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# Induced Protic Behaviour in Aprotic Ionic Liquids by Anion Basicity for Efficient Carbon Dioxide Capture

Darius J. Yeadon,<sup>a,b,\*</sup> Johan Jacquemin,<sup>a,b,c,\*</sup> Natalia V. Plechkova,<sup>a</sup> Manuel Maréchal<sup>d</sup> and Kenneth R. Seddon<sup>a,e</sup>

**Abstract:** The interactions between aprotic tetrabutylphosphonium carboxylate ionic liquids (ILs),  $[P_{4.4.4.4}][C_nCOO]$  ( $n = 1, 2$  and  $7$ ), and water were investigated. The cation-anion interactions occur *via* the  $\alpha$ - $^1H$  on  $[P_{4.4.4.4}]^+$  and the carboxylate headgroup of the anion. Upon addition,  $H_2O$  localises around the carboxylate headgroups, inducing an electron inductive effect towards the oxygens, leading to ion-pair separation. Studies with  $D_2O$  and  $[P_{4.4.4.4}][C_nCOO]$  revealed protic behaviour of the systems, with proton/deuterium exchange occurring at the  $\alpha$ - $^1H$  of the cation, promoted by the basicity of the anion, forming an intermediate ylide. The greater influence of van der Waals forces of the  $[P_{4.4.4.4}][C_7COO]$  system allows for re-orientation of the ions through larger interdigitation. The protic behaviour of the neat ILs allows for  $CO_2$  to be chemically absorbed on the ylide intermediate, forming a phosphonium-carboxylate zwitterion, signifying proton exchange occurs even in the absence of  $H_2O$ . The absorption of  $CO_2$  in equimolar IL- $H_2O$  mixtures forms a hydrogen carbonate, through a proposed reaction of the  $CO_2$  with an intermediate hydroxide, and carboxylic acid.

## Introduction

Over the last two decades, ionic liquids (ILs) have been promoted as “*designer solvents*” with the allure of tailoring their physicochemical properties, through a myriad of possible cation and anion combinations and structural changes.<sup>[1]</sup> Despite the burgeoning interest, tuning the desired properties has proven difficult, especially in terms of viscosity. In recent years, a new strategy has emerged of mixing stoichiometric quantities of molecular solvents, in particular water, with ILs in order to obtain desired physicochemical properties.<sup>[2, 3]</sup>

[a] Dr. D. J. Yeadon\*, Dr. N. V. Plechkova, Dr. J. Jacquemin\*, Prof. K. R. Seddon  
The QUILL Research Centre  
The School of Chemistry & Chemical Engineering  
Queen's University of Belfast, Belfast, BT9 5AG, United Kingdom  
E-mail: DYeadon01@qub.ac.uk

[b] Dr. D. J. Yeadon\*, Dr. J. Jacquemin\*  
Laboratoire PCM2E  
Université de Tours, Parc de Grandmont, 37200 Tours, France  
E-mail: JJ@univ-tours.fr

[c] Dr. J. Jacquemin  
Materials Science and Nano-engineering (MSN) Department  
Mohammed VI Polytechnic University (UM6P), Lot 660 – Hay Moulay Rachid, 43150, Benguerir, Morocco

[d] Dr. M. Maréchal  
Univ. Grenoble Alpes, CNRS, CEA, IRIG-SyMMES, 38000 Grenoble, France

[e] Deceased

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Water is the most common impurity found in ILs, even for hydrophobic ones which are able to dissolve appreciable amounts.<sup>[4]</sup> The presence of impurities is known to have significant effects on their physicochemical properties, due to the strong influence on cation-anion association.<sup>[5]</sup> The presence of water has shown in some cases to enhance performance of an IL,<sup>[6, 7]</sup> which in turn has prompted research into studying the hydrogen bonding in such systems,<sup>[8]</sup> an approach that combines two alternative solvent strategies for developing potential replacements of VOCs.<sup>[9]</sup> In addition, it has been proposed that water may be used as a probe for polarity in ILs.<sup>[10]</sup>

The study of hydrogen bonding in ILs is thus essential to aid in developing “*task specific*” liquids. The vast majority of papers available in literature focus primarily on physical properties of IL-water mixtures, which observe the effects of hydrogen bonding rather than directly studying the interactions. While such studies provide valuable information on the bulk behaviour, they provide little information on the molecular environments. Spectroscopic studies on the other hand, can provide a clear and direct insight into the Coulombic forces and hydrogen bonding of these systems. Despite this, there are only few studies that utilise spectroscopic techniques to probe the interactions with water,<sup>[11, 12]</sup> and even fewer full systematic studies.

