1. INTRODUCTION

Most of the steps of the carbon capture and storage (CCS) chain, such as transportation, compression, and storage, are established and technologically available. One of the main obstacles hampering the exploitation of CCS is the capture stage, which represents almost two-thirds of the total costs of the CCS. This pending issue requires a swift solution. Postponing leads to continuation of the climate change as a result of the increasing consumption of fossil fuels, which accounts for 86% of the anthropogenic greenhouse gas emissions complemented by deforestation and chemical processing. The prevalent public concern is justified considering the drastic increase of the annual global CO$_2$ emissions by approximately 80% between 1970 and 2004.3

In carbon capture the energy needed for solvent regeneration has a major impact on costs. This energy is directly related to the separation efficiency of the solvent and the nature of interaction with CO$_2$. Therefore, improving the separation efficiency will have a significant impact of the capture costs.4

Development, evaluation, and application of novel, more efficient and sustainable solvents have been of broad and current interest in various scientific and technological areas, among which is gas separation. One of the remarkable achievements in this context is the application of the nonvolatile ionic liquids (ILs) and their potential to replace volatile organic solvents for CO$_2$ capture.5–7 ILs possess unique physicochemical properties, which are tunable by combining different cations and anions as well as inserting different functional groups in either the cation or the anion or in both. Deep eutectic solvents (DESs) are another class of novel solvents that have similarities with ILs. Generally, DESs are prepared by mixing two solid constituents, a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA). Liquefaction occurs as a result of association by means of hydrogen bonds.8,9 Moreover, DESs composed of multi-component mixtures have been reported in the literature.10,11 The ease of preparation and the elimination of purification steps significantly reduce the production costs and the impact on the environment making the DESs a very promising economical alternative for the currently used solvents.12 This is in line with the objectives of green chemistry and green engineering. Both reach for safety, maximum efficiency, and minimum health and environmental impact at all stages of a chemical’s life cycle.13

So far, CO$_2$ solubilities in DESs reported in the literature have been limited to hydrophilic ones and to the best of our knowledge hydrophobic DESs have not been studied as potential solvents for CO$_2$ capture. In this work, for the first time the CO$_2$ solubility is determined in hydrophobic DESs. The hydrophobic DESs were prepared by combining decanoic acid (DecA), which acts as HBD, with various halide anions and alkyl chain lengths. The measured CO$_2$ solubilities are similar to those found in renowned fluorinated ILs, while the heats of CO$_2$ absorption are in the range of nonpolar solvents. The presented DESs show good potential to be used as CO$_2$ capture agents.

ABSTRACT: The solubility of CO$_2$ in hydrophobic deep eutectic solvents (DESs) has been measured for the first time. Six different hydrophobic DESs are studied in the temperature range from 298 to 323 K and at CO$_2$ pressures up to 2 MPa. The results are evaluated by comparing the solubility data with existing hydrophilic DESs and currently applied physical solvents and fluorinated ionic liquids. The DESs are prepared by mixing decanoic acid with a quaternary ammonium salt with different halide anions and alkyl chain lengths. The measured CO$_2$ solubilities are similar to those found in renowned fluorinated ILs, while the heats of CO$_2$ absorption are in the range of nonpolar solvents. The presented DESs show good potential to be used as CO$_2$ capture agents.
selected due to its ability to form hydrogen bonds, its dominating nonpolar domains, and its low water solubility (e.g., 0.15 mg·g⁻¹ at 20 °C).¹⁵ Five different quaternary ammonium salts act as HBAs: tetrabutylammonium chloride (N₄₄₄₄⁻Cl), methyltrioctylammonium chloride (N₈₈₈₁⁻Cl), methyltrioctylammonium bromide (N₈₈₈₁⁻Br), tetraoctylammonium chloride (N₈₈₈₈⁻Cl) and tetraoctylammonium bromide (N₈₈₈₈⁻Br).

The HBD has been used in different molar ratios with the HBAs. The effects of the halide ion, the alkyl chain length of the quaternary ammonium salts, and the HBD:HBA ratio on the CO₂ solubility are evaluated. In addition, a comparative study based on Henry's law and the heat of solution has been conducted to assess their CO₂ solubility compared to existing state-of-the-art physical solvents for CO₂ capture.

