganic formate salt ($\text{Na}[\text{HCO}_2]$) was tested for comparison. Sodium is much smaller and lighter than any of the phosphonium cations used for the generation of ionic liquids, and hence, it requires much larger mass (and volume) fractions of water to achieve the same molar ratios. To produce a liquid $\text{Na}[\text{HCO}_2]/\text{H}_2\text{O}$ blend at room temperature, a minimum of ca. 50 % water (in mass fraction, equating to almost 4:1 H₂O/ $\text{Na}[\text{HCO}_2]$ molar ratio) was needed, and its capacity to dissolve CO₂ under identical conditions was 0.17 mol L^{-1} . This is markedly inferior to phosphonium formate ionic liquids. At an even higher hydration degree, albeit a significantly lower mass fraction of water (22.8 %) $[P_{4.4.4.4}][\text{HCO}_2] \cdot 5\text{H}_2\text{O}$ absorbs 0.72 mol L^{-1} , i.e. $0.30 \text{ mol}_{\text{CO}_2} \text{ mol}_{\text{H}_2\text{O}}^{-1}$ (see Table 2). This

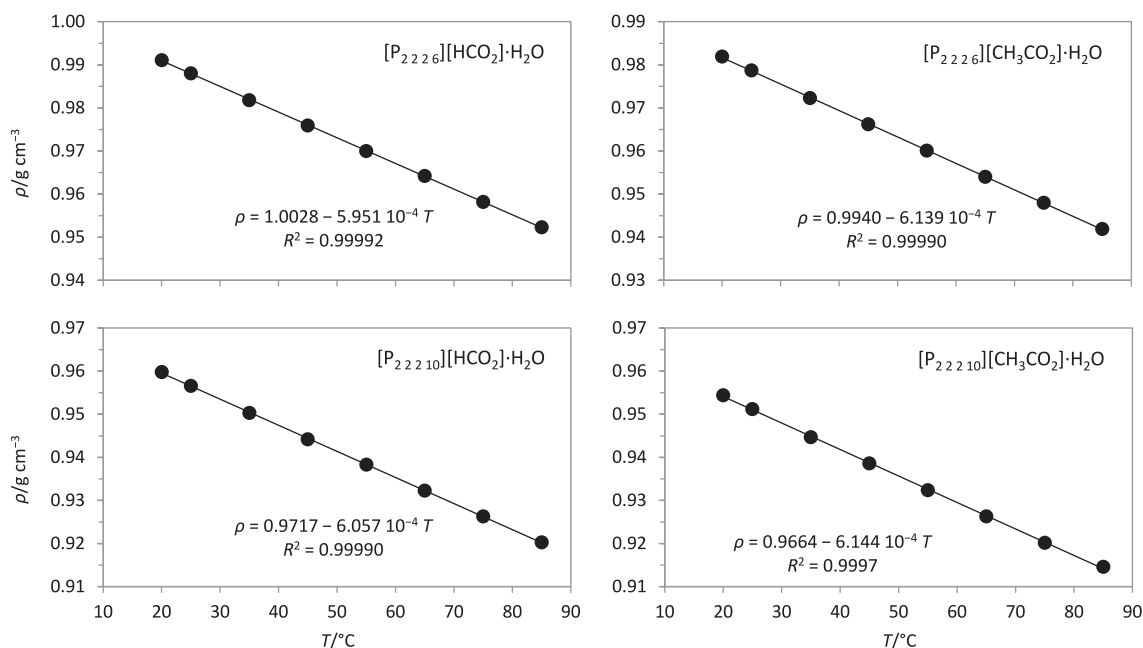


Fig. 2. Density plots as a function of temperatures (data from Table S1), and linear fit equations and goodness-of-fit data for triethylhexyl- and decyl-triethylphosphonium formate or acetate ionic liquid monohydrates.

Table 2

Density and CO₂ solubility (5 bar, 25 °C) in various carboxylate ionic liquids at different hydration degrees.

ionic liquid, salt or amine	water content molar ratio/ mol _{H₂O} mol _{IL} ⁻¹	mass fraction/ g _{H₂O} g _{liquid} ⁻¹ (%)	ρ/g cm ⁻³	CO ₂ solubility C _{CO₂,l} ^a / mol L ⁻¹	molar ratio/ mol _{CO₂} mol _{IL} ⁻¹	mass ratio/ g _{CO₂} g _{liquid} ⁻¹ (%)
[P _{4 4 4 4}][HCO ₂]	0.46	2.6	0.9493	1.58	0.52	7.34
	1.00	5.66	0.9489	2.16	0.73	10.0
	2.00	10.6	0.9515	1.74	0.62	8.06
	5.00	22.8	0.9627	0.72	0.30	3.3
	10.0	37.3	0.9749	0.34	0.17	1.5
[P _{4 4 4 4}][CH ₃ CO ₂]	3.37	16.0	0.9545	1.81	0.72	8.36
	4.70	21.0	0.9599	1.47	0.62	6.74
	7.08	39.9	1.0390	0.13	0.04	0.54
[P _{2 2 2 2}][HCO ₂]	1.00	6.77	0.9874	2.32	0.63	10.3
[P _{2 2 2 6}][HCO ₂]	0.10	0.63	0.9684	0.38	0.11	1.7
[P _{2 2 2 8}][HCO ₂]	1.00	6.13	0.9705	1.90	0.58	8.63
[P _{2 2 2 10}][HCO ₂]	1.00	5.59	0.9563	1.88	0.89	8.66
[P _{2 2 2 2}][CH ₃ CO ₂]	3.21	21.9	1.0356	2.18	0.56	9.26
[P _{2 2 2 6}][CH ₃ CO ₂]	1.00	6.44	0.9787	3.07	0.88	13.8
[P _{2 2 2 8}][CH ₃ CO ₂]	0.01	0.07	0.9546	0.36	0.11	1.7
	1.01	5.87	0.9638	2.55	0.82	11.6
	1.14	6.59	0.9651	2.48	0.80	11.3
[P _{2 2 2 10}][CH ₃ CO ₂]	1.00	5.37	0.9512	2.52	0.88	11.7
Na[HCO ₂]	3.89 ^b	50.8	1.3467	0.17	0.02	0.57
MEA ^c	7.91 ^b	70.0	1.0108	3.54	0.72	15.4