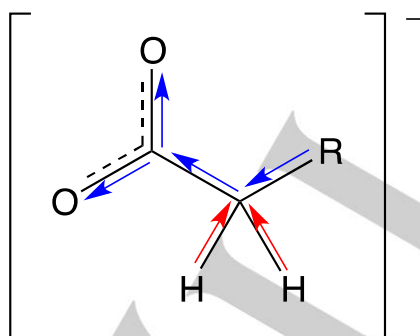
In this work, we extend our study into the interactions between tetrabutylphosphonium carboxylate ILs,  $[P_{4.4.4.4}][C_nCOO]$  ( $n = 1, 2$  and  $7$ ), and water by employing Nuclear Magnetic Resonance (NMR), Infrared (IR) spectroscopy and Small- and Wide- Angle X-ray Scatterings (SWAXS). This builds upon the physical properties previously reported,<sup>[13]</sup> and provides an insight into the interactions on a molecular scale. In addition,  $CO_2$  gas absorption provides an additional perspective in probing the interactions.

The initial focus of the study was to investigate anion-water interactions by coupling a basic anion with a weaker-interacting cation. Thus, the  $[P_{4.4.4.4}]^+$  cation was selected due to its tetrahedral symmetry with lower cation-anion interaction than any other asymmetrical shorter alkyl chains phosphonium cations, whilst also having medium hydrophobicity preventing phase separation contrary to bigger phosphonium cation like  $[P_{6.6.6.14}]^+$ .  $[C_nCOO]^-$  anions were selected to promote the formation of strong hydrogen bonds with water thanks to their basic nature. Moreover, previous research has shown phosphonium carboxylates are able to efficiently capture  $CO_2$  in the presence of water,<sup>[6]</sup> signifying a potential competition of interaction sites. The range of  $x_w$  0.1-0.95 of IL-water mixtures was selected in order to investigate the addition of stoichiometric quantities of water, as opposed to typical salt in aqueous solutions or pure ILs mainly reported, to date.

## Results and Discussion

The interactions of the three  $[P_{4.4.4.4}][C_nCOO]$  ( $n = 1, 2$  and  $7$ ) IL-water mixtures were studied by peak shift analysis of the  $^1H$ ,  $^{13}C$  and  $^{31}P$  nuclei at varying water concentrations, with the chemical shifts ( $\delta$ ) listed in **Tables S1.1-S1.15** of the ESI. Deviations in the chemical shifts ( $\Delta\delta = \delta_0 - \delta_1$ ) were calculated based on the dry IL for the octanoate, and at water content  $x_w$  0.3 and 0.2 respectively, for the ethanoate and propanoate samples due to their melting points. Changes in the interactions induced by the addition of water are reflected in the chemical shifts, as a result of increased or decreased shielding of inner-shell of electrons of the nuclei.

The addition of water to all three  $[P_{4.4.4.4}][C_nCOO]$  samples sees weakening of cation-anion interactions (**Figures S1.1-S1.5**), with the upfield shift of the protons on the  $\alpha$ -carbons of the cation, as water is preferentially solvating the hydrophilic carboxylate anions, which is reflected in the  $^{13}C$  and  $^{31}P$  NMR spectra (**Figures S1.6 and S1.10**). This coincides with the conclusions of Kim *et al.*<sup>[11]</sup>, with the high dielectric constant of water reducing Coulombic interactions.<sup>[14]</sup> The  $\alpha$ - $^1H$  of the  $[P_{4.4.4.4}]^+$  cation are, therefore, the most acidic as they are the most affected, suggesting it is the main interaction site with the carboxylate anions. This is in agreement with the crystal structure of  $[P_{4.4.4.3}]Cl$  reported by Adamová *et al.*<sup>[15]</sup> IL-water studies predominantly focus on anion-water interactions,<sup>[2]</sup> as in most cases they are favoured over cation-water,<sup>[16, 17]</sup> which are often neglected. The favourable anion-water interactions are reflected in the  $^{31}P$  NMR spectra (**Figure S1.10**), with the ethanoate and propanoate anions having similar behaviours, shifting upfield up to  $x_w \sim 0.75$  and  $0.70$ , before returning downfield suggesting reorganisation of the cation. The octanoate system, however, shares the initial upfield shift before plateauing and continuing upfield. The larger hydrophobic moiety of the octanoate undoubtedly allows for van der Waals to play a greater role in cation-anion association.



**Figure 1.** Illustration of the electron inductive effect on the carboxylate anion with increasing water content, as interpreted from deviations in chemical shifts,  $\Delta\delta$ , of  $(-)$   $^1H$  and  $(-)$   $^{13}C$  NMR spectra.