Table 1. Substances and DESs (Including Molar Ratio of HBD:HBA) Used in This Study, Including Their Source, Purity, Molecular Weight (M), Density (ρ) at 298.15 K and pH Values of the Aqueous Phase after Mixing with Water

| component                | source          | purity/wt % | M/g·mol⁻¹ | ρ/kg·m⁻³ (298.15 K) | pH of the water phase |
|--------------------------|-----------------|-------------|-----------|---------------------|-----------------------|
| DecA (C₁₀H₂₀O₂)         | Sigma-Aldrich   | ≥98         | 172.16    | 4                   |
| N₈₈₈₁⁻Cl                | Sigma-Aldrich   | ≥97         | 404.16    | 4                   |
| N₈₈₈₁⁻Br                | Sigma-Aldrich   | ≥97         | 448.61    | 3.9                 |
| N₈₈₈₁⁻Cl                | Sigma-Aldrich   | ≥97         | 502.34    | 5.3                 |
| N₈₈₈₁⁻Br                | Sigma-Aldrich   | ≥98         | 546.80    | 5.5                 |
| N₈₈₈₈⁻Cl                | Merck           | ≥95         | 277.92    | 4.5                 |
| DecA:N₈₈₈₁⁻Cl (2:1)¹⁶   | prepared by mixing | ≥98     | 249.49    | 896.4               | 1.6                   |
| DecA:N₈₈₈₁⁻Br (2:1)¹⁶   | prepared by mixing | ≥98     | 264.31    | 942.2               | 1.7                   |
| DecA:N₈₈₈₈⁻Cl (2:1)¹⁶   | prepared by mixing | ≥97     | 207.41    | 916.8               | 1.7                   |
| DecA:N₈₈₈₈⁻Br (2:1)¹⁶   | prepared by mixing | ≥98     | 297.04    | 929.8               | 1.6                   |
| DecA:N₈₈₈₈⁻Cl (1.5:1)¹⁶ | prepared by mixing | ≥98     | 304.23    | 888.1               | 1.7                   |
| DecA:N₈₈₈₈⁻Cl (2:1)¹⁶   | prepared by mixing | ≥98     | 282.22    | 888.9               | 1.6                   |
| CO₂                      | Linde AG        | ≥99.995     | 44.01     |                     |

Figure 1. Molecular structures of the HBD and the HBAs used in this work.
2. EXPERIMENTAL SECTION

2.1. Materials and Preparation of Hydrophobic DESs.

Tetrabutylammonium chloride (N_{4444}^−\text{Cl}, ≥ 95%) was purchased from Merck. Methyltrioctylammonium chloride (N_{8881}^−\text{Cl}, 97%), methyltrioctylammonium bromide (N_{8881}^−\text{Br}, 97%), tetraoctylammonium chloride (N_{8888}^−\text{Cl}, 97%), tetraoctylammonium bromide (N_{8888}^−\text{Br}, 98%), and decanoic acid (C_{10}H_{20}O_{2} (DecA), 98%) were purchased from Sigma-Aldrich, The Netherlands. The CO₂ used for the measurements was supplied by Linde AG, The Netherlands, and has an ultrahigh purity of 99.995%. The molecular structures of the DES constituents are shown in Figure 1.

The DESs were prepared by weight using an analytical balance (Sartorius Extended ED224S) with 0.1 mg readability. The HBD (decanoic acid) and the HBA (quaternary ammonium salt) were added to a capped glass bottle. To obtain a homogeneous mixture, the constituents were thoroughly mixed using a vortex mixer (VWR) at room temperature before heating at 308 K in the thermostatic oil bath with a temperature controller (IKA ETS-D5) until a clear liquid was observed. The mixture is magnetically stirred during the heating. Subsequently, the formed DESs were cooled to room temperature and stored in a vacuum desiccator until use.

Table 1 presents the DESs prepared including their abbreviations, purity, molecular weights of the HBD, the HBAs, density at 298.15 K and the average molecular weights of the formed DESs. Experimental density data of the prepared DESs are reported in our previous work\textsuperscript{16} and the data of the newly prepared DES (DecA: N_{8888}^−\text{Cl} (1.5:1)) is given in Table S1 of the Supporting Information. The water content in the prepared DESs was measured with the Karl Fischer titration method (795 KFT Titrino Metrohm Karl Fischer) and was in all cases less than 1 wt \% see Table S1.

