Pentaerythritol-Based Molecular Sorbent for CO₂ Capturing: A Highly Efficient Wet Scrubbing Agent Showing Proton Shuttling Phenomenon

Abdussalam K. Qaroush,§† Khaleel I. Assaf,§,* Ala’a Al-Khateeb,§ Fatima Alsoubani,§ Enas Nabih,§ Carsten Troll,‖ Bernhard Rieger,‖* and Ala’a F. Eftaiha*a,†‡§⊥

Abstract: Pentaerythritol (PE) is considered a biodegradable material that combines the ease of synthesis, nonvolatility, and extra stability under basic conditions (acidic gas sequestration, e.g., CO₂), which makes it a useful candidate for postcombustion capture (PCC) application. To overcome corrosion problems associated with CO₂ binding organic liquids, a binary mixture comprised of PE/1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU) (1:4 molar ratio) dissolved in dimethyl sulfoxide (DMSO) was exploited for CO₂ capturing. The formation of ionic alkyl organic carbonate (RCO₃⁻) was confirmed using ¹³C NMR (157.4 ppm) and ex situ attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) (two peaks were identified, viz., 1670 and 1630 cm⁻¹, which were ascribed to the symmetric and asymmetric stretching of both C=O and O=C=O⁻ within RCO₃H and RCO₃⁻, respectively). The charged adduct was measured using a thermostated beaker coupled with conductivity and pH meter probes. The sorption capacity of a 5.0% PE (w/v) solution was measured volumetrically with high efficiencies as, ca. 16 and 18.5 wt %, for wet and dry conditions, respectively. In addition, density functional theory (DFT) performed to understand the mechanism of action in the case of H₂O, and simple alcohols, e.g., methanol and ethanol. Moreover, we reported on the newly discovered medium-dependent proton shuttling phenomenon that was verified experimentally and theoretically.

Carbon dioxide (CO₂), is considered to be the most prominent greenhouse gas, which is attributed as the main cause of anthropogenic climate change.¹⁻² The expected increase in the atmospheric CO₂ concentration to an unprecedented level (up to 430 ppm in 2060)³ makes boosting CO₂ capturing strategies, viz., precombustion, postcombustion, oxy-fuel combustion, and electrochemical separation, necessary to guarantee a sustainable and resilient future. For governmental and industrial sectors, postcombustion capture (PCC) is of particular interest because it does not require additional capital investments in comparison with other sequestration strategies (see the review by Kenarsari et al.¹ and others †§⊥ for more details). In this regard, carbon capture and storage or sequestration (CSS)⁶ together with carbon capture and utilization (CCU)⁷ are potential approaches to mitigate global warming.⁸

Amine scrubbing via monoethanolamine (MEA) is the most mature technology for CO₂ capturing due to its effectiveness toward dilute CO₂ streams and commercial availability.⁹⁻¹¹ The chemisorption of CO₂ by aqueous amine-based solvents takes place through the formation of the carbamate anion following a 1:2 mechanism, viz., 1 mol of CO₂ reacts with 2 mol of amine functional groups, or the formation of inorganic bicarbonate ion via a 1:1 mechanism (chemical structures are shown in Scheme 1AB). There are several drawbacks associated with amine-based sorbents such as corrosiveness, toxicity, intensive energy required to regenerate aqueous amine solutions, and chemical degradation upon successive absorption—desorption cycles.¹²⁻¹³ Ammonia (NH₃) scrubbing has several merits over amine-based sorbents in terms of cost, loading capacity and less-corrosive character; however, the high volatility of NH₃ addresses several technical problems.¹⁴⁻¹⁵ This highlights the potential importance of implementing other alternative technologies such as solid sorbents¹⁶⁻¹⁷ and membranes¹⁸⁻¹⁹ and paving the way to less energy demanding scrubbing agents upon regeneration through the formation of ionic organic carbonate.²⁰⁻²¹ In this context, Sir J. Fraser Stoddart (Chemistry Nobel Laureate, 2016) reported that cyclodextrin based metal organic frameworks (CD-MOFs) chemisorbed CO₂ selectively and reversibly at low pressures by the free hydroxyl group(s) of the glucopyranose ring.²²⁻²³ Very recently, our group has reported on the supramolecular chemisorption of CO₂ through organic alkyl carbonate formation, adopting a benign-by-design approach using green
chemistry guidelines by applying safer chemicals and the use of biorenewables, namely, chitin acetate oligomer dissolved in dimethyl sulfoxide (DMSO). The formation of chitin-CO$_2$ adduct (Scheme 1C) was confirmed experimentally and verified by density functional theory (DFT) calculations. The use of DMSO (aprotic and hydrogen bond acceptor solvent) was necessary to activate the primary hydroxyl group (C-6) of the ammonium/amide pyranose repeating units to become more susceptible toward nucleophilic attack.$^{24,25}$

