ARCHIVIO ISTITUZIONALE
DELLA RICERCA

Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

Physical absorption of CO2 in betaine/carboxylic acid-based Natural Deep Eutectic Solvents

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:
Gabriella Siani, M.T. (2020). Physical absorption of CO2 in betaine/carboxylic acid-based Natural Deep Eutectic Solvents. JOURNAL OF MOLECULAR LIQUIDS, 315, 1-7 [10.1016/j.molliq.2020.113708].

Availability:
This version is available at: https://hdl.handle.net/11585/767506 since: 2020-11-10

Published:
DOI: http://doi.org/10.1016/j.molliq.2020.113708

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (https://cris.unibo.it/).
When citing, please refer to the published version.

(Article begins on next page)

16 September 2026

This manuscript is the faithful reproduction of the one published in the Journal of Molecular Liquid in post-print version (G. Siani, M. Tiecco, P. Di Profio, S. Guernelli, A. Fontana, M. Ciulla, V. Canale, Physical absorption of CO_2 in betaine/carboxylic acid-based Natural Deep Eutectic Solvents, J. Mol. Liq. 315, 2020, 113708)

Physical absorption of CO_2 in betaine/carboxylic acid-based Natural Deep Eutectic Solvents

Gabriella Siani,[a] Matteo Tiecco,[b] Pietro Di Profio,[a] Susanna Guernelli,[c] Antonella Fontana,[a] Michele Ciulla[a] and Valentino Canale[a]*

[a] Dipartimento di Farmacia, Università "G. d'Annunzio", via dei Vestini n° 31, 66013 Chieti, Italia. E-mail: siani@unich.it

[b] Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto n° 8, 06123 Perugia, Italia.

[c] Dipartimento di Chimica "Giacomo Ciamician", Università degli Studi di Bologna, Via S. Giacomo n° 11, 40126 Bologna, Italia

ABSTRACT: The ability of some zwitterionic natural deep eutectic solvents (NADESs) based on N,N,N-trimethylglycine (TMG) and carboxylic acids (oxalic, glycolic and phenylacetic) to act as environmentally friendly solvents for CO_2 capture has been investigated. The solubility of CO_2 in the NADESs was measured gravimetrically at different temperatures in the range 298.15 - 333.15 K, and at different pressures in the range 0.1 - 4 MPa. The effect of the adopted experimental conditions has been discussed. The highest uptake has been observed for phenylacetic acid/TMG DES at 313.15 K and 4 MPa (45.5 mg CO_2/g DES). The efficiency of this NADES as CO_2 sorbent when reused in subsequent capture cycles has been evaluated. This work might open new perspectives in developing the most appropriate combination of HBA and HBD components of the DESs and the most appropriate operative conditions for an environmentally friendly CO_2 capture.

Keywords: Natural Deep Eutectic Solvents; CO_2 capture; green chemistry

1. Introduction

Global warming and the