The changes in the chemical shifts of  $^1H$  and  $^{13}C$  environments (**Figures S1.11-S1.16**) of the anions reveal hydrogen-bonding of the water is heavily localised around the carboxylate headgroup, regardless of the alkyl chain. The presence of water appears to have an inductive effect with electron density shifting towards the oxygen atoms (**Figure 1**), as implied by the continuous downfield shifting of the  $-COO^-$  environment (**Figure S1.17**). This is further implied by the upfield shifts of the remaining  $^{13}C$  environments (**Figures S1.14-S1.16**), with the anions being

continuously solvated. The chemical shifts of the  $-COO^-$  environments have the following trend at  $x_w$  0.5: propanoate > octanoate > ethanoate (176.61, 175.86 and 173.53 ppm, respectively), suggesting hydrogen-bonding acceptability (basicity) between the propanoate anion and water is the highest followed by octanoate and ethanoate. This is not surprising considering the  $pK_a$  values of the ethanoic (4.76), propanoic (4.88) and octanoic (4.89) acids, with the conjugated bases being more basic for the longer alkyl-chained anions. The comparable  $pK_a$  values of propanoic and octanoic acid would imply similar basicity of the conjugated bases, however the hydrophobic effects of the extended alkyl chains cannot be neglected, which could potentially hinder interactions.

The  $\Delta\delta$  in  $^1H$  NMR of the water were calculated relative to that of the pure ( $x_w$  1,  $\delta = 3.26$  ppm) at 300 K. All three IL-water systems exhibit strong hydrogen bonding between anion and water at low concentrations ( $x_w < 0.5$ ) with negative  $\Delta\delta$  (**Figure S1.18**). An increase in water content sees a gradual decrease in average anion-water interaction, up to  $x_w$  0.8, which is reflected in the upfield shifts before plateauing. This can be envisaged as multiple water molecules aggregating around a single carboxylate headgroup, up to  $x_w$  0.8, promoted by repulsion of the hydrophobic alkyl chains of the cation and anion with water.<sup>[18]</sup> Thus, resulting in delocalisation of the negative charge of the anions causing the system to expand resulting in a “swelling effect”, inducing water separated ion-pairs.<sup>[19]</sup> This is corroborated by the  $^1H$ - $^1H$  NOESY spectra, with water correlating to all  $^1H$  environments of the cation, and becomes more evident with increasing water concentration (**Figures S1.19-S1.36**). The swelling behaviour and formation of IL aggregates has previously been reported for aqueous  $[P_{4.4.4.4}][CF_3COO]$ .<sup>[20]</sup>

At higher water content ( $x_w > 0.8$ ), water-water association begins to dominate for all three IL systems, with the formation of a secondary solvation layer (**Figure S1.18**). Interestingly, excess molar volumes have previously shown a maximum compactness at  $x_w$  0.8.<sup>[13]</sup> The cross peaks in the NOESY NMR spectra indicate that the IL structures of the ethanoate and propanoate begin to deteriorate at  $x_w$  0.67 (**Figures S1.22 and S1.28**), with no correlation seen at  $x_w$  0.8 (**Figures S1.23 and S1.29**), whereas for the octanoate system it is maintained (**Figure S1.35**). This combined with the difference in  $^{31}P$  NMR suggests a potential re-arrangement of  $[P_{4.4.4.4}]^+$  cation and  $[C_7COO]^-$  anion structure; stabilised by the van der Waals forces.

The IR vibrational modes of the dry  $[P_{4.4.4.4}][C_nCOO]$  ( $n = 1, 2$  and  $7$ ) were assigned with the aid of  $[P_{4.4.4.4}]Cl$  and the group one metal carboxylates, and are detailed in **Tables S2.1-S2.3** and **Figures S2.1-S2.12**. There has been little evidence in literature that tetraalkylammonium and tetraalkylphosphonium cations are involved in significant hydrogen bonding in any known salts.<sup>[21]</sup> This is reflected in the NMR studies of the  $[P_{4.4.4.4}]^+$  cation, with no significant changes in stretching modes to be expected. As has previously been reported, carboxylate anions are strong hydrogen bond acceptors and in the free state have a  $C_{2v}$ , which makes them IR active,<sup>[22]</sup> and are sensitive to changes in their environment. The asymmetric ( $\nu_{as}$ ) and symmetric ( $\nu_s$ ) stretching modes of the carboxylate ( $COO^-$ ) groups are clearly visible for the  $[P_{4.4.4.4}][C_nCOO]$  ILs between 1577 and 1366  $cm^{-1}$  (**Figures S2.2, S2.4 and S2.6**), and their differences, ( $\Delta\nu_{a-s}$ ) =  $\nu_{as}(COO^-) - \nu_s(COO^-)$ , have frequently been used to assess the coordination of anions.<sup>[23, 24]</sup> For unidentate

coordination,  $\Delta\nu_{\text{as-s}}$  is typically  $> 200 \text{ cm}^{-1}$ , whereas bidentate have a smaller  $\Delta\nu_{\text{as-s}}$ , typically  $< 150 \text{ cm}^{-1}$ .<sup>[24]</sup> The  $\Delta\nu_{\text{as-s}}$  values of the dry ethanoate, propanoate and octanoate ILs are: 225, 199 and  $203 \text{ cm}^{-1}$ , respectively, implying unidentate coordination with the  $[\text{P}_{4.4.4.4}]^+$  cation.