2.2. Carbon Dioxide Solubility Measurements. CO₂ solubilities in all systems were measured with a magnetic suspension balance (MSB, Rubotherm GmbH). The MSB and the experimental procedures have been described in detail in previous works\textsuperscript{17,18} The evacuation step prior to the start (to remove volatiles and water) of an absorption measurement and after the end of the absorption process (mainly to remove the absorbed CO₂) was performed at 308 K under reduced pressure. The CO₂ solubility isotherms were measured at 298.15, 308.15, and 323.15 K and in the pressure range from 0.1 to 2 MPa.

3. RESULTS AND DISCUSSION

The results of the CO₂ solubilities measured using the MSB at several temperatures and pressures up to 2 MPa are shown in
Figure 2. It can be observed that at higher pressures and lower temperatures higher CO₂ solubilities are obtained. In Figure 2A,B the results show that the effect of the halide anions chloride and bromide of the quaternary ammonium salts on the CO₂ solubility is negligible. The molar volumes of both DESs are virtually identical and therefore it can be expected that the available free volume to host solute molecules is not significantly different for these DESs. Nevertheless, with increasing alkyl chain length from methyltrioctyl- to tetraoctylammonium, the CO₂ solubility increases as was already observed in solubility measurements using ILs. Increasing the ratio of the quaternary ammonium salt (see Figure 2C) results in higher CO₂ solubilities as was expected from an earlier work. Because of the lack of theoretical insight concerning the exact interactions between CO₂ and the DESs and the assumption that only dispersion forces govern the interactions between the solvent and CO₂, we can relate this increase to the lower molar density of the 1.5:1 ratio, which indicates the availability of more space in the bulk of the liquid to host the CO₂ molecules than in the 2:1 ratio solvent.

The absorbed CO₂ by the DESs could be regenerated at 308.15 K under reduced pressure as shown in Figure 3. Moreover, the regenerated DESs have been repeatedly recycled for CO₂ absorption without the observed loss of sample mass or efficiency, demonstrating that the DESs are stable at the experimental conditions and that the CO₂ absorption process is reversible. A thorough study on the thermal behavior has been performed in our previous work.

In addition, ¹³C NMR spectra were taken of the prepared systems before and after CO₂ solubility measurements. Both spectra were compared and there is no change between the spectra before and after the CO₂ measurements (Figures S1–S16, Supporting Information). Herein, we can conclude that the prepared systems are stable under the experimental conditions and are recovered after CO₂ absorption measurements. Furthermore, no color change and no signs of corrosion were observed.

One of the additional topics we have investigated in this study is the change in the pH value of the water phase after being in contact with the prepared DESs. After mixing water (Milli-Q) either with the prepared systems or their constituents a decrease in pH was measured, see Table 1. The pH-dependence will not affect the CO₂ capture at precombustion conditions (very low H₂O concentration) and by no means under the water free environment of the CO₂ absorption measurements of the present work. However, this will have a more significant affect in the case of extracting chemicals from aqueous solutions. Therefore, we recommend taking this issue seriously into account when hydrophobic DESs are intended to be applied for other applications (e.g., metal ion extraction from aqueous solutions). This is more critical when proton donating constituents with high dissociation constants (e.g., acids) are involved. Consequently, dissociation of HBD will change the molar ratio of the DESs and regeneration of the original DES will be challenging. On the other hand, leaching of the HBA into the water phase will also alter the molar ratio of the DES. Since hydrophobicity of a compound is relative, we would recommend analysis of the water phase using proper techniques available such as total organic carbon (TOC), ion chromatography (IC), NMR, and pH measurements. This is necessary to evaluate the behavior of hydrophobic DES with water. We have applied the first three techniques in our previous works on the extraction of fatty acids from aqueous solutions using the same DESs reported here and extraction of metal ions with DESs. Therefore, as an extension of our former works, the pH of the water phase after being mixed with the investigated DESs has been measured.