^a Amounts of CO₂ calculated as the difference between the total CO₂ fed into the system (as measured by a mass flow controller) and the amount of CO₂ in the gas phase after the equilibrium is reached, based on the ideal gas law; molar concentrations based on the sorbent volume and assuming no volume change during absorption. ^b Molar ratio relative to the used salt or amine, instead of IL. ^c MEA: monoethanolamine.

reveals that not only the [RCO₂]⁻/H₂O ratio affects the effectiveness of chemical CO₂ absorption; the nature, structures and molar volumes of the cations also have influence on solubilities. There is no evidence for the direct participation of ionic liquid cations in the chemistry of CO₂ capture, given that water prevents the formation of C-nucleophilic cationic moieties such as ylides or carbenes [36,37], but they may favour absorption by more physical factors. For example, cation asymmetry and packing inefficiency with cations may leave interstitial spaces for CO₂ [9]. Moreover, the larger molar masses and volumes of [P_{n n n m}]⁺ (and by extension, other typical ionic liquid cations) as compared to simple alkali metal cations may disrupt carboxylate-water interaction to some extent, thus enhancing anion basicity.

Anion effects are studied by only comparing the two simplest carboxylates, that is, formate and acetate. The latter is more basic, and hence, is presumably more efficacious for chemical absorption of CO₂. The results in Table 2 confirm this: for a given cation, solubilities are higher for acetate (e.g. 3.07 and 2.32 mol L⁻¹ for [P_{2 2 2 6}][CH₃CO₂]₂·H₂O and [P_{2 2 2 6}][HCO₂]₂·H₂O, respectively at 5 bar and 25 °C). It is worth noting that nearly equimolar capture (≈ 0.9 mol_{CO₂} mol_{IL}⁻¹) is attained for some of the formulations, e.g. [P_{2 2 2 10}][HCO₂]₂·H₂O, [P_{2 2 2 6}][CH₃CO₂]₂·H₂O and [P_{2 2 2 10}][CH₃CO₂]₂·H₂O (Table 2). This is in agreement with results in the literature for other related ionic liquid hydrates [44,47]. One key advantage of this lies in the possibility to achieve high capture performances even for more hydrated ionic liquids.

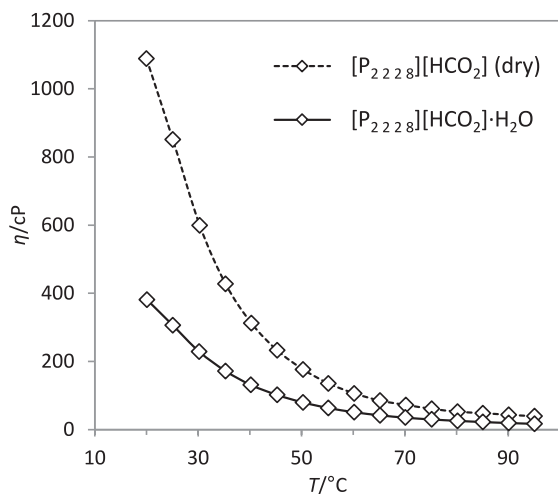


Fig. 3. Comparison of experimental viscosity data plots for dry (water content ≈ 340 ppm dashed trace) and monohydrated (solid trace) $[P_{2,2,2,8}][HCO_2]$, showing the drastic reduction upon water introduction.

For example, $[P_{2,2,2,2}][CH_3CO_2] \cdot 3.21H_2O$ absorbs 2.18 mol L^{-1} under the same conditions. The CO_2 solubilities achieved for acetate ionic liquid hydrates are remarkably high as compared to typical amine sorbents employed commercially. This is illustrated by the data for aqueous monoethanolamine (30 % weight ratio), which exhibits a marginally higher CO_2 absorption capacity than that of $[P_{2,2,2,6}][CH_3CO_2] \cdot H_2O$, i.e. the best performing ionic liquid hydrate (15.4 % vs. 13.8 % CO_2 /liquid mass ratio, Table 2). Interestingly, molar capacity is even higher for the hydrated ionic liquids as compared to the aqueous amine (0.88 vs. 0.72 $\text{mol}_{CO_2} \text{ mol}_{IL}^{-1}$, respectively, Table 2). Despite the still superior solubility in the amine sorbent on a volume basis, and the possibility to enhance performance by advanced amine formulations, the present results for carboxylate ionic liquid hydrates are encouraging with regards to further sorbent development based on them by judicious structural design.

Structural design versatility of ionic liquids allows nearly countless variations to be performed on cation and/or anion. Playing with alkyl chain lengths is an obvious manner to explore possibilities. The set of ionic liquid cations presented herein span from highly symmetric (e.g. $[P_{4,4,4,4}]^+$) to asymmetric (e.g. $[P_{2,2,2,8}]^+$). Asymmetry helps preventing crystallisation (see Section 3.1) thus widening low temperature ranges. The effect of asymmetry on CO_2 solubility is less apparent, according to the limited amount of data presented herein. Further systematic investigations will surely establish more solid trends. Regarding chain lengths and cation sizes, two opposing effects may be at play, as discussed above: Smaller cations entail higher concentrations of the chemically active carboxylate cations, whilst larger ones leave broader interstices for physical dissolution and minimise the basicity-deactivation effect of water. A close inspection of the solubility results in Table 2 for the $[P_{2,2,2,m}]^+$ series indicate highest CO_2 solubilities for $[P_{2,2,2,6}]^+$ ionic liquid hydrates. Therefore, the strategy of making cations smaller and more asymmetric is successful. Although this study must be competed with more ionic liquid hydrate formulations, the results indicate that concentrating the anions enhances chemical absorption of CO_2 , provided packing inefficiencies compensate for the more intense electrostatic cation–anion interactions to suppress or minimise crystallisation events.