The IR spectrum of water has been intensely studied and reported in literature, to elucidate its interactions in various solvents and materials.<sup>[25]</sup> The  $C_{2v}$  symmetry allows the water three IR active vibration modes, however in the case of liquid water one can observe more than three bands, due to inhomogeneous hydrogen-bonding,<sup>[26]</sup> intermolecular vibrations,<sup>[27]</sup> coupling to delocalised symmetric and asymmetric vibrational modes<sup>[28]</sup> and Fermi resonance caused by coupling with bending overtones.<sup>[29]</sup> The  $\nu(\text{OH})$  vibrational modes are, therefore, very sensitive to the environment and intermolecular interactions.<sup>[8, 29, 30]</sup>

The presence of water in the  $[\text{P}_{4.4.4.4}][\text{C}_n\text{COO}]$  IL systems is revealed by the formation of a broad  $\nu(\text{OH})$  band between  $3660\text{--}3000 \text{ cm}^{-1}$  (Figures S2.13–S2.15), which becomes more pronounced with increasing water content. The band interestingly resembles that of pure water up to  $x_w 0.75$ , where  $\nu_{\text{as}}(\text{OH})$  and  $\nu_{\text{s}}(\text{OH})$  are not distinguishable. Similar observations have been reported for  $[\text{CF}_3\text{COO}]^-$  and  $[\text{NO}_3]^-$  anions,<sup>[12]</sup> which have been attributed to strong hydrogen bonds and the formation of water clusters or aggregates around the anions, causing a redshift of the  $\nu_{\text{as}}(\text{OH})$  and a blueshift of the first overtone of the HOH bending vibration. This causes the bands to approach one another and overlap. The broad  $\nu(\text{OH})$  vibrational modes begin to deviate from that of pure water above  $x_w 0.8$ , with the  $\nu_{\text{as}}(\text{OH})$  at  $3400 \text{ cm}^{-1}$  becoming more pronounced, signifying the formation of less tightly bound water.<sup>[10]</sup> This unsurprisingly is reflected in the  $^1\text{H}$  environments of neat water with the saturation of the carboxylate anions (Figures S1.18).

A number of IR studies have previously reported the formation of symmetric 2:1 complexes, with water hydrogen-bonding to two anions and *vice versa*,<sup>[12, 31]</sup> based on the differences of  $\nu_{\text{as}}(\text{OH})$  and  $\nu_{\text{s}}(\text{OH})$ . This, however, has been disputed by Ludwig *et al.*,<sup>[10]</sup> for water forming two hydrogen bonds with a single anion yielding comparable  $\Delta\nu(\text{OH})$  values. The broad  $\nu(\text{OH})$  vibrational modes makes it impossible to determine with certainty the formation of 2:1 symmetrical complexes, but more likely the formation of water aggregates or the  $[\text{P}_{4.4.4.4}][\text{C}_n\text{COO}]$  systems.

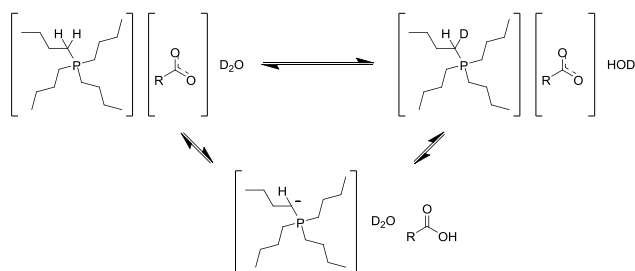
Analysis of the (COO) modes provides direct evidence of the strong hydrogen-bonding between the carboxylate anions and water, with the  $\nu_{\text{as}}(\text{COO})$  redshifting as the water content is increased (Figures S2.16–S2.18). The decrease in wavenumber is the result of the C–O covalent bond weakening, as electron density is being shifted towards oxygens that are hydrogen-bonding to the water molecules. This corroborates the findings from  $^{13}\text{C}$  NMR of the  $-\text{COO}^-$  with continuous downfield shift. The convergence of the (COO) stretching modes,  $\Delta\nu_{\text{as-s}}(\text{COO})$ , represents a change in coordination of the carboxylate anions to the  $[\text{P}_{4.4.4.4}]^+$  cation, likely from a unidentate of the dry IL to that of a polydentate with multiple water molecules aggregating around a single  $-\text{COO}^-$  head group. It should be reminded that the mixtures studied here contain stoichiometric quantities of water and should not be viewed as traditional aqueous salt and water solutions. However even at high water content ( $x_w > 0.9$ ), there is no clear evidence to

suggest the re-formation of the carboxylic acids from NMR and IR spectra (Figures S2.19–S2.21).