Unlike the previously discussed structural motifs, small organic molecules combine facile synthesis, well-defined chemical structure and the ease of chemical analysis of intermediates and reaction products. Phillip Jessop’s research group reported that exposing a mixture of 1-hexanol and 1,8-diazabicyclo-[5,4.0]-undec-7-ene (DBU, Scheme 1D) to the atmospheric CO$_2$ resulted in the formation of amidinium hexylcarbonate ([DBUH$^+$][O$_2$COHex]) adduct. The reaction mixture could be regenerated by applying external stimuli such as bubbling nitrogen or heating. $^{38}$ This reversible reaction with CO$_2$ was exploited to engineer a wide spectrum of species that can reversibly change their ionic character for different applications such as solvents,$^{27}$ solutes,$^{28}$ surfactants,$^{29}$ coagulatable/dispersible polymers,$^{30}$ catalysts,$^{31}$ sensors,$^{32}$ etc. Following Jessop’s concept, Anugwom et al. reported a switchable ionic liquid comprised of glycerol and DBU to capture acidic gases such as CO$_2$ and sulfur dioxide. $^{33}$ However, glycerol can undergo dehydration reaction in basic media $^{34}$ together with the formation of cyclic carbonates,$^{35}$ which might limit its practical usage for CO$_2$ capturing in the presence of DBU. In order to eliminate the possibility of side reactions of multifunctionalized alcohol together with increasing the potential sorption capacity of CO$_2$ compared with other alcohol/DBU mixtures reported elsewhere in the literature,$^{18,19,33}$ we have chosen to examine a multiarmed hydroxyl-terminated organic moiety, viz., pentaerythritol (PE, Scheme 1E) due to the lack of $\beta$-H adjacent to the hydroxyl groups. PE is a commercially available small molecule that was synthesized by Tollens and Wigand in 1891. $^{36}$ The ability of PE to participate in condensation reactions was utilized to build up several structural motifs for CO$_2$ fixation.$^{37,38}$

To the best of our knowledge, this is the first report on exploiting PE as a small molecular sorbent for CO$_2$ capturing in the presence of DBU through alkyl carbonate formation. The chemisorption of CO$_2$ by the tetra-functionalized substrate was investigated by using nuclear magnetic resonance (NMR) and ex situ attenuated total reflectance-Fourier transform infrared (ATR-FTIR). The sorption capacity was measured volumetrically using in situ ATR-FTIR. Furthermore, DFT was used to understand the mechanism and energetics of CO$_2$ sorption at different molar ratios between PE and DBU.

### MATERIALS AND METHODS

#### Chemicals

Unless otherwise stated, all chemicals were handled under Schlenk line. PE and DBU were purchased from Sigma-Aldrich. Dimethyl sulfoxide-d$_6$ (DMSO-d$_6$, 99.5+% atom D) was purchased from ACROS Organics. DMSO used for ex situ ATR-IR measurements was purchased from TEDIA, while the wet and dry (anhydrous) grades used for volumetric uptake measurements were obtained from Grüssing GmbH and Sigma-Aldrich, respectively. CO$_2$ (99.95%, Food grade) was purchased from Advanced Technical Gases Co. (Amman, Jordan). Methanol (MeOH) and ethanol (EtOH) were purchased from Sigma-Aldrich.

#### Instruments

Solution $^1$H and $^{13}$C NMR spectra were collected at room temperature using (AVANCE-III 400 MHz ($^1$H: 400 MHz, $^{13}$C: 100 MHz)) FT-NMR NanoBay spectrometer (Bruker, Switzerland) in DMSO-d$_6$. In situ attenuated total reflectance-Fourier transform infrared (ATR-FTIR) measurements were carried out using a MMR45m RB04-50 (Mettler-Toledo, Switzerland) with an MCT detector, and a silicon window probe connected via pressure vessel; sampling 3500 to 650 cm$^{-1}$ at 8 wavenumber resolution; scan option: 64; gain: 1X. Ex situ ATR-FTIR spectra were recorded on a Bruker Vertex 70-FT-IR spectrometer at room temperature coupled with a Vertex Pt-ATR accessory. pH measurements were obtained via an RL 150-Russel pH meter. Conductivity measurements were carried out using a 712 conductometer (Metrohm, Switzerland). Water content was determined using a Karl Fischer titrator (TZ 1753 with Diaphragma, KF1100, TitroLine KF).

#### Computational Method

Calculations were performed within Gaussian 09.$^{39}$ The full optimization was performed using the DFT method (B3LYP/6-31+G*). Different starting geometries were considered for each system. Minima were characterized by the absence of imaginary frequencies. A polarizable continuum model was used for implicit solvent calculations. $p_K_a$ calculations were performed in DMSO according to the literature.$^{40,41}$

### EXPERIMENTAL PROCEDURES

#### NMR

In an NMR tube, 30 mg of the PE was dissolved in 0.5 mL of DMSO-d$_6$. Upon dissolution, CO$_2$ was bubbled into the NMR tube via a long cannula for 20 min. A white precipitate was formed as a result of [DBUH$^+$][O$_2$COHex], which settles down in the NMR tube.