Upon CO_2 absorption, the supramolecular ionic liquid hydrate structure changes radically. The extent of the chemical absorption reaction is significant even at moderate partial pressures of carbon dioxide (typically $> 0.5 \text{ mol}_{CO_2} \text{ mol}_{IL}^{-1}$ at 1 bar, see Section 3.4). The resulting accumulation of hydrogencarbonate entails more hydrogen-bonding sites and enables the likely formation of adducts either with itself or

with the protonated carboxylate. At the same time, water is consumed. On occasions, formation of solids has been observed upon CO_2 capture (Scheme 1) [41,44]. Even in the absence of solids, the absorption of CO_2 generally leads to increases in viscosity. To quantify such effect, viscosity measurements were performed at increasing temperatures (Table S3). A comparison of the results before and after capture is shown in the plots in Fig. 4 for selected ionic liquid hydrates. Viscosity increases are clear in all studied cases, and more marked for the formate ionic liquid hydrates. Upon heating, sudden viscosity increases are observed, most likely owing to the onset of CO_2 release by desorption, as suggested by the apparition of gas bubbles. The temperatures at which this phenomenon starts are higher the higher the viscosity of the ionic liquid. Release starts at temperatures as low as 30 °C for $[P_{2,2,2,6}][HCO_2]$, reflecting the ease of regeneration of this sorbent family [49]. The maximum rate of release takes place at higher temperature for acetate (50 °C for $[P_{2,2,2,8}][CH_3CO_2]$), a fact that can be ascribed to higher anion basicity. At the end of the measurement (90 °C), viscosities had fallen close to those of the fresh ionic liquid hydrate, revealing almost complete CO_2 desorption.

3.3. Chemical absorption: Isotherms and speciation

Isotherms have been recorded for some selected cases by measuring CO_2 solubilities in increasing pressure steps. The obtained data is listed in Table S4 and plotted in Fig. 5. The possible interference of water on pressure readings is not significant, as assessed by vapour pressure measurements of hydrated ionic liquids under study herein ($P_{vap,H_2O} = 1.6$ mbar for $[P_{4,4,4,4}][CH_3CO_2] \cdot 1.5H_2O$ at 25 °C, or < 0.02 bar for $[P_{2,2,2,6}][CH_3CO_2] \cdot H_2O$ at 90 °C, Figure S4). The use of $[P_{4,4,4,4}][CH_3CO_2]$ at low hydration degrees is somewhat restricted by the formation of crystallites after prolonged periods at room temperature, most likely consisting of $[P_{4,4,4,4}][H(CH_3CO_2)_2]$ [44], whereas more hydrated samples show much lower propensity toward crystallisation. The isotherm for $[P_{4,4,4,4}][CH_3CO_2] \cdot 3.4H_2O$ at 25 °C (Fig. 5, top) is a curve revealing significantly higher increases in solubility at moderate pressures, and sign of saturation at $P_{CO_2} > 1.5$ bar. As previously observed for similar carboxylate ionic liquid hydrates, such behaviour is consistent with chemical absorption of CO_2 in the form of $[HCO_3]^-$. Another ionic liquid hydrate tested, primarily owing to the availability of its methylcarbonate precursor that greatly facilitates synthesis, was $[P_{4,4,4,1}][HCO_2] \cdot 0.96H_2O$. At slightly higher temperatures (40 °C), and in addition considering that formate is less basic than acetate, a noticeable chemical CO_2 absorption is suggested by its isotherm, despite the less favourable conditions. A region at low pressures (< 1 bar) where the CO_2 uptake shows a pronounced increase is observed, followed by a region where the increase in solubility is more moderate. In both cases, physical absorption might be of relevance after saturation at higher pressures, as suggested by the steady increase in solubility.

Isotherms at different pressures were recorded for $[P_{2,2,2,6}][CH_3CO_2] \cdot 0.96H_2O$, with the ultimate objective of estimating the related enthalpy of CO_2 absorption. The data clearly reveals how the chemical and physical absorption processes take place in parallel, as for the ionic liquids discussed above, but to different extents depending on temperature and pressure. Thus, at 25 °C the CO_2 uptake rapidly increases at low pressures (< 1 bar), while it increases more slowly (but steadily) at higher pressures. The resulting exponential-like curve is a clear indication of strong chemical absorption, due to the basicity of acetate, the nearly equimolar hydration ratio and the moderate temperature. Further support to the relevance of chemical absorption is derived from CO_2 /IL molar ratios, surpassing 0.5 and approaching 0.9 $\text{mol}_{CO_2} \text{ mol}_{IL}^{-1}$ at 1 and 6 bar, respectively, at 25 °C (see Table S4). The result at atmospheric pressure is remarkable, since it represents a capture effectiveness on a par with strongly chemically absorbing amine-based ionic liquids that exert a saturation capacity at 0.5 $\text{mol}_{CO_2} \text{ mol}_{amine}^{-1}$ according to the ammonium carbamate mechanism operating in such sorbents [10,58]. Overall, $[P_{n,n,n,m}][RCO_2] \cdot xH_2O$ in general