Mixtures of  $[\text{P}_{4.4.4.4}][\text{C}_n\text{COO}]$  with deuteriated water provides an additional dimension to the study of the interactions, however the inherent basicity of the carboxylate anions adds an extra layer of complexity. While the expected (OD) vibrational modes of the  $\text{D}_2\text{O}$  are clearly present ( $2728\text{--}2160 \text{ cm}^{-1}$  and  $1205 \text{ cm}^{-1}$ ), the signature of (OH) vibrational bands is visible in all three IL systems at  $3625\text{--}3040 \text{ cm}^{-1}$  (Figures S3.1–S3.6). These bands are seen to increase with increasing  $\text{D}_2\text{O}$  content up to  $x_D 0.67$  before decreasing and disappearing completely, inferring the involvement of non-deuteriated water at lower concentrations. Conversely, the (OD) vibrational modes only become evident at  $x_D 0.67$  and above. Interestingly, for the  $[\text{P}_{4.4.4.4}]\text{Cl}$  IL– $\text{D}_2\text{O}$  mixtures, the formation of supposed  $\nu(\text{OH})$  stretching modes appears significantly reduced and localised at  $3400 \text{ cm}^{-1}$ , with  $\nu(\text{OD})$  being significantly more pronounced (Figures S3.7 and S3.8).

$^1\text{H}$  NMR spectra of the  $[\text{P}_{4.4.4.4}][\text{C}_n\text{COO}]\text{--D}_2\text{O}$  mixtures indicate the involvement of non-deuteriated water through proton/deuterium exchange of the  $\alpha\text{--}^1\text{H}$  on the  $[\text{P}_{4.4.4.4}]^+$  cation, with a maximum occurring at  $x_D 0.67$  determined from peaks integration (Tables S3.1–S3.3). The different alkyl chain lengths of the anion have a negligible effect. Interestingly, this is the same concentration at which mixing enthalpy is most energetically favourable, as previously reported.<sup>[13]</sup> At  $\text{D}_2\text{O}$  content above  $x_D 0.67$ , the proton/deuterium exchange immediately decreases, as exemplified by the peak splitting in  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectra (Figures S3.9–S3.14). Further evidence of the displacement of the  $\alpha\text{--}^1\text{H}$  on the  $[\text{P}_{4.4.4.4}]^+$  can be seen in the deuterium ( $^2\text{H}$ ) NMR spectrum of  $x_D 0.67$  mixture of the ethanoate-based IL (Figure S3.15). Electrospray mass spectra in the positive mode reveals the extent of the substitution, with an initial  $259 m/z$  for the non-deuteriated cation and between two and five deuterium atoms on the cation at  $260\text{--}264 m/z$  (Figures S3.16–S3.18). Furthermore, as no evidence of proton/deuterium exchange is observable in the case of  $[\text{P}_{4.4.4.4}]\text{Cl}\text{--D}_2\text{O}$  mixture by NMR spectroscopy and mass spectrometry (Figures S3.19–S3.21), this phenomenon could be directly related to the anion (structure, property) and thus on interaction changes on  $[\text{P}_{4.4.4.4}][\text{C}_n\text{COO}]$  in the presence of water. The interactions of the  $[\text{P}_{4.4.4.4}][\text{C}_n\text{COO}]\text{--water}$  mixtures are more complex than initially believed, with a dynamic equilibrium between cation, anion and water. The initial approach that water is primarily hydrogen-bonding to the anion is therefore false, with the  $[\text{P}_{4.4.4.4}]^+$  actively participating through proton abstraction, induced by the basicity of the carboxylate, forming an intermediate ylide. The formation of phosphonium ylides have shown to be stable in water under basic conditions.<sup>[32]</sup> Imidazolium ILs have shown to undergo facile proton exchange on the C2 position.<sup>[33]</sup> The absence of the acidic ring of protons in the phosphonium ILs greatly contributes to the stability.<sup>[34]</sup> However, it also leads to weaker cation-anion interactions and in turn an increase in basicity of the system.<sup>[16]</sup> The presence of water above  $x_w 0.67$  sufficiently weakens cation-anion interactions, effectively “switching off” proton exchange. We propose a possible resonance mechanism, *vide infra*, for proton/deuterium substitution on the  $[\text{P}_{4.4.4.4}]^+$  cation (Figure 2). Phosphonium-based ILs coupled with basic anions, should therefore more correctly be described as protic.



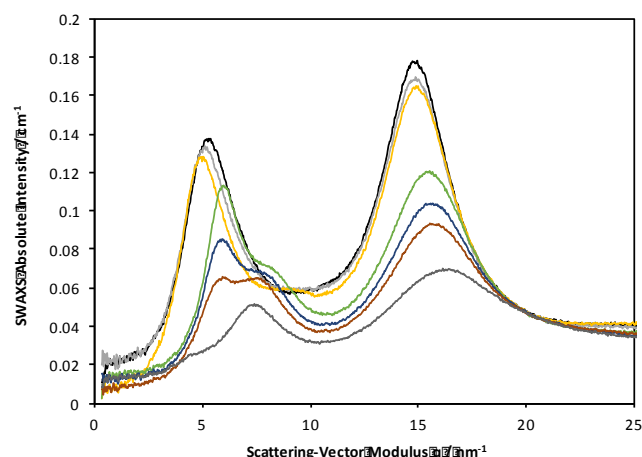


**Figure 2.** Schematic of the proton-deuterium exchange mechanism at the  $\alpha$ -position for  $[P_{4444}][C_nCOO]$ - $D_2O$  mixtures below  $x_D$  0.75.

