

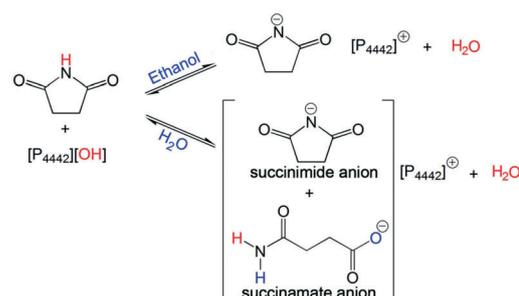
Reply to the Correspondence on “Preorganization and Cooperation for Highly Efficient and Reversible Capture of Low-Concentration CO₂ by Ionic Liquids”

Yanjie Huang, Guokai Cui,* Yuling Zhao, Huiyong Wang, Zhiyong Li, Sheng Dai, and Jianji Wang*

carbon capture · carbon dioxide · ionic liquids · water

We would like to thank Prof. Dupont and co-workers^[1] for their interest in our Communication,^[2] and appreciate their concerns regarding the development of CO₂ capture by ionic liquids (ILs).^[3] In a previous study,^[2] we had reported a preorganized imide-based IL [P₄₄₄₂][Suc] with the tri-*n*-butylethylphosphonium cation and the succinimide anion for highly efficient and reversible capture of low-concentration CO₂ through cooperative interactions between CO₂ and multiple active sites in the anion. In this reply to the Correspondence of Dupont and co-workers, we show that the water content is crucial to the preparation of the IL and its performance in the capture of CO₂.

First, the preparation procedures of [P₄₄₄₂][Suc] described in two different publications were compared. It is well known that neutral succinimide (Suc) contains an imide group (-CO-NH-CO-), and its treatment with mild bases in the presence of water yields the corresponding salt of succinamic acid through a ring-opening reaction.^[4] Therefore, in our work, [P₄₄₄₂][Suc] was prepared through a neutralization reaction between Suc and a solution of phosphonium hydroxide ([P₄₄₄₂][OH]) in anhydrous ethanol (Scheme 1). In this way, only a small amount of Suc was hydrolyzed to produce succinamic acid. It has been calculated from the ¹H NMR spectrum of the IL in Figure S1 of this Reply that the succinamate anion by-product



Scheme 1. Effect of water on the preparation of [P₄₄₄₂][Suc].

amounts to only 3.2 mol % in our prepared IL. However, we were surprised to find that the “IL” given by Dupont et al.^[1] was prepared through neutralization of [P₄₄₄₂][OH] and Suc in water/ethanol (10:1), where many more succinamate anions would be produced in the “IL” (calculated to be about 18.1 mol % from their ¹H NMR spectra (Figure S2)). Therefore, it is very difficult to remove the water in the “IL”, and the “IL” easily absorbs water owing to the production of an amino acid anion (Scheme 1).

In order to investigate whether the addition of water to our IL can restart the basic hydrolysis of succinimide anions ([Suc]), we added different amounts of water to our IL (water contents: 3.3, 8.8, and 17.6 wt %). It can be seen from Figure 1 that the intensity of the new resonance at about $\delta = 3.5$ ppm in the ¹H NMR spectra, which can be assigned to the H₂O hydrogen atoms, increased with an increasing amount of added water in [P₄₄₄₂][Suc]. No other new resonances or obvious changes in the peak intensities and positions were observed, indicating that there is almost no change in the composition and structure of the IL during the addition of H₂O. In other words, the added water in the IL does not restart the basic hydrolysis, thus the succinamate anion may only be produced in the neutralization reaction.

Next, FTIR spectra of the IL from different sources were compared. It is clear from Figure 2a that there are significant differences at wavenumbers from 3000 to 3750 cm⁻¹, which were ascribed to the hydrogen-bonded OH stretching vibration of H₂O,^[5] and the water content of the “IL” prepared by Dupont and co-workers was much higher than that of our IL. To estimate the content of water in the “IL”, FTIR spectra of our [P₄₄₄₂][Suc] samples prepared by addition of water (water

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<https://doi.org/10.1002/anie.201808486>.