#### In Situ ATR-FTIR

Dry or wet solvents were used according to the run of interest. A 1:4 molar solution of PE/DBU was prepared by dissolving 0.5 g of PE in 5 mL of DMSO. Similarly, an appropriate amount of DBU (2.2 mL) was introduced in 5 mL of DMSO. Both solutions were mixed and sonicated until complete dissolution occurred and then transferred into the ATR-FTIR autoclave. CO$_2$ was introduced at 25 °C, and the drop-in pressure was measured while scanning every 15 s until a constant value (bars) was reached. Initial and final pressures for each run are shown in Table 1. For correction purposes, CO$_2$ was purged into 10 mL of DMSO in the ATR-FTIR autoclave, and the solvent contribution through physisorption of CO$_2$ was measured at the centered peak of 2337 cm$^{-1}$. For wet samples, the chemisorbed CO$_2$ with bicarbonate formation was measured within the blank run and corrected accordingly, and all values are reported in Table 1. For both MeOH and EtOH, 4 mol of the alcohol was mixed with 2.2 mL of DBU using the previously mentioned procedures.

---

Scheme 1. Chemical Structures of (A) Carbamate-Amide Adduct for MEA: R$_1$ = H, R$_2$ = CH$_2$OH. (B) Bicarbonate-Amide Adduct. (C) Chitin-Acetate Oligomer (x and y are 0.6 and 0.4, respectively). (D) 1,8-Diazabicyclo-[5,4.0]-undec-7-ene (DBU). (E) Pentaerythritol (PE)
RESULTS AND DISCUSSION

In this work, DMSO was chosen as a polar aprotic, high dielectric constant, nonvolatile solvent to solubilize PE (a white crystalline solid that melts at \(\sim 253-258 \degree C\)) and to stabilize the anticipated organic carbonate adduct (if any) upon bubbling CO2. As an aside, the high boiling point of DMSO (bp 189 \degree C) and DBU (bp 261 \degree C) is beneficial upon sorbent regeneration to avoid evaporation losses, which decreases the operational costs and enables greener and sustainable media for such process. Moreover, the smaller specific heat of DMSO compared to H2O (1.96 and 4.18 J g\(^{-1}\) K\(^{-1}\), respectively) makes the use of the former less energy consuming upon regeneration. It is anticipated that the use of DMSO which has a smaller specific heat (1.96 J g\(^{-1}\) K\(^{-1}\)) will be less energy consuming.

\(^{13}\)C NMR spectra of the neat PE dissolved in DMSO-\(d_6\) were similar before and after bubbling CO2 with a difference of emergence of a peak at ca. 124.7 ppm, that corresponds to physisorbed CO2 (Figure 1A), which highlights the importance of activating the substrate toward nucleophilic attack prior the exposure to CO2 using an auxiliary base, viz., DBU. Notably, bubbling the base dissolved in DMSO-\(d_6\) (used as received with no drying attempted) resulted in a white precipitate, due to the reaction between DBU and CO2 in the presence of H2O to form amidinium bicarbonate salt ([DBUH]\([\neg O_2COH]\)], an insoluble white precipitate. The \(^{13}\)C NMR spectrum of the precipitate dissolved in D\(_2\)O is shown in the Supporting Information (Figure S1). This explained the absence of the

<table>
<thead>
<tr>
<th>run</th>
<th>sorbent</th>
<th>(P_1)</th>
<th>(P_f)</th>
<th>sorbed CO2 (bar)</th>
<th>sorption capacity (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMSO (as received)</td>
<td>4.6</td>
<td>3.2</td>
<td>1.4</td>
<td>14.66</td>
</tr>
<tr>
<td>2</td>
<td>PE/DBU/DMSO (as received)</td>
<td>4.6</td>
<td>0</td>
<td>4.6</td>
<td>15.93</td>
</tr>
<tr>
<td>3</td>
<td>DMSO (as received)</td>
<td>10.8</td>
<td>8.0</td>
<td>2.8</td>
<td>18.48</td>
</tr>
<tr>
<td>4</td>
<td>PE/DBU/DMSO (as received)</td>
<td>10.6</td>
<td>5.6</td>
<td>5.0</td>
<td>15.77</td>
</tr>
<tr>
<td>5</td>
<td>DMSO (dry)(^{b})</td>
<td>10.8</td>
<td>7.8</td>
<td>3.0</td>
<td>21.88</td>
</tr>
<tr>
<td>6</td>
<td>PE/DBU/DMSO (dry)(^{b})</td>
<td>10.6</td>
<td>4.8</td>
<td>5.8</td>
<td>21.88</td>
</tr>
<tr>
<td>7</td>
<td>MeOH/DBU/DMSO (dry)(^{c})</td>
<td>10.6</td>
<td>5.4</td>
<td>5.2</td>
<td>15.77</td>
</tr>
<tr>
<td>8</td>
<td>EtOH/DBU/DMSO(^{d})</td>
<td>10.4</td>
<td>5.0</td>
<td>5.4</td>
<td>21.88</td>
</tr>
</tbody>
</table>