SWAXS patterns of all three ionic liquid-water systems exhibit three peaks in the  $q$  range of 5.51 to 17.08 nm<sup>-1</sup> (Figures S4.1-S4.2, Figure 3, and Tables S4.3). The pre-peak arises from segregation of the alkyl chains of the cation and/or anion to form non-polar/polar domains,<sup>[35]</sup> and can probe the distance between the charged head groups of the ions, separated by the alkyl chains, resulting in low  $q$  values (low compactness). The principal peaks with  $q$  values around 15 nm<sup>-1</sup> are attributed to intramolecular interactions and nearest neighbours; greater compactness. The shouldering peak at ca. 7.5 nm<sup>-1</sup>, is normally seen for aprotic analogues,<sup>[36]</sup> which are associated to charge alternation.

The SWAXS patterns of the ethanoate- and propanoate-water mixtures are very similar, whereas for the octanoate system, a noticeable decrease in the pre-peak intensity and an increase in principal peak can be seen. We attribute this to the increased presence of van der Waals forces, contributing to an enhanced packing of the alkyl chains enabling the formation of liquid crystalline phases.

The addition of water to each  $[P_{4444}][C_nCOO]$  sample induces a decrease of the intensity of each diffraction peak, due to a dilution effect. The lowering of the  $q$  values with increasing water content of the pre-peak for the ethanoate and propanoate ILs suggests ion-pair separation, as the polar domains enlarge.<sup>[19]</sup> The repulsion between water and the alkyl chains dominates, causing the polar head group to expand, which has been regarded as a “swelling effect”.<sup>[18]</sup> The analysis of effect of the addition of water to the octanoate IL sample is more complicated, with the diffraction of the pre-peak initially moving to lower  $q$  values until  $x_w$  0.41 (less compact) before jumping to significantly higher values at  $x_w$  0.67 (greater compactness) and returning downfield (Table S4.3, Figure 3). This dramatic change suggests a re-orientation of the ions moving closer to one another, probably through greater interdigitation of the alkyl chains of the cation and anion promoted by van der Waals forces. For both the propanoate and octanoate IL-water mixtures, the pre-peak disappears at  $x_w$  0.9, as has been reported by Greaves *et al.*<sup>[37]</sup> The persistence of the pre-peak of the  $[P_{4444}][C_1COO]$  is likely due to the smaller anion being able to remain closer to the  $[P_{4444}]^+$  cation at high water content, having a more globular interaction.



**Figure 3.** SWAXS patterns of  $[P_{4444}][C_7COO]$ -water mixtures, at: (—)  $x_w$  0.00; (—)  $x_w$  0.20; (—)  $x_w$  0.41; (—)  $x_w$  0.67; (—)  $x_w$  0.75; (—)  $x_w$  0.80; and (—)  $x_w$  0.90.

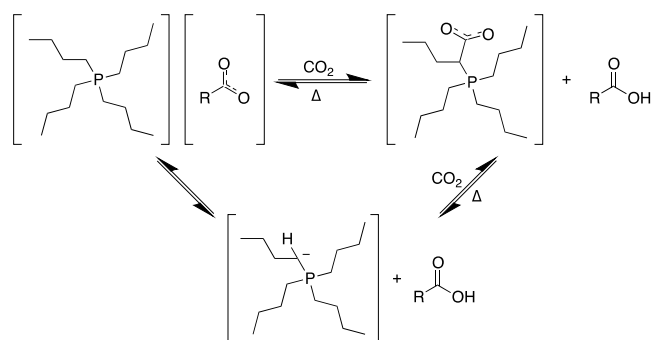
The chemisorption of  $CO_2$  in neat phosphonium azolide IL has previously been reported by Brennecke *et al.*<sup>[38]</sup> on the cation via an intermediate ylide at elevated temperatures. Considering the protic behaviour exhibited by the  $[P_{4444}][C_nCOO]$ , we are keen to see whether this behaviour is reflected in the ILs studied here, to further probe the interactions using  $CO_2$  in both the dry and water mixtures. Moreover, to our knowledge, the study of  $CO_2$  in long-alkyl-chain carboxylate ILs have not been reported in literature, to date.