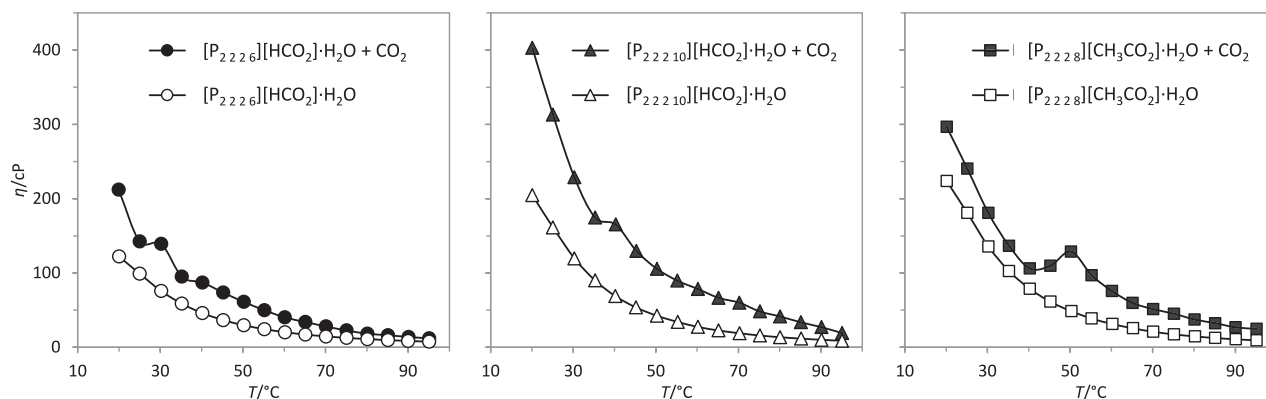


Fig. 4. Comparison of experimental viscosity data plots for $[P_{2,2,2,6}][HCO_2] \cdot H_2O$, $[P_{2,2,2,10}][HCO_2] \cdot H_2O$ and $[P_{2,2,2,8}][CH_3CO_2] \cdot H_2O$, as fresh liquids and after CO_2 absorption experiments (5 bar) at increasing temperatures. Higher viscosities for CO_2 -laden liquids are ascribed to the formation of hydrogencarbonate, which might strengthen the hydrogen bond network. The incremental discontinuity upon heating is related to the onset of CO_2 desorption.

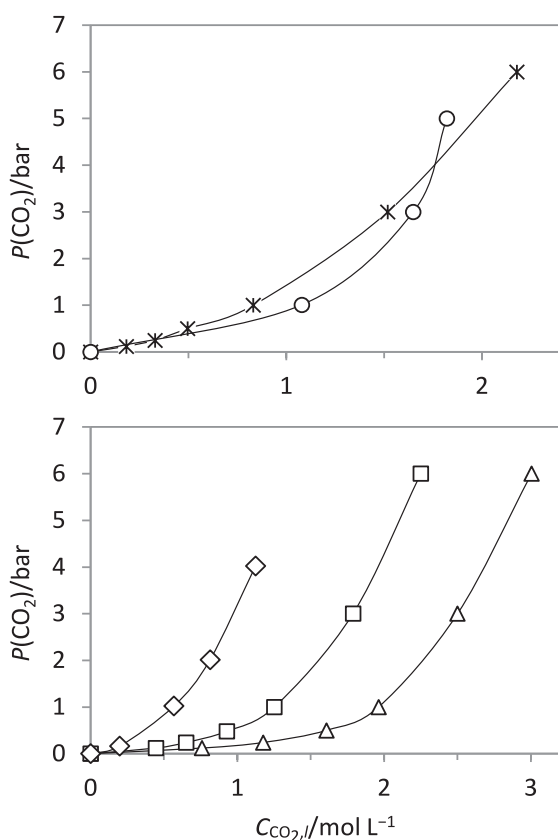


Fig. 5. Carbon dioxide solubility ($C_{CO_2,l}$ in $mol\ L^{-1}$) isotherms for various ionic liquid hydrates. Top: $[P_{4,4,4,4}][CH_3CO_2] \cdot 3.4H_2O$ (circles, 25 °C) and $[P_{4,4,4,1}][HCO_2] \cdot 0.96H_2O$ (stars, 40 °C). Bottom: $[P_{2,2,2,6}][CH_3CO_2] \cdot 0.96H_2O$ (triangles, 25 °C; squares, 50 °C; diamonds, 90 °C). The marked curves displayed by all liquids prove their behaviour as chemical CO_2 absorbers. Lines are a guide to the eye.

absorb CO_2 chemically with increasing pressure until the reaction approaches saturation; then, the chemical absorption declines but the physical absorption continues, dominating the uptake at higher pressures.

Transformation of CO_2 it into $[HCO_3]^-$ has been unambiguously proven by spectroscopic techniques, especially FTIR and NMR, for a range of carboxylate ionic liquids in the presence of water [36,44,49]. Furthermore, the identification of small amounts physically dissolved CO_2 has been performed by NMR and Raman spectroscopies [45,59].

The relative quantification of both unreacted carbon dioxide and the derived hydrogencarbonate in the liquid phase is surely a worthwhile topic of future research. In this work, ^{13}C NMR and ATR-FTIR