\(^{a}\)Applied conditions: \(T = 298 K\), \(V_{\text{autoclave}} = 50.0\) mL. The amount of CO2 absorbed by the binary system was calculated using the equation of state of the ideal gas (\(PV = nRT\)). The contribution of DMSO was taken in consideration while calculating the sorption capacity. Sample calculation is shown in Supporting Information. \(^{b}\)Water content measured by Karl Fischer titrator was 2.6 ppm. \(^{c}\)Water content measured by Karl Fischer titrator was 10.2 ppm. \(^{d}\)Water content measured by Karl Fischer titrator was 22.6 ppm.

"Figure 1. \(^{13}\)C NMR spectra of (A) PE, (B) DBU and (C) 1:4 PE/DBU dissolved in DMSO-\(d_6\) before (black) and after (red) bubbling CO2 for 20 min at 25 \degree C."
CO₂ peak (≈124.7 ppm) in the ¹³C NMR spectrum of the DBU solution (Figure 1B), presumably due to the salting out effect.

DBU alkyl-carbonate adduct was synthesized by bubbling CO₂ through a 1:4 molar mixture of PE/DBU dissolved in DMSO at room temperature as shown in Scheme 2.

The ¹³C NMR spectrum of the mixture (Figure 1C) showed the emergence of a new peak at 157.4 ppm together with a peak shifted from 160.5 to 165.0 ppm upon bubbling CO₂. While the former can be explained by the formation of organic carbonate species, the latter shifted peak can be attributed to the bridgehead amidinium carbon of DBUH⁺ upon complexation to the PE-carbonato anion. A similar, chemical shift was reported by Phan et al.44 after bubbling CO₂ through a 1-hexanol-DBU binary mixture.44

¹H NMR spectra were measured for PE/DBU binary mixture before and after bubbling CO₂. Upon bubbling, the spectrum of the binary mixture showed a broadened peak centered at 10.8 ppm due to NH proton transfer (vide infra) and the asymmetric stretching of O–C–O⁻ within the organic carbonate anion, respectively.45

The interaction between PE/DBU binary system with CO₂ was further investigated by monitoring the variation in temperature, pH, and conductance as a function of bubbling time as shown in Figure 4. Expectedly, the reaction is exothermic. The pH of the solution was decreased to a minimum of 14.88, and the conductance was increased to a maximum of 2.3 mS throughout the experiment progress. On one side, the increase in conductance might be attributed to the weaker ion pairing tendency due to increasing the bulkiness of the counteranion after the chemisorption of CO₂ rather than increasing the ionic mobility.46 On the other side, the decrease in pH over time pointed to a proton transfer from the amidinium cation to the organic carbonato species as verified by DFT calculations (vide infra). Subsequently, as the solution temperature went down due to reaction completion, the pH and conductance values rose and dropped, respectively.

Similarly to a previously reported protocol of volumetric uptake experiment, the sorption capacity was evaluated using an in situ ATR-FTIR autoclave by following the evolution of the asymmetric stretching frequency of O–C–O at 1630 cm⁻¹ as a function of time as shown in Figure 5A. The amount of the chemisorbed CO₂ was calculated by plugging the drop-down in pressure (recorded by a digital manometer) in the equation of state of the ideal gas (PV = nRT). Correction with respect to solvent was carried out using neat DMSO (physisorbed). Table 1 shows the sorption capacity at different conditions.

The uptake of a 5.0% (w/v) PE solution (Run 2, Table 1) was 4.6 bar (sample calculation is shown in Supporting Information). Doubling the CO₂ pressure increased the amount of the physisorbed CO₂ by 2-fold (Run 1 and 3, respectively), as well as the sorption capacity by ca. 9%, which can be attributed to the enhanced physisorption at higher pressure. Unexpectedly, the removal of water from the system should decrease the sorption capacity (due to the extra contribution of [DBUH⁺]⁻·O₂COH⁻), on the contrary, the increased sorption could be explained by the more favorable physisorption over chemisorption at dry conditions. From a comparison point of view, a dry MeOH based system (Run 7, Table 1) gave almost the same sorption capacity as the wet PE based system (Run 2, Table 1), which emphasizes the idea of using our system for wet scrubbing in PCC without drying or volatility losses, which is a major concern.