The  $CO_2$  absorption measurements in the dry  $[P_{4444}][C_1COO]$  and  $[P_{4444}][C_7COO]$  ILs were performed at 338 K in order to promote chemisorption onto the cation to form a zwitterionic carboxylate.<sup>[38]</sup> In addition, it allowed for the ethanoate system to be in the liquid state. The  $CO_2$  absorption quantities are reported in Tables S5.1 and S5.2, and Figure S5.1. The initial  $CO_2$  absorption in both the ethanoate and octanoate ILs is rapid, due to physisorption. The rate of uptake significantly reduces after the first 15 minutes, and further decreases after 60 minutes for both systems. However, in both cases, the equilibrium is almost reached after 8 h of bubbling  $CO_2$ , with results being within the experimental errors, as illustrated in Figure S5.1. Uptake of  $CO_2$  for the ethanoate and octanoate ILs are  $x_{CO_2}$  of 0.22 and 0.19, respectively, which is an order of magnitude greater than that typically reported for physisorption.<sup>[39]</sup>

The  $^1H$  NMR spectrum of the  $[P_{4444}][C_1COO]$  IL after being exposed to  $CO_2$  for 8 h shows the presence of two additional peaks on either side of the  $\alpha$ - $^1H$  of the cation (Figure S5.2), as well as a new acidic environment at 15.55 ppm. However, these peaks are not clearly visible for the  $[P_{4444}][C_7COO]$  sample (Figure S5.3). The  $^{13}C$  NMR spectra of both the ethanoate and octanoate systems show the formation of a new peak between 166-165 ppm (Figures S5.4 and S5.5), as well as, a new peak in the  $^{31}P$  NMR; identical to that reported by Brennecke *et al.*<sup>[38]</sup> (Figures S5.6 and S5.7).

IR spectra, prior to and after exposure to  $CO_2$ , sees the presence of a new vibrational mode at 1635 cm<sup>-1</sup>, adjacent to the  $\nu_{as}(COO)$  of the carboxylate anions (Figures S5.8 and S5.9), strongly resembling that previously reported for  $CO_2$  chemisorption on the phosphonium cation.<sup>[38]</sup> Whilst no significant change is observed between 3600-2400 cm<sup>-1</sup> (Figures S5.10 and S5.11), the structure of a

[P<sub>4444</sub>]-carboxylate adduct is verified by electrospray ionisation mass spectrometry in the positive mode, with a peak of 561.50 *m/z* for both ethanoate and octanoate ILs (**Figures S5.12-S5.15**). The peak is the result of two [P<sub>4444</sub>]<sup>+</sup> cations, one in the ylide form (259.43 and 258.42 *m/z*), and CO<sub>2</sub> (44.01 *m/z*). A proposed mechanism for the chemisorption of CO<sub>2</sub> in dry [P<sub>4444</sub>][C<sub>*n*</sub>COO] ILs is proposed in **Figure 4**, *vide infra*.



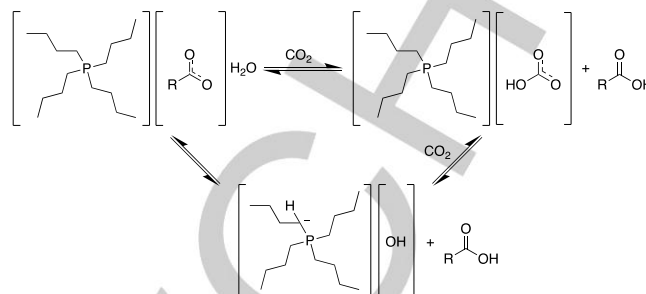
**Figure 4.** Schematic of the proposed chemisorption of CO<sub>2</sub> in neat [P<sub>4444</sub>][C<sub>*n*</sub>COO] ILs, at 338.15 K.

The protic behaviour of the [P<sub>4444</sub>]<sup>+</sup> suggests that there is no competition between the carboxylate anions and CO<sub>2</sub> for the interaction site on the cation, but rather that they are complimentary. The chemisorption is a two-step process, with the [C<sub>*n*</sub>COO]<sup>-</sup> abstracting an α-<sup>1</sup>H from the cation enabling CO<sub>2</sub> interaction. This may account for the slow rate of CO<sub>2</sub> absorption in selected IL media.

The solubility of CO<sub>2</sub> in equimolar mixtures of [P<sub>4444</sub>][C<sub>1</sub>COO] and [P<sub>4444</sub>][C<sub>7</sub>COO] with water, *x<sub>w</sub>* 0.5, are reported in **Tables S5.3 and S5.4**, and **Figure S5.16**. The absorption of CO<sub>2</sub> of the binary IL-water mixtures was found to be *x*<sub>CO<sub>2</sub></sub> 0.40 and 0.41 for the ethanoate and octanoate-based ILs, respectively. A comparison of the amount of CO<sub>2</sub> captured by chemisorption in the dry ILs, not only sees a noticeable increase with the equimolar IL-water mixtures, but also significantly improved absorption rate, with saturation being reached within the first 15 minutes. Despite the increased alkyl chain length of the octanoate anion, CO<sub>2</sub> solubilities are comparable between the two ILs. Saturation of the ethanoate system is reached after 15 minutes, with further absorption prevented by the solidification. The octanoate system on the other hand sees a gradual loss in mass after the initial 15 minutes, likely due to evaporation of water.