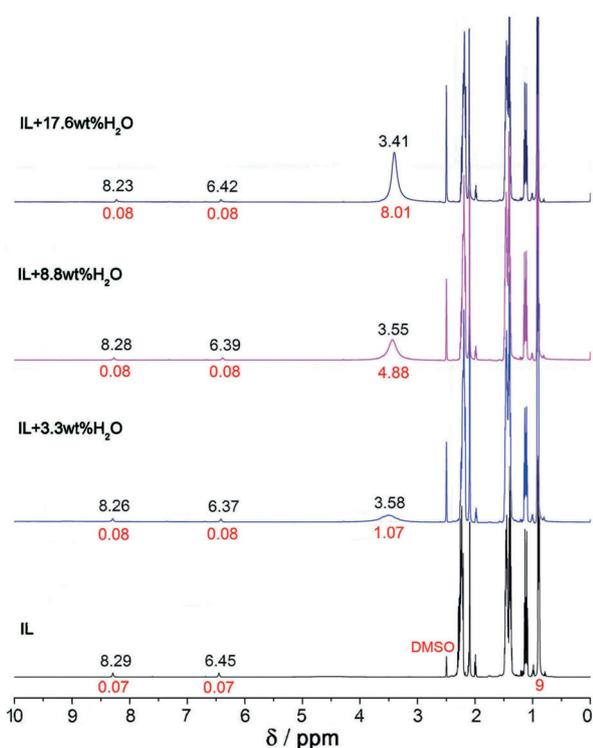


Figure 1. 1H NMR spectra of $[P_{4442}][Suc]$ prepared by our group with the addition of different amounts of water. Values in wt% are water contents in samples.

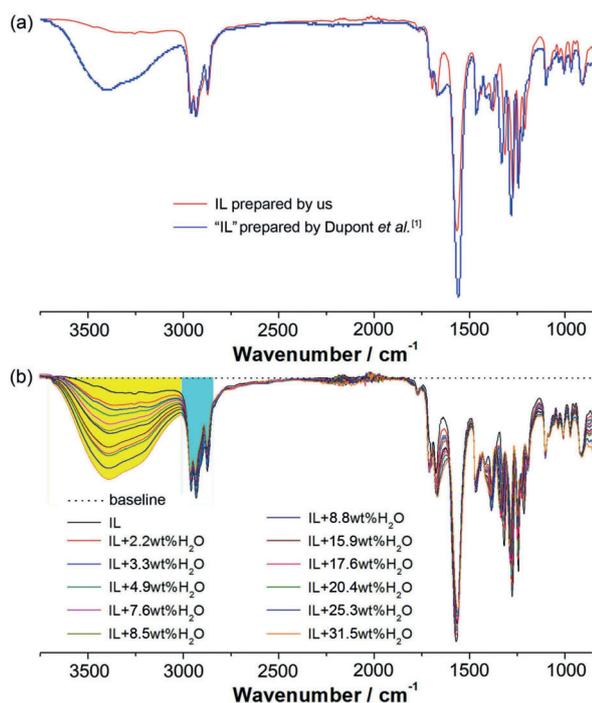


Figure 2. a) Comparison of the FTIR spectra of the ILs prepared by our group and by Dupont and co-workers. b) FTIR spectra of our $[P_{4442}][Suc]$ samples with different amounts of water added. Values in wt% are the water contents of the samples.

contents: 2 to 32 wt%) were recorded (Figure 2b). The intensity of the broad peak in the range from 3000 to

3750 cm^{-1} dramatically increased with an increasing water content in the sample. However, there was almost no change for the typical peaks of $[P_{4442}][Suc]$ in the range from 850 to 3000 cm^{-1} , indicating that the effect of added water on the composition of our IL is very small. As the positions and intensities of the aliphatic C–H stretching vibration bands in the range of 2850 – 3000 cm^{-1} were well maintained during the increase of the water content, we utilized the peak area of C–H to quantify the peak area of -OH in the corresponding samples.

The quantitative relationship between area of the -OH IR band and the content of water added to our IL was established by using the peak area integration method as described in the literature.^[6] For this purpose, 2850 and 3000 cm^{-1} were chosen as the upper and lower limits of the C–H stretching bands, while 3000 and 3750 cm^{-1} were chosen as the upper and lower limits of the hydrogen-bonded OH stretching bands, respectively. Then, the peak areas based on the above limits were used to measure the water content in the IL samples (see Table S1 and Figure S3). Figure 3a shows the relationship between the area ratio and the content of added water in our samples. A linear relationship between the area ratio and the content of water added to our IL sample was clearly established ($r^2 = 0.9888$), which is similar to a result previously reported.^[6] According to this linear relationship and Figure 3b, the “IL” used in Dupont’s work was similar to a mixture of our IL with 17.6 wt % H_2O .