The ATR-FTIR spectra of the reaction mixture before and after bubbling CO₂ (Figure 3) fortified the chemisorption of CO₂ through the appearance of two peaks at 1670 and 1630 cm⁻¹ ascribed to the symmetric stretching of C=O (in the acidic form as a result of proton shuttling, vide infra) and the asymmetric stretching of O–C–O⁻ within the organic carbonate anion, respectively.45

The formation of alkyl-carbonate was further explored using ex situ ATR-FTIR spectroscopy. In agreement with NMR measurements, the spectra of the neat materials indicated that neither PE nor DBU reacted with CO₂ (Figure S2A,B), although a white precipitate was formed when DBU was exposed to CO₂ (vide supra).

Figure 4. Reaction temperature, conductance, and pH of 1:4 PE/DBU mixture dissolved in DMSO as a function of CO₂ time.

Figure 5. (A) Partial in situ IR spectrum for the 5% (w/v) PE/DBU in DMSO as a function of time carried out at 298 K, 4.6 bar. The red asterisk denotes the followed-up peak at 1630 cm⁻¹ absorption profiles as a function of time. (B) Physisorbed CO₂ monitored at 2327 cm⁻¹ by neat DMSO. (C) Organic carbonate monitored at 1630 cm⁻¹ using a 2.5% (w/w) (navy) and 5.0% (blue) of PE/DBU dissolved in DMSO.
as in the case of MeOH. Although the EtOH/DBU neat system has the previously mentioned limitation (volatility issues), it gave a sorption capacity of 21.88% (Run 8, Table 1), which might be explained by the higher nucleophilicity of the corresponding alkoxide together with the less repulsion among arms once compared to PE/DBU. Assuming a 1:4 reaction stoichiometry between PE and CO\textsubscript{2} (Scheme 2), the theoretical sorption capacity should be 23.62 wt %. However, the volumetric uptake measurements provided smaller numbers for both wet and dry conditions at different CO\textsubscript{2} pressure as well as sorbent concentrations. DFT calculations (Table 4, vide infra) indicated that the relative equilibrium constants of the first mole of CO\textsubscript{2} to be absorbed are much larger than the second one and so on, which justified the volumetric uptake results.

The regeneration of PE/DBU binary mixture upon binding CO\textsubscript{2} was achieved either by bubbling N\textsubscript{2} gas through the reaction mixture at room temperature, or heating at 100 °C. The reversibility character was confirmed using \textsuperscript{13}C NMR, which indicated a massive reduction in the intensity of the chemical shift of the carbonate carbon (ca. 157 ppm) in comparison with the corresponding peak of the central carbon of [DBUH\textsuperscript{+}+] (ca. 165 ppm).

In comparison with CO\textsubscript{2} binding organic liquids (CO\textsubscript{2}BOLs), the PE/DBU binary system required only 5.0% PE, while neat liquids are needed in the case of CO\textsubscript{2}BOLs (Table 2), which will be reflected on the total cost of the sorbent used versus its abundance. It is noteworthy that we used diluted PE/DBU solutions, which will lower the corrosive character once compared to neat alcohols/DBU mixtures. For example, the concentration of DBU required to prepare a 1:1 hexanol/DBU using a 10 mL of hexanol (as the active material within the sorbent that bears CO\textsubscript{2}) is 122% (w/v) compared to 22% (w/v) needed to make a 5.0% (w/v) solution of PE in DMSO of the same volume. Furthermore, CO\textsubscript{2}BOLs are more volatile, and thus higher losses upon regeneration are expected. In our system, PE possesses low vapor pressure (bp = 270 °C, 30 mmHg), which makes it useful for the regeneration process, e.g., upon heating. In addition, the use of DMSO as green solvent with a high boiling point is another advantage compared to other commercial solvents.\textsuperscript{47} Extra merit can be drawn for the studied material which is its utilization without further purification. Extra precautions should be taken into consideration in the case of CO\textsubscript{2}BOLs. In this context, Heldebrant et al.\textsuperscript{18} reported that the equilibrium constant for the reaction between H\textsubscript{2}O, DBU, and CO\textsubscript{2} with respect to that of MeOH (K\textsubscript{eq}(H\textsubscript{2}O)/K\textsubscript{eq}(MeOH)) was 1.43, which emphasizes that the formation of [DBUH\textsuperscript{+}][\textsuperscript{-}O\textsubscript{2}COH] is more preferred over the alkyl carbonate.

### Table 2. Comparison between the CO\textsubscript{2} Binding Organic Liquids (CO\textsubscript{2}BOLs) and PE/DBU Binary System

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Jessop’s system</th>
<th>PE/DBU in DMSO (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat liquids</td>
<td>37% (w/v) (relative to MeOH)</td>
<td>5.0 wt %</td>
</tr>
<tr>
<td>superbase concentration\textsuperscript{a}</td>
<td>12% (w/v) (relative to HexOH)</td>
<td>22% (based on 5 wt % solution)</td>
</tr>
<tr>
<td>volatility</td>
<td>more volatile\textsuperscript{b}</td>
<td>less volatile due to the use of DMSO (bp = 189 °C)</td>
</tr>
<tr>
<td>drying and ease of handling</td>
<td>dry conditions, requires extra precautions</td>
<td>DMSO was used as received (wet)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Values in DMSO are given in parentheses.