Absorption of CO<sub>2</sub> in equimolar phosphonium carboxylate-water mixtures has conclusively shown the formation of hydrogen carbonate and the re-constitution of carboxylic acid.<sup>[6]</sup> This is confirmed for systems studied here from NMR and IR spectra (**Figures S5.17-S5.26**), which resemble to those previously reported.<sup>[6, 40]</sup> A competition between the chemisorption *via* the hydrogen carbonate and the phosphonium-carboxylate cation does not appear to be a factor, as suggested by <sup>31</sup>P NMR (**Figure S5.21**), with no additional phosphorous environments observed. To our knowledge the CO<sub>2</sub> chemisorption mechanism in binary phosphonium carboxylate-water mixtures has not been discussed or investigated in any significant detail. The ability of hydroxides to chemically absorb CO<sub>2</sub> to form hydrogen carbonates is well documented,<sup>[41]</sup> however it does not seem to

have been recognised by the IL community, or at least mentioned in publications. As such, we propose a chemisorption mechanism of CO<sub>2</sub> *via* a hydroxide anion intermediate, induced by the basicity of the anion for [P<sub>4444</sub>][C<sub>*n*</sub>COO] IL-water systems **Figure 5**.



**Figure 5.** Schematic of the proposed chemisorption mechanism of CO<sub>2</sub> in equimolar [P<sub>4444</sub>][C<sub>*n*</sub>COO]-water mixtures.

The chemisorption is promoted by the proximity of water to both the carboxylate head group and the α-<sup>1</sup>H, as previously found, *vide supra*. This combined with the propinquity of the CO<sub>2</sub> to the α-<sup>1</sup>H of the cation, allows for more favourable interactions with the intermediate [OH]<sup>-</sup> anion, as opposed to the ylide. Further evidence of the complex reaction mechanism is seen in the deuterium NMR spectrum of [P<sub>4444</sub>][C<sub>7</sub>COO]-D<sub>2</sub>O mixture after being bubbled with CO<sub>2</sub> (**Figure S5.26**). The presence of both deuterated octanoic acid and α-positions on the cation suggests direct reaction between D<sub>2</sub>O and CO<sub>2</sub> has not occurred.

## Conclusion

This work provides a better understanding of the interactions between [P<sub>4444</sub>][C<sub>*n*</sub>COO] and water, and the changes to the environments that impact their ability to capture CO<sub>2</sub>. Spectroscopic studies reveal cation-anion interactions occur *via* the α-protons on the [P<sub>4444</sub>]<sup>+</sup> and the carboxylate head group of the anion. The addition of water results in weakening cation-anion association, with water aggregating around the carboxylate head group, causing electron negativity to shift towards the oxygen atoms and inducing ion-pair separation. The hydrogen-bonding acceptability (basicity) of the anions promotes proton exchange between the α-protons on the [P<sub>4444</sub>]<sup>+</sup> and water below *x<sub>w</sub>* 0.75, stabilised by a ylide intermediate. This exchange mechanism was found to also occur in the absence of water at elevated temperatures, allowing for CO<sub>2</sub> to chemically absorb onto the ylide, forming a phosphonium-carboxylate zwitterion. In equimolar mixtures of [P<sub>4444</sub>][C<sub>*n*</sub>COO] and water, the proximity of water to the carboxylate headgroup and the α-protons allow for more favourable CO<sub>2</sub> absorption *via* the intermediate [OH]<sup>-</sup> anion, to form a hydrogen carbonate. The increased alkyl chain length of the octanoate anion facilitates greater influence of van der Waals forces, allowing for re-orientation upon the addition of water through larger interdigitation. This neoteric description and its crucial role in promoting the CO<sub>2</sub> capture are of particular interest for a range of applications in the field of energy and environmental science.

## Acknowledgements

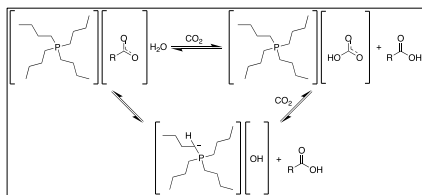
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**Keywords:** Ionic liquid • Water • CO<sub>2</sub> • NMR • IR • SWAXS

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## Entry for the Table of Contents



Darius J. Yeadon\*, Johan Jacquemin\*, Natalia V. Plechkova,  
Manuel Maréchal and Kenneth R. Seddon

An in-depth insight into the interactions between “aprotic” ionic liquids with water mixtures, which questions our fundamental understanding of what is considered a protic and aprotic ionic liquid depends on anion selection. The presence of strong hydrogen bond accepting (basic) anions allows for induced protic behaviour in a typically considered aprotic cation. This in turn promotes significantly greater CO<sub>2</sub> uptake by chemisorption.