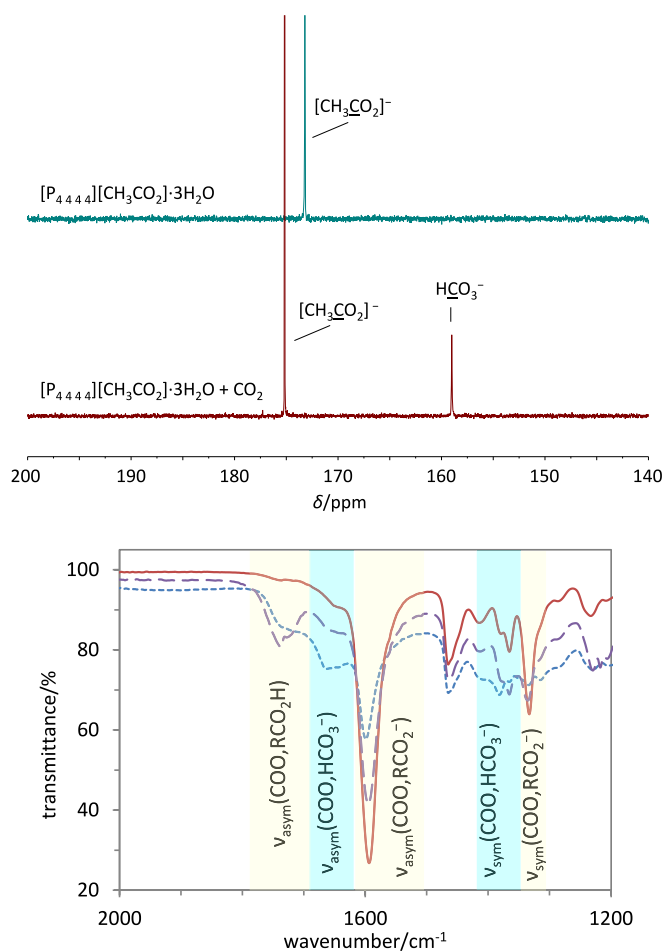


Fig. 6. Top: ^{13}C NMR spectra of hydrated $[P_{4,4,4,4}][CH_3CO_2]$ before and after CO_2 capture (dmsd- d_6 as external standard, 400 MHz), showing the emerging peak due to $[HCO_3]^-$ and shifting of the carboxylate signal. Bottom: ATR spectra of $[P_{4,4,4,4}][HCO_2] \cdot H_2O$ before (red trace) and after CO_2 (dotted blue trace) or $^{13}CO_2$ (dashed purple trace) absorption; after CO_2 absorption, bands associated to HCO_2H and $[HCO_3]^-$ can be clearly observed, whereas the latter are not visible since they are red-shifted. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

measurements have been undertaken to confirm the formation of $[\text{HCO}_3]^-$ as the trapped CO_2 species. The ^{13}C NMR spectra of hydrated $[\text{P}_{4444}][\text{CH}_3\text{CO}_2]$, both prior to and subsequently to CO_2 capture (1 bar) are shown in Fig. 6 (top). A distinctive peak at 173.2 ppm is indicative of the presence of the carboxylate carbon atom of acetate. After CO_2 capture, the emergence of a discernible peak at approximately 159 ppm corresponds to the hydrogencarbonate carbon, thereby providing conclusive evidence of carbon dioxide absorption by the hydrated carboxylate ionic liquid via the expected mechanism (Scheme 1). Moreover, the carboxylate carbon signal of acetate slightly shifted to lower field.

In addition to NMR, ATR-FTIR measurements with or without isotopic labelling were recorded to deepen in the understanding of the CO_2 capture process in $[\text{P}_{nnnm}][\text{RCO}_2] \cdot x\text{H}_2\text{O}$. A comparison of the ATR-FTIR spectra of $[\text{P}_{4444}][\text{HCO}_2] \cdot \text{H}_2\text{O}$ before and after equilibration with either CO_2 or $^{13}\text{CO}_2$ (1 bar) is shown in Fig. 6, bottom. The presence of broad bands typical of bicarbonate in the 1640–1670 and 1360–1400 cm^{-1} ranges, due to asymmetric and symmetric COO^- stretching, respectively [37], is clearly noticeable after absorption of conventional carbon dioxide. The shoulder around 1720 cm^{-1} is due to the presence of formic acid as a hydrogen-bonded species, also supporting the suggested mechanism (Scheme 1). Moreover, weak signals at ca. 2340 cm^{-1} (not shown) are attributable to the C–O stretching of the free CO_2 molecule, which could be due to physical absorption or to *in-situ* reversal of the reaction with the corresponding release of gas. It is also worthwhile mentioning that the O–H stretching band of water (broad between 3000 and 3500 cm^{-1}), is greatly diminished after CO_2 absorption, which might indicate the transformation into hydrogencarbonate anions and formic acid. Further studies should help confirm these conclusions.

The ATR-FTIR spectrum recorded after either CO_2 or $^{13}\text{CO}_2$ absorption into $[\text{P}_{4444}][\text{HCO}_2] \cdot \text{H}_2\text{O}$ (Fig. 6, bottom) show marked differences in the hydrogencarbonate regions. The asymmetric COO^- stretching band are essentially absent (the residual shoulder at $\approx 1640 \text{ cm}^{-1}$ is consistent with the H–O–H bending mode of water) in the case of carbon-13 labelling, suggesting that $[\text{H}^{13}\text{CO}_3]^-$ is formed instead. Its analogous asymmetric $^{13}\text{COO}^-$ stretching signal is expected to red-shift with respect to that for $[\text{H}^{12}\text{CO}_3]^-$, and consequently, to severely overlap with the asymmetric COO^- stretching band of the carboxylate anion. In fact, the intensity of the signal at ca. 1590 cm^{-1} is higher for the experiment using $^{13}\text{CO}_2$. A similar phenomenon is observed for the symmetric stretching bands at around 1400 cm^{-1} . These observations further provide evidence about the formation of hydrogencarbonate in hydrated carboxylate ionic liquids upon CO_2 capture. The predominance of chemical absorption is supported by spectroscopy. However, physical dissolution cannot be neglected. The challenge of quantifying both unreacted carbon dioxide and hydrogencarbonate prevents a more precise understanding of the extent of physical and chemical absorption. Advanced NMR procedures might help in this regard. Notwithstanding, the current knowledge and data obtained in this work are suitable to undertake thermodynamic modelling to estimate enthalpies of CO_2 absorption, as described below.

3.4. Absorption models and enthalpies of absorption

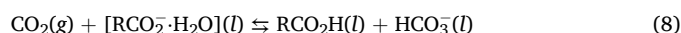
The equilibrium constants were calculated based on the chemical CO_2 sorption mechanism described in general terms in Scheme 1, that is, the reaction of a carboxylate-water adduct with carbon dioxide giving rise to the protonated carboxylate and a hydrogencarbonate anion, well-supported by spectroscopic measurements in this work and in the prior art [41,44,45,48,53,60,61]. This is admittedly a simplified view of the real situation, most likely entailing a complex, highly ionic, hydrogen bond network whereby discrete protonic species are shared by anions. Given this complexity, implementing a universal thermodynamic model for the absorption of CO_2 in hydrated carboxylate ionic liquids is challenging, especially for wide ranges of hydration ratios or CO_2 partial pressures. To assess the validity of different models with the purpose of