### Table 3. Calculated Gas-Phase Proton Affinities\textsuperscript{*} (PAs) and pK\textsubscript{a} values\textsuperscript{b} in DMSO for Different Substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Representative equation</th>
<th>PA/kcal mol\textsuperscript{-1}</th>
<th>pK\textsubscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBU</td>
<td>DBU + H\textsuperscript{+} → DBUH\textsuperscript{+}</td>
<td>247.66</td>
<td>12.95 (12)</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>OH\textsuperscript{−} + H\textsuperscript{+} → H\textsubscript{2}O</td>
<td>382.96</td>
<td>27.94 (31.4)</td>
</tr>
<tr>
<td>MeOH</td>
<td>CH\textsubscript{3}OH\textsuperscript{−} + H\textsuperscript{+} → CH\textsubscript{3}CH\textsubscript{2}OH</td>
<td>373.20</td>
<td>28.00 (29.0)</td>
</tr>
<tr>
<td>EtOH</td>
<td>CH\textsubscript{3}CH\textsubscript{2}OH\textsuperscript{−} + H\textsuperscript{+} → CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}OH</td>
<td>369.88</td>
<td>28.11 (29.8)</td>
</tr>
<tr>
<td>PE-(OH)\textsubscript{1}</td>
<td>C(CH\textsubscript{2}OH\textsubscript{2})\textsubscript{−} + H\textsuperscript{+} → C(CH\textsubscript{2}OH\textsubscript{2})\textsubscript{2}</td>
<td>336.65</td>
<td>19.85</td>
</tr>
<tr>
<td>PE-(OH)\textsubscript{2}</td>
<td>C(CH\textsubscript{2}OH\textsubscript{2})\textsubscript{−} + H\textsuperscript{+} → C(CH\textsubscript{2}OH\textsubscript{2})\textsubscript{2}</td>
<td>449.39</td>
<td>32.37</td>
</tr>
<tr>
<td>PE-(OH)\textsubscript{3}</td>
<td>C(CH\textsubscript{2}OH\textsubscript{2})\textsubscript{−} + H\textsuperscript{+} → C(CH\textsubscript{2}OH\textsubscript{2})\textsubscript{2}</td>
<td>528.57</td>
<td>37.07</td>
</tr>
<tr>
<td>PE-(OH)\textsubscript{4}</td>
<td>C(CH\textsubscript{2}OH\textsubscript{2})\textsubscript{−} + H\textsuperscript{+} → C(CH\textsubscript{2}OH\textsubscript{2})\textsubscript{2}</td>
<td>631.90</td>
<td>49.11</td>
</tr>
</tbody>
</table>

\textsuperscript{*}PA was calculated by using the Gaussian 09 software (B3LYP/6-31+G\textsuperscript{*} level of theory) as the negative of the enthalpy change (ΔH) of the gas phase reaction, A\textsuperscript{−} (g) + H\textsuperscript{+} (g) → AH (g). Under standard conditions, the value of the enthalpy of the gas-phase proton was taken as 1.48 kcal mol\textsuperscript{-1}.\textsuperscript{48}\textsuperscript{b}Calculated pK\textsubscript{a} values for the conjugated acids in water, see Computational Method for details.\textsuperscript{48}\textsuperscript{c}Taken from an online document provided by D. A. Evans and co-workers, Harvard University.\textsuperscript{49}\textsuperscript{d}Taken from ref 50.

### Table 4. Calculated Thermodynamic Parameters\textsuperscript{*} (in Both Gas Phase and DMSO\textsuperscript{b}) for the Capture of CO\textsubscript{2} by PE, H\textsubscript{2}O, MeOH, and EtOH, as well as tert-Butanol (tert-BuOH)

According to the Following Reaction:

ROH + CO\textsubscript{2} + DBU → [DBUH\textsuperscript{+}][\textsuperscript{-}O\textsubscript{2}COR]