### 3.1. Henry’s Law Constant

The Henry’s law constants can be obtained from the solubility data determined using the MSB to evaluate the solubility of a certain gaseous solute in a solvent. According to the Henry’s law the fraction of the gas dissolved in a liquid is proportional to its fugacity in the gas phase. The proportionality constant is Henry’s law constant:

\[
H_{x_2}(T, P) = \lim_{x_2 \to 0} \frac{\frac{\dot{f}_x(T_{eq}, P_{eq}, x_2)}{x_2}}{\frac{\dot{\phi}_2(T_{eq}, P_{eq})}{P_{eq}}}
\]

where \(H_{x_2}(T,P)\) is the Henry’s constant, \(x_2\) is the mole fraction of CO₂ dissolved in the DES, \(\dot{f}_x\) is the fugacity of CO₂ (component 2) in the gas phase, \(\dot{\phi}_2\) is its fugacity coefficient calculated using the Peng–Robinson equation of state (EoS) and \(P_{eq}\) is the CO₂ pressure at phase equilibrium. Assuming that DESs have a negligible vapor pressure at the experimental conditions, the fugacity of the gas in the CO₂ + DES system is assumed to be equal to that of pure CO₂. Henry’s law constants are determined from the slope of the solubility data (l’Hopital’s rule) at relatively low pressures (≤0.5 MPa), see Table 2.

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Table 2. Henry’s Law Constants ($H_{2,1}$) of CO$_2$ in the Prepared DESs and in DESs and ILs Reported in Literature at Different Temperatures

| solvent                      | $H_{2,1}$/MPa |
|------------------------------|---------------|
| DecA:$\text{N}_{8888}$−Br (2:1) | 7.15          |
| DecA:$\text{N}_{8888}$−Cl (2:1) | 7.18          |
| DecA:$\text{N}_{4444}$−Cl (2:1) | 7.55 ± 0.08   |
| DecA:$\text{N}_{8888}$−Br (2:1) | 6.17 ± 0.20   |
| DecA:$\text{N}_{8888}$−Br (1.5:1) | 6.26 ± 0.07   |
| urea:choline chloride (2:1)$^{12}$ | 5.90 ± 0.09   |
| [C$_{4}$mim][BF$_{4}$]−Cl (2:1)$^{18}$ | 14.46         |
| [C$_{4}$mim][BF$_{4}$]−Br (2:1) | 8.27          |
| [C$_{4}$mim][BF$_{4}$] (1.5:1) | 8.74 ± 0.04   |
| [C$_{4}$mim][BF$_{4}$] (2:1) | 7.18          |
| [C$_{4}$mim][BF$_{4}$] (1.5:1) | 8.42 ± 0.14   |
| [C$_{4}$mim][BF$_{4}$] (2:1) | 8.49 ± 0.16   |
| [C$_{4}$mim][Tf$_{2}$N]−Cl (2:1)$^{23}$ | 7.55          |
| selexol$^{24}$ | 3.3 ± 0.03    |
| heptane$^{25}$ | 5.0 ± 0.26    |
| benzene$^{25}$ | 15.1          |

Table 3. Partial Molar Enthalpy $\Delta_{sol}H$ and entropy $\Delta_{sol}S$ of Solution of CO$_2$ in the Investigated DESs at Fixed Composition and in a Selection of Well-Known Chemical and Physical Solvents

| solvent                      | $T_{intens}$/K | $\Delta_{sol}H$/kJ mol$^{-1}$ | $\Delta_{sol}S$/J mol$^{-1}$K$^{-1}$ |
|------------------------------|---------------|-------------------------------|---------------------------------|
| DecA:$\text{N}_{8888}$−Cl (2:1) ($x_{\text{CO}_2} = 0.1$) | 298 to 323 | $-11.6 \pm 0.3$ | $-37.3 \pm 0.9$ |
| DecA:$\text{N}_{8888}$−Br (2:1) ($x_{\text{CO}_2} = 0.1$) | 298 to 323 | $-10.5 \pm 0.5$ | $-33.9 \pm 1.5$ |
| DecA:$\text{N}_{8888}$−Cl (1.5:1) ($x_{\text{CO}_2} = 0.1$) | 298 to 323 | $-10.4 \pm 0.2$ | $-33.6 \pm 0.7$ |
| DecA:$\text{N}_{8888}$−Cl (2:1) ($x_{\text{CO}_2} = 0.1$) | 298 to 323 | $-10.3 \pm 0.3$ | $-33.9 \pm 0.9$ |
| benzene$^{25}$ | 298 | $-9.34$ | $-31.4$ |
| heptane$^{25}$ | 298 | $-9.67$ | $-32.4$ |
| ethanol$^{25}$ | 298 | $-12.8$ | $-42.9$ |
| selexol$^{24}$ | 294 to 357 | $-13.4 \pm 0.9$ | $-41.3 \pm 1.4$ |
| [C$_{4}$mim][Tf$_{2}$N]$^{23}$ | 283 to 323 | $-12.5 \pm 0.4$ | $-84.2$ |
| MEA (30 wt %, $x_{\text{CO}_2} = 0.1$)$^{27}$ | 313 | $-84.2$ | $-84.2$ |