determining enthalpies of absorption, three approaches are herein adapted from previous studies in the literature for similar carboxylate ionic liquid systems. Minor modifications have been introduced to better account for the particular composition of the ionic liquid hydrate under study herein ($[\text{P}_{2226}][\text{CH}_3\text{CO}_2] \cdot 0.96\text{H}_2\text{O}$, hereinafter $[\text{P}_{2226}][\text{CH}_3\text{CO}_2] \cdot \text{H}_2\text{O}$, for simplicity) or to maintain consistency. For the sake of comparison and exploration of possibilities, each approach is further submitted to slight variations resulting in distinct models, as specifically described in detail in the following paragraphs. In each case, equilibrium constants have been calculated at each temperature, and subsequently, reaction enthalpies have been determined by applying the van't Hoff equation (see extended discussion in the Supplementary Data) as follows:

$$R \ln K = \Delta S^\circ - \frac{1}{T} \Delta H^\circ \quad (7)$$

3.4.1. Associated carboxylate-hydrate (based on Quinn et al.) [41]

The seminal investigations by Quinn et al. considered carboxylate-water entities as adducts and hydrogencarbonate as free anions [41]. The general reaction equation (8) is considered to obtain the corresponding equilibrium constant on a molar concentration basis (9), and subsequently, a linear-fit model equation (10).

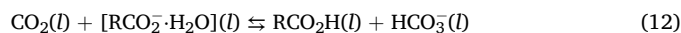


$$K_8 = \frac{c_{\text{RCO}_2\text{H}} c_{\text{HCO}_3^-}}{c_{\text{CO}_2,\text{g}} c_{[\text{RCO}_2 \cdot \text{H}_2\text{O}]}} \quad (9)$$

$$C_{\text{CO}_2,\text{l}}^2 / (c_{\text{IL},0} - C_{\text{CO}_2,\text{l}}) = K_8 c_{\text{CO}_2,\text{g}} (\text{model Ia}) \quad (10)$$

Fitting according to model Ia results in reasonably linear trends (Figure S5 and Table S5), demonstrating that the chemical CO_2 absorption by $[\text{P}_{2226}][\text{CH}_3\text{CO}_2] \cdot \text{H}_2\text{O}$ follows the expected stoichiometry described in reaction equation (8). Table 3 lists the results of this and the forthcoming models along with related literature data for comparison. The heat of absorption of CO_2 in $[\text{P}_{2226}][\text{CH}_3\text{CO}_2] \cdot \text{H}_2\text{O}$ was estimated as ca. -39 kJ mol^{-1} by model Ia, which is slightly higher than that measured for $[\text{N}_{2222}][\text{CH}_3\text{CO}_2] \cdot 4\text{H}_2\text{O}$ by calorimetry [41], a fact that might be rationalised due to the lower basicity of acetate upon further dilution. Moreover, the enthalpy of absorption according to model Ia is remarkably close to the estimation performed by Chinn et al. by a similar data treatment procedure [62].

Considering carbon dioxide as a gas phase reactant in model Ia is a convenient simplification. Aiming at a stricter thermodynamic description of CO_2 absorption, a modification was done by considering a two-step dissolution-reaction process, as described by equations (11) and (12). The equilibrium constant of the latter reaction, namely K_{12} , now considers the concentration of unreacted CO_2 in the hydrated ionic liquid phase ($C_{\text{CO}_2,\text{l}}$) and implies that the total concentration of absorbed CO_2 ($C_{\text{CO}_2,\text{l}}$) is equal to the sum of $C_{\text{CO}_2,\text{l}}$ and $c_{\text{HCO}_3^-}$. After estimating $C_{\text{CO}_2,\text{l}}$ (see extended details in the Supplementary Data) and rearranging as done above for equation (10), the fitting equation for model Ib (equation (15)) is obtained.



$$K_{12} = \frac{c_{\text{RCO}_2\text{H}} c_{\text{HCO}_3^-}}{c_{\text{CO}_2,\text{l}} c_{[\text{RCO}_2 \cdot \text{H}_2\text{O}]}} \quad (13)$$

$$C_{\text{CO}_2,\text{l}} = c_{\text{CO}_2,\text{l}} + c_{\text{HCO}_3^-} \quad (14)$$

$$c_{\text{HCO}_3^-}^2 / (c_{\text{IL},0} - c_{\text{HCO}_3^-}) = K_{12} c_{\text{CO}_2,\text{l}} (\text{model Ib}) \quad (15)$$

Fitting the data according to model Ib is acceptable (Figure S5), although marginally less satisfactory than for model Ia. The actual $C_{\text{CO}_2,\text{l}}$

Table 3

Summary of enthalpies of CO₂ absorption determined by means of the van't Hoff equation after fitting experimental [P₂₂₂₆][CH₃CO₂]-H₂O data to different thermodynamic models, and comparison to related literature systems.

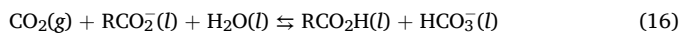
Model	Step ^a	ionic liquid hydrate sorbent	$\Delta S^\circ /$ J K ⁻¹ mol ⁻¹	$\Delta H^\circ /$ kJ mol ⁻¹	R ²	Reference
Ia	r	[P _{2 2 2 6}][CH ₃ CO ₂]-H ₂ O	-96	-39.3	0.996	this work
Ia	r	[N _{2 2 2 2}][CH ₃ CO ₂]-4H ₂ O	-	-35 ^b	0.998	[41]
Ib	r	[P _{2 2 2 6}][CH ₃ CO ₂]-H ₂ O	-101	-38.5	0.9994	this work
IIa	r	[P _{2 2 2 6}][CH ₃ CO ₂]-H ₂ O	-161	-60.2	0.990	this work
IIa	r	[P _{4 4 4 4}][HCO ₂]-H ₂ O	-	-61	-	[46]
IIb	r	[P _{2 2 2 6}][CH ₃ CO ₂]-H ₂ O	-129	-47.7	0.97	this work
IIb	r	[P _{4 4 4 4}][HCO ₂]-H ₂ O	-	-46	-	[46]
IIIa	d	[P _{2 2 2 6}][CH ₃ CO ₂]-H ₂ O	-53	-12.5	0.97	this work
	r		-96	-33.7	0.98	
	o		-149	-46	-	
IIIa	d	[N _{2 2 2 4}][CH ₃ CO ₂]-H ₂ O	-91	-21	-	[48]
	r		-	-29	-	
	o		-	-50	-	
IIIb	d	[P _{2 2 2 6}][CH ₃ CO ₂]-H ₂ O	-46	-9.9	0.98	this work
	r		-104	-36.5	0.990	
	o		-150	-46	-	