<table>
<thead>
<tr>
<th>Peptide</th>
<th>ΔH\textsuperscript{a}</th>
<th>−7ΔS\textsuperscript{c}</th>
<th>ΔG\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-(CO\textsubscript{2})\textsubscript{2}</td>
<td>−4.18 (−5.09)</td>
<td>−0.76 (−0.59)</td>
<td>−4.94 (−5.68)</td>
</tr>
<tr>
<td>PE-(CO\textsubscript{2})\textsubscript{3}</td>
<td>−4.05 (−5.28)</td>
<td>−0.34 (−0.20)</td>
<td>−4.39 (−5.48)</td>
</tr>
<tr>
<td>PE-(CO\textsubscript{2})\textsubscript{4}</td>
<td>−3.32 (−5.52)</td>
<td>−0.39 (−0.07)</td>
<td>−3.71 (−5.27)</td>
</tr>
<tr>
<td>PE-(CO\textsubscript{2})\textsubscript{5}</td>
<td>−1.33 (−3.95)</td>
<td>−0.21 (0.13)</td>
<td>−1.54 (−3.82)</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>−3.80 (−4.50)</td>
<td>−1.80 (−2.15)</td>
<td>−5.60 (−6.65)</td>
</tr>
<tr>
<td>MeOH</td>
<td>−4.81 (−5.79)</td>
<td>−0.88 (−0.48)</td>
<td>−5.69 (−6.27)</td>
</tr>
<tr>
<td>EtOH</td>
<td>−4.28 (−5.30)</td>
<td>−0.50 (−0.94)</td>
<td>−4.78 (−6.24)</td>
</tr>
<tr>
<td>tert-BuOH</td>
<td>0.00 (0.00)</td>
<td>0.00 (0.00)</td>
<td>0.00 (0.00)</td>
</tr>
</tbody>
</table>

\textsuperscript{*}Values are given relative to tert-butanol, per CO\textsubscript{2} units in kcal mol\textsuperscript{-1}. Values in DMSO are given in parentheses.
compared to EtOH (taken as a model due to its possession of an equivalent number of carbons as in one arm of PE), the $K_{eq}(\text{ROH})/K_{eq}(\text{H}_2\text{O})$ value is larger for the PE based system, and this makes our system much better at coping in the presence of water compared to CO$_2$BOLs. One aspect that is superior to CO$_2$BOLs is the sorption capacity of different alkylcarbonates as measured by $^1$H NMR from the reaction of a set of primary alcohols, DBU, and CO$_2$, which increases from 17.3 to 20.7% as a function of the molar mass of the homologous series.$^{18,19}$ In our case it was ca. 18.5 wt %.

**DFT Calculations.** The first mechanistic step for the CO$_2$ capture using alcohols, to form the organic carbonato-species, requires the formation of an alkoxide using a strong base, viz., DBU.$^4$ For PE, all hydroxyl groups are equivalent, and upon reacting with DBU, they give equivalent alkoxide anions (black trace, Figure 2). We have accessed the basicity of each hydroxyl group through calculating the gas-phase proton affinity (PA) and the $pK_a$ value in DMSO (Table 3). For comparison, PA and $pK_a$ values of DBU$^+$ (conjugated acid of DBU), H$_2$O, MeOH, and EtOH were also calculated. The calculated $pK_a$ values were in a good agreement with experimental data. The PE-(OH)$_4$ shows the highest PA value of 631.9 kcal mol$^{-1}$, which is almost twice that for the formation of PE-(OH)$_1$. Furthermore, the $pK_a$ values were calculated as 19.85, 32.37, 37.07, and 49.11 for PE-(OH)$_1$, PE-(OH)$_2$, PE-(OH)$_3$, and PE-(OH)$_4$ respectively. Therefore, the order of reactivity toward CO$_2$ capturing follows this order: PE-(OH)$_1$ > PE-(OH)$_2$ > PE-(OH)$_3$ > PE-(OH)$_4$. Interestingly, PE-(OH)$_1$ shows lower basicity (lower $pK_a$ value in DMSO) once compared to ethanolate and hydroxide, which clearly indicates that PE (at least the first arm) has a stronger ability to lose the proton and capture CO$_2$ in DMSO once compared to EtOH and H$_2$O. For CO$_2$ capturing purposes, the consecutive formation of the first carbonate adduct (PE-(CO$_2$)$_1$, vide infra) makes the next nucleophilic attack less susceptible towards CO$_2$.

Thermodynamics for the CO$_2$ capturing by PE, MeOH, and EtOH, as well as H$_2$O, were calculated in both gas phase and DMSO to mimic our experimental results. Table 4 shows the thermodynamic parameters relative to tert-butanol. In general, the reaction shows favorable enthalpic contributions ($\Delta H$) associated with large entropic penalties ($T\Delta S$) (see Table 4 and Supporting Information for the absolute values). The change in the Gibbs free energy ($\Delta G$) indicated that the consecutive CO$_2$ capturing becomes less favorable, viz., PE-(CO$_2$)$_1$ is the most favored adduct (Table 4). In the gas phase, PE-(CO$_2$)$_1$ showed a more favorable $\Delta G$ value compared to EtOH, but less favorable compared to H$_2$O and MeOH by only 0.66 and 0.75 kcal mol$^{-1}$, respectively. In DMSO, the trend was different due to its higher dielectric constant compared to gas phase, in which H$_2$O shows the lowest free energy, followed by MeOH, EtOH, and PE-(OH)$_1$. The same observation was obtained experimentally for H$_2$O and methanol by Jessop and co-workers.$^{18}$ tert-Butanol showed the least favorable $\Delta G$ value, which is known to be so experimentally, due to both steric and electronic effects.$^{18}$

Optimization of the possible adduct(s) formation of the ionic organic alkylcarbonate anions on each arm of PE’s hydroxyl groups and their complexes with BD$_2$U$^+$ were calculated in both gas phase and DMSO. The optimized structures in the gas phase are shown in Figure 6A–D. No significant structural changes were observed when going from gas phase to DMSO. In the case of PE-(CO$_2$)$_1$ and PE-(CO$_2$)$_4$, the depictions of the tri- and
tetra-carbonato species showed the occurrence of a proton shuffling between the formed carbonic acid and the DBU when changing the medium from gas phase (E) to DMSO (F). In which, the carbonic acid is formed in gas phase, while the carbonate adduct is formed in DMSO. A similar result was observed experimentally by H NMR (red trace, Figure 2, broadening of peak corresponding to the amidinium cation-carbonic acid ca. 10 ppm is due to hydrogen bonding), together with a supporting evidence using an ATR-FTIR spectrum (Figure 3) with a centered peak at 1670 cm⁻¹ as a result of carbonic acid contribution. The same phenomenon was reported by Cantu et al. via a single component CO₂BOL using ab initio molecular dynamics simulation.

**CONCLUSIONS**

A new binary system comprised of 5.0% (w/v) PE in the presence of DBU (1:4 molar ratio) dissolved in DMSO was reported for CO₂ capturing. The formation of ionic alkyl organic carbonate ([DBUH⁺][O₂COR]) was confirmed using ¹³C NMR, ex situ ATR-FTIR. Further, the charged basic species was confirmed using a thermochromated conductivity and pH meter couple. The sorption capacity of 5.0% PE (w/v) solution was measured volumetrically with high efficiency using an ATR-FTIR autoclave. In addition, DFT was used to justify the reason behind the different reactivities of all arms toward CO₂ capturing both in the gas phase and DMSO. For the [DBUH⁺][O₂COR], different substrates were taken into consideration for comparison reasons, viz., PE together with H₂O₂ and simple alcohols, as in MeOH and EtOH. Moreover, we report on the newly discovered proton shuttling, medium-dependent phenomenon, that was verified both experimentally and theoretically.

**ASSOCIATED CONTENT**

Supporting Information The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energy-fuels.7b01125.

**AUTHOR INFORMATION**

Corresponding Authors

*(A.K.Q.) E-mail: s.qroush@ju.edu.jo.
*(K.L.A.) E-mail: k.assaf@jacobs-university.de.
*(A.F.E.) E-mail: alaa.eftaiha@hu.edu.jo; aeftaiha@ucsb.chem.edu (Fulbright Visiting Scholar).

Khaleel I. Assaf:0000-0003-4331-8492
Bernhard Rieger:0000-0002-0023-884X
Ala’a F. Eftaiha:0000-0003-4285-2546

**Funding** Financial support has been provided by the Deanship of Scientific Research at the Hashemite University.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

A.F.E. acknowledges the Deanship of Scientific Research at the Hashemite University and the Binational Fulbright Commission (BFC) in Jordan. Marina Reiter (TUM, Germany) is acknowledged for performing the volumetric uptake measurements using the in situ ATR-FTIR autoclaves.

**ABBREVIATIONS**

PE, pentaerythritol; PCC, postcombustion capture; DBU, 1,8-diazabicyclo-[5,4,0]-undec-7-ene; DMSO, dimethyl sulfoxide; [DBUH⁺][O₂COR], ionic alkyl organic carbonate; NMR, nuclear magnetic resonance; ATR-FTIR, attenuated total reflectance-Fourier transform infrared; DFT, density functional theory; CCS, carbon capture and storage or sequestration; CCU, carbon capture and utilization; MEA, monoethanolamine; NH₃, ammonia; MOFs, metal organic frameworks; SO₂, sulfur dioxide; MeOH, methanol; EtOH, ethanol; CO₂BOLs, CO₂ binding organic liquids; Kₑq, equilibrium constant; PA, proton affinity; ΔH, enthalpy; ΔS, entropy; AG, Gibbs free energy

**REFERENCES**

(2) Thorns, J. E.; Pope, F. D. Chapter 1. Why Do We Need Solutions to Global Warming? In Geoengeering of the Climate System; The Royal Society of Chemistry, 2014; pp 1–21.
(13) Reynolds, A. J.; Verheyen, T. V.; Adelouj, S. B.; Meuleman, E.; Feron, P. Towards Commercial Scale Postcombustion Capture of CO₂


(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Fox, D. J. et al. Gaussian 09 Gaussian Inc.