Higher Henry’s coefficients correspond to lower solubilities. To the best of our knowledge, the hydrophobic DESs investigated in this work show the highest solubility of CO$_2$ as compared to any other DES reported in literature so far. In fact, they are even better than some fluorinated ILs. For instance DecA:$\text{N}_{8888}$−Cl (1.5:1) has a lower value of the Henry’s coefficient than [C$_{4}$mim][BF$_{4}$] at 323.15 K. Furthermore, incorporating [BF$_{4}$]$^-$ and [PF$_{6}$]$^-$ anions makes the ILs susceptible to hydrolysis, releasing highly corrosive hydrogen fluoride (HF), which is also a disadvantage of fluorine containing ILs.$^{21}$

3.2. Enthalpy and Entropy of Solvation. From the effect of temperature on the solubility, the partial molar enthalpy ($\Delta_{sol}H$) and the partial molar entropy ($\Delta_{sol}S$) of solution can be calculated using the Clausius–Clapeyron and the Clapeyron equation, respectively.$^{26}$ These parameters are calculated for systems where the CO$_2$ solubilities are measured at three different temperatures. $\Delta_{sol}H$ indicates the strength of the intermolecular interactions between the solvent and the solute and $\Delta_{sol}S$ provides information about the degree of ordering upon dissolution of the gas in the liquid medium. The changes in enthalpy and entropy are calculated from the solubility data at a fixed composition ($x_{\text{CO}_2}$)$^{26}$

$$\Delta_{sol}H = R \left( \frac{\partial \ln P}{\partial (\frac{1}{T})} \right)_{x_{\text{CO}_2}}$$

(2)

$$\Delta_{sol}S = \frac{\Delta_{sol}H}{T_{eq}} = -R \left( \frac{\partial \ln P}{\partial \ln T} \right)_{x_{\text{CO}_2}}$$

(3)

where $R$ is the universal gas constant, $T$ is the absolute temperature, $P$ is the CO$_2$ pressure at phase equilibrium, and $x_{\text{CO}_2}$ is the mole fraction of CO$_2$ in the liquid mixture at equilibrium. The solubility decreases with increasing temperature, resulting in an exothermal absorption process. The values, presented in Table 3, are in the range typically found for physical solvents and are much lower than those found in chemically active solvents (e.g., monoethanolamine, MEA). The enthalpy and entropy of solution are similar to those of the nonpolar solvents (e.g., benzene and heptane) where the molecular interactions are limited to dispersion forces. The high solubilities in combination with weak molecular interactions increase the solvent efficiency. Further studies are necessary to investigate the nature of interactions within the DESs and their interactions with CO$_2$.

Heat of solution is an important parameter in determining the total heat load and thus the amount of energy necessary to regenerate the solvent and also in deciding which configuration fits the absorption/desorption process the best, that is, pressure swing or temperature swing or a combination of the two. The latter saves compression and heating expenditures.

4. CONCLUSIONS

CO$_2$ solubilities in various hydrophobic DESs have been measured for the first time. The effect of the halide anion in the quaternary ammonium salts (HBA) is not significant. The CO$_2$
solubilities increase by increasing the alkyl chain length and by lowering the ratio of HBD to HBA. The molar ratio of the HBD and the HBA is, unlike the ratio of cations and anions in ILs, not necessarily 1:1. The performance of DecA:N8888−Cl (1.5:1) is better than [Cmim][BF4], which is a good perspective for improving solvent performances without the need of complex synthesis and the subsequent purification steps. The solubility trends and the enthalpies and entropies of solvation indicate the physical nature of the absorption process. Moreover, the enthalpies and entropies of CO2 absorption are similar to those of the nonpolar solvents heptane and benzene, indicating that the molecular interactions are governed by dispersion forces. The hydrophobic DESs studied show good solvation properties and can be considered as promising candidates for CO2 capture.

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**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.7b00534.

Experimental density data of the DESs, CO2 solubilities in the prepared DESs, 13C NMR spectra of the DESs before and after CO2 solubility measurements (PDF)

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The authors declare no competing financial interest.

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