^a d: physical dissolution of CO₂; r: chemical absorption reaction leading to HCO₃⁻; o: overall. ^b Experimental enthalpy, measured by calorimetry; fitting was performed only to confirm reaction stoichiometry, not for determination of thermodynamic parameters.

could be overestimated given that part of the interstitial cavities prone for hosting dissolved CO₂ are expected to be occupied by water, and to the basicity of acetate driving reactive transformation into [HCO₃]⁻. In fact, our own results (see above) and prior literature reports [45,59] are consistent about the minor presence of free CO₂ in the hydrated carboxylate ionic liquids. It is remarkable, though, that the correlating equilibrium constants and reciprocal temperatures is even better than for model Ia (see Table 3 and Figure S5). More interestingly, the final enthalpy of absorption is essentially identical, or marginally lower for model Ib (ca. -39 kJ mol⁻¹). Similar consistency in entropies is observed (Table 3), further supporting the comparable validity of both associated carboxylate-hydrate models (Ia and Ib).

3.4.2. One-step, dissociated carboxylate-hydrate (based on Yasaka and Kimura) [46]

This approach considers one-step chemical CO₂ sorbent models (*i.e.* no physisorption was contemplated), yet with significant differences over the I models discussed above. The hydrogencarbonate and protonated carboxylate products were modelled in two different ways (see Supplementary Data for further details) [46]. The first of these models (IIa) considers that all reactants and products occur as independent entities, according to the following stoichiometry and equilibrium constant expressions, which results in fitting equation (18).



$$K_{16} = \frac{c_{\text{RCO}_2\text{H}} c_{\text{HCO}_3^-}}{c_{\text{CO}_2,\text{g}} c_{\text{RCO}_2^-} c_{\text{H}_2\text{O}}} \quad (17)$$

$$c_{\text{CO}_2,\text{l}}^2 / (c_{\text{IL},0} - c_{\text{CO}_2,\text{l}})^2 = K_{16} c_{\text{CO}_2,\text{g}} (\text{model IIa}) \quad (18)$$

Conversely, the hydrogencarbonate and protonated carboxylate products are regarded as bound to each other in the form of a hydrogen-bonded adduct between in model IIb; for simplicity and consistency, the concentration of the adduct is designated as $c_{\text{HCO}_3^-}$. The corresponding stoichiometry, equilibrium constant and linear fit equations are indicated below.



$$K_{19} = \frac{c_{[\text{RCO}_2\text{H} \cdots \text{HCO}_3^-]}}{c_{\text{CO}_2,\text{g}} c_{\text{RCO}_2^-} c_{\text{H}_2\text{O}}} \quad (20)$$

$$c_{\text{CO}_2,\text{l}} / (c_{\text{IL},0} - c_{\text{CO}_2,\text{l}})^2 = K_{19} c_{\text{CO}_2,\text{g}} (\text{model IIb}) \quad (21)$$

Fitting results (Table 3, Figure S6 and Table S6) are acceptable, especially for model IIa (see Figure S6 and data in Table 3). The derived heats of absorption of CO₂ are quite different depending on the model. The fully dissociative model IIa results in a noticeably higher ΔH° than the IIb counterpart, *i.e.* -60 and -48 kJ mol⁻¹, respectively. These values are remarkably close that the analogous enthalpies determined by Yasaka and Kimura for their monohydrate system ([P_{4 4 4 4}][HCO₂]-H₂O), *i.e.* -61 and -46 kJ mol⁻¹, respectively. Hence, the determination of CO₂ absorption enthalpies appears to be greatly dependent on the stoichiometry model chosen. Despite the significantly different experimental conditions as compared to reference [46], that is, single versus variable pressure measurements, none of these one-step models (IIa and IIb, and by extension, also Ia) is clearly unsuccessful. Even if Ia gives better correlation, all of them are valid, probably due to their similarity regarding stoichiometry. The real speciation might be a hybrid between the different models whereby hydrogen bonds are dynamically and continuously being formed, broken and re-formed, probably via different topologies. The main issue that remains to be ascertained is which model (models) better predicts (predict) the enthalpies of CO₂ absorption. A dedicated experimental study involving calorimetric measurements, currently considered as a research task in our laboratories, would shed light into this.

3.4.3. Two-step, associated carboxylate-hydrate (based on Wang et al.) [48]

Thermodynamically, it is arguable more appropriate to decouple physical absorption of CO₂ from its chemical reaction with the hydrated carboxylate to give rise to hydrogencarbonate as the main carbonic species in the ionic liquid medium. This is suitably described by reaction equations (11) and (12). The downside of this two-step approach is the minor significance of unreacted CO₂ in the liquid, as discussed above for model Ib. However, typical chemical absorbent liquids such as aqueous amines have also been modelled taking into consideration this pathway [63,64]. In this context, Wang et al. developed a simple two-step model for hydrated carboxylate ionic liquids, namely [N_{2 2 2 4}][CH₃CO₂]-xH₂O [48], based on Henry's constants (k_{H}) to account for the physical dissolution step, *i.e.* equation (11).