It is known that the presence of water in ILs may significantly affect the physical properties of the ILs,^[7] and

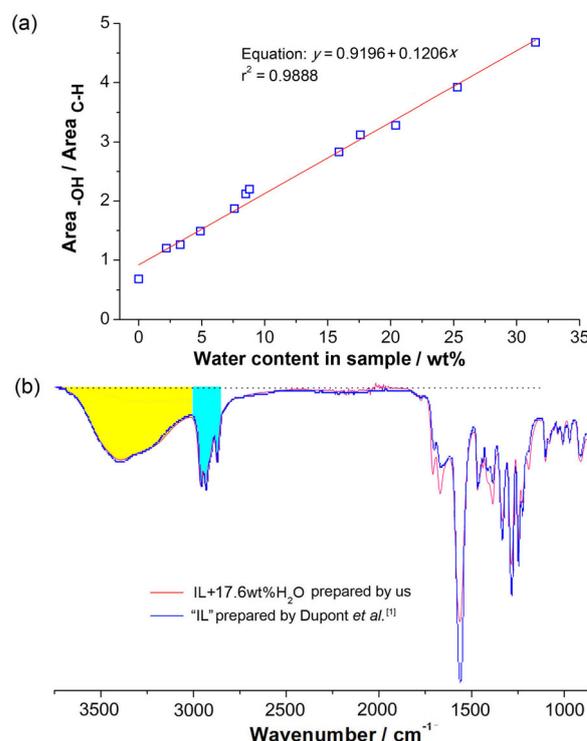


Figure 3. a) Linear relationship between the area ratio and the water content in the sample. b) Comparison of the FTIR spectra of our IL+17.6 wt% H_2O sample and the “IL” prepared by Dupont and co-workers.

therefore may have a considerable impact on the CO₂ capture (rate, capacity, and mechanism).^[8] Thus CO₂ capture by [P₄₄₄₂][Suc] with different contents of added water (0, 3.3, 8.8, and 17.6 wt %) was investigated (Figure 4). The presence of

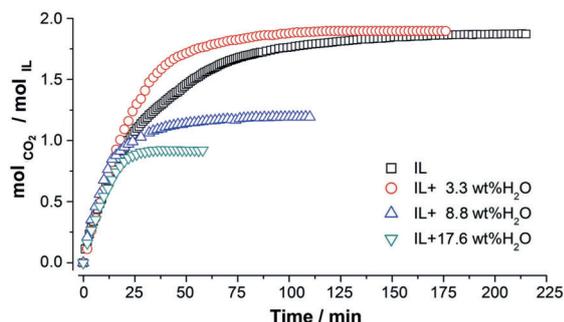
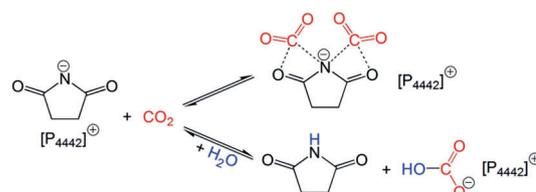


Figure 4. CO₂ absorption capacities (in mol CO₂ mol⁻¹ IL) of our [P₄₄₄₂][Suc] samples with different water contents (in wt%) at 20°C and 1 bar as a function of absorption time.

a small amount of water has a negligible effect on the CO₂ absorption capacity, but the impact is significant if the water content is high. For example, the molar ratios of the absorbed CO₂ to [P₄₄₄₂][Suc] at 20°C were 1.87, 1.90, 1.19, and 0.92 for IL, IL + 3.3 wt % H₂O, IL + 8.8 wt % H₂O, and IL + 17.6 wt % H₂O, respectively. With addition of 3.3 wt % H₂O, the effect in the equilibrium absorption capacity was within experimental error, but its absorption rate was much faster than that of the neat IL. A similar result was reported by Brennecke and co-workers,^[9] who studied a series of [P₆₆₆₁₄][2-CNPyrr]/H₂O mixtures (1–4.5 wt % H₂O) for CO₂ capture; they observed only a slightly increased solubility of CO₂ with increasing H₂O content, which was ascribed to the stronger water solvation of the [2-CNPyrr]-CO₂ anion compared to that of the [2-CNPyrr] anion.^[10] Therefore, the CO₂ absorption mechanism was marginally affected by the addition of a small amount of water to the IL under ambient pressure.^[9] On the other hand, the CO₂ capacity dramatically decreased when large amounts of water (8.8 wt %, 17.6 wt %) were added to the IL, suggesting a different absorption mechanism. Recently, CO₂ capture by aqueous solutions of ILs has been investigated,^[11] and it has been suggested that the CO₂ solubility is mainly determined by the basicity of the anions, which can activate the reaction between water and CO₂ to form bicarbonate anions and the conjugate acid of the basic anion. Based on the above absorption experiments and previous reports, we believe that bicarbonate anions (HCO₃⁻) and neutral succinimide (Suc) are formed during the absorption of CO₂ in the presence of large amounts of water owing to the basicity of [Suc] anion (Scheme 2).

To study the effect of added water on the absorption mechanism, CO₂ capture by our [P₄₄₄₂][Suc] samples with different water contents (0, 3.3, 8.8, and 17.6 wt %) was investigated by ¹³C NMR spectroscopy (Figure 5). Compared with the ¹³C NMR spectra of the neat IL, a new resonance at about 159 ppm was observed in the spectrum of every CO₂-saturated absorbent. This peak in the spectra of IL + CO₂ and IL + 3.3 wt % H₂O + CO₂ could be ascribed to the absorbed



Scheme 2. Effect of water on the CO₂ absorption mechanism.

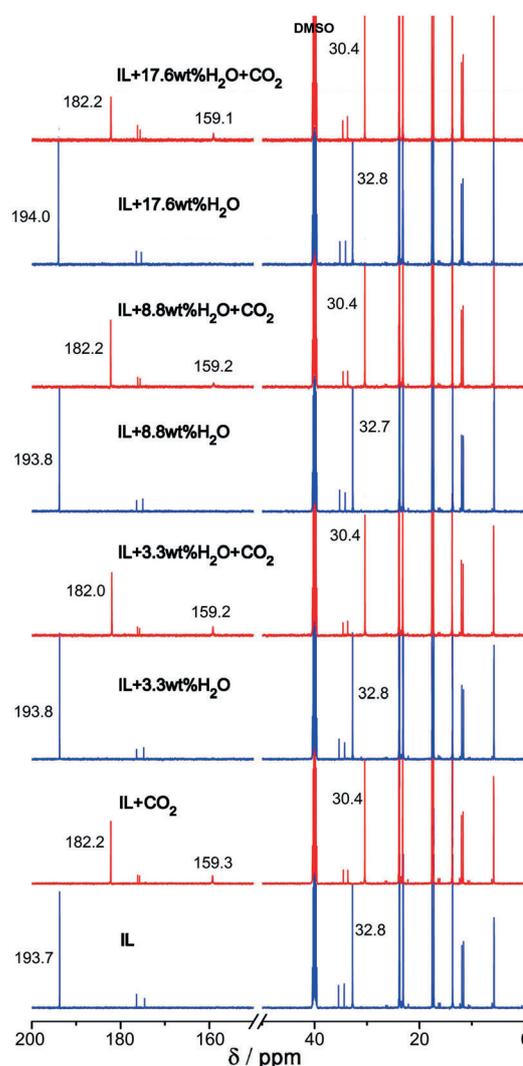


Figure 5. ¹³C NMR spectra of our [P₄₄₄₂][Suc] samples with different water contents (in wt%) before and after the absorption of CO₂ at 20°C and 1 bar.

CO₂,^[12] while the peak in the spectra of IL + 8.8 wt % H₂O + CO₂ and IL + 17.6 wt % H₂O + CO₂ was attributed to HCO₃⁻.^[11] Typical peaks at about 194 ppm (C=O carbon atom in [Suc]) and 33 ppm (CH₂ carbon atom in [Suc]) in the spectra of the absorbents moved upfield to about 182 and 30 ppm, respectively, after the absorption of CO₂. These shifts in the spectra of IL and IL + 3.3 wt % H₂O after the absorption of CO₂ were due to the reaction between [Suc] and CO₂ to form a [Suc]-2CO₂ complex,^[12b] while the shifts in the spectra of IL + 8.8 wt % H₂O and IL + 17.6 wt % H₂O

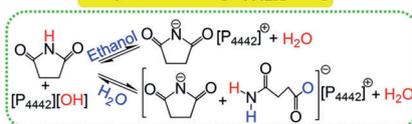
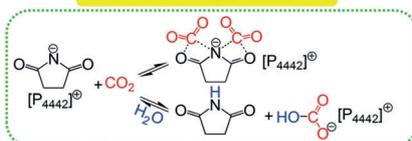
Correspondence



Ionic Liquids II

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Reply to the Correspondence on
“Preorganization and Cooperation for
Highly Efficient and Reversible Capture of
Low-Concentration CO₂ by Ionic Liquids”

Preparation of [P₄₄₄₂][Suc]CO₂ capture by [P₄₄₄₂][Suc]

The water content is crucial to the preparation of [P₄₄₄₂][Suc] and its capture of CO₂. The use of a large amount of water in the preparation of this ionic liquid results in the significant formation of the byproduct succinamate anions and difficulties in water removal, which strongly reduces the capacity of CO₂ absorption through a bicarbonate mechanism. By contrast, the addition of a small amount of water maintains a high absorption capacity through cooperation.