The procedure entails the use of Henry's constants (k_{H}) to account for the physical dissolution step, *i.e.* equation (11), whereas K_{12} is used as in equation (13), combined with equation (22) to isolate $c_{\text{HCO}_3^-}$.

$$k_{\text{H},11} = K_{11}^{-1} = \frac{P_{\text{CO}_2}}{c_{\text{CO}_2,\text{l}}} \quad (22)$$

$$c_{\text{HCO}_3^-} = \left(\frac{P_{\text{CO}_2} K_{12} (c_{\text{IL},0} - c_{\text{HCO}_3^-})}{k_{\text{H}}} \right)^{1/2} \quad (23)$$

Two variants of this approach are herein tested. The first (model *IIIa*) considers that the amount of physically dissolved CO_2 is significantly smaller than that of $[\text{HCO}_3^-]$, and hence, equation (14) becomes $C_{\text{CO}_2,l} \approx c_{\text{HCO}_3^-}$. Then, the above and results in the equation below.

$$\frac{C_{\text{CO}_2,l}}{P_{\text{CO}_2}} = \frac{1}{k_{\text{H}}} + \left(\frac{K_{12}}{k_{\text{H}}} \right)^{1/2} \left(\frac{c_{\text{IL},0} - C_{\text{CO}_2,l}}{P_{\text{CO}_2}} \right)^{1/2} \quad (\text{model IIIa}) \quad (24)$$

A variation of this model by estimating the concentration of unreacted CO_2 in the ionic liquid hydrate ($C_{\text{CO}_2,l}$) based on Henry's constant data of a reference ionic liquid (see [Supplementary Data](#) for details) [65]. The model *IIIb* derived reflects more closely the two-step absorption mechanism.

$$\frac{C_{\text{CO}_2,l}}{P_{\text{CO}_2}} = \frac{1}{k_{\text{H}}} + \left(\frac{K_{12}}{k_{\text{H}}} \right)^{1/2} \left(\frac{c_{\text{IL},0} - c_{\text{HCO}_3^-}}{P_{\text{CO}_2}} \right)^{1/2} \quad (\text{model IIIb}) \quad (25)$$

The main advantage of the two-step approach of these models lies in the possibility to assess in one single fit the relative influence of physical dissolution in the liquid and chemical reaction on heats of absorption. The fittings obtained for models *IIIa* and *IIIb* ([Figure S7](#) and [Table S7](#)) suggest overestimation of physical absorption, as discussed in more detail in the [Supplementary Data](#). However, their overall validity is not severely compromised. The obtained enthalpies are reasonably close to those obtained by other methods ([Table 3](#)). Model *IIIb*, which fits better to linearity among the two, gives physical and chemical heats of absorption around -10 and -36 kJ mol^{-1} . This result is in agreement with a more significant impact of chemical sorption, as also suggested for aqueous amines [63,64] and amine-based ionic liquids [17]. Overall enthalpies and entropies of absorption are remarkably similar (ca. -46 kJ mol^{-1} and $-150 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively) for both models *IIIb* and *IIIb* (see [Table 3](#)). These overall absorption enthalpies are within the range of those estimated by other models, and close to the original model by Wang *et al.* [48], reinforcing the observation that the final estimate heavily depends on the modelling approach.

Whilst more experimental data must be acquired to further assess the validity of the different methods, all of them are useful and reasonable to estimate enthalpies of CO_2 absorption of carboxylate hydrates. This is in spite of the inherent limitations of each model, as discussed above. The range of enthalpies obtained (average between -40 and -45 kJ mol^{-1}) are within the range of other hydrated carboxylate ionic liquid systems reported in the literature (see [Table S8](#)). By comparison with typical CO_2 absorbents, these enthalpies are, in absolute values, clearly below those for primary and secondary amines ($<65 \text{ kJ mol}^{-1}$), and significantly below those for tertiary amines ($<50 \text{ kJ mol}^{-1}$) [2,3], confirming that these ionic liquid sorbents behave as mild chemical absorbers for CO_2 with low regeneration heat requirements [49].

4. Conclusions

The validity of carboxylate ionic liquid hydrates as feasible candidates for CO_2 capture technologies is reinforced and supported by the CO_2 solubility results obtained in this work. Several of a series of tetraalkylphosphonium formate or acetate ionic liquids, in hydrated form, absorb significant amounts of carbon dioxide. The expected chemisorption mechanism leading to hydrogencarbonate is confirmed by nuclear magnetic resonance and infrared spectroscopy by isotopic labelling. Capture capacities are optimum for monohydrates, reaching 3 mol L^{-1} (ca. $0.9 \text{ mol CO}_2 \text{ mol IL}^{-1}$) for triethylhexylphosphonium acetate hydrate ($[\text{P}_{2226}][\text{CH}_3\text{CO}_2] \cdot \text{H}_2\text{O}$) at 5 bar and 25°C , although solubilities are significant for a wide range of hydration degrees. This system combines the optimal of several trends drawn by critically examining

solubility data, that is, asymmetric cations enhance liquid ranges at low temperatures by preventing crystallisation for monohydrates, smaller cations with shorter alkyl chains result in concentration of the chemisorption-active anions, and the higher basicity of acetate vs. formate further enhances CO_2 capture. Remarkably, carboxylate ionic liquid performance approaches that of commercial aqueous amine sorbents (13.8 % and 15.4 % CO_2 /liquid mass ratio, respectively). Isotherm data are used to assess thermodynamic models, varied according to one-step or two-step absorption mechanisms and relative consideration of physical dissolution and chemical reaction, for the estimation of enthalpies of absorption. Values of ΔH° range between -30 and -60 kJ mol^{-1} , in line with results for similar models reported in the literature. The most likely heats of absorption are expected to be in the range from -40 to -45 kJ mol^{-1} ; further experimental studies will surely help refining the models. The key advantage of hydrated carboxylate ionic liquids for CO_2 capture lies in these readily attainable heats, making regeneration feasible at moderate temperatures ($<70^\circ\text{C}$).

CRedit authorship contribution statement

Alberto Puga: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Mohammad Yousef:** Methodology, Investigation, Formal analysis. **Katarzyna Glińska:** Methodology, Investigation, Formal analysis. **Ricard Garcia-Valls:** Resources, Formal analysis. **Marta Giamberini:** Writing – review & editing, Validation, Resources, Formal analysis.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2024.128443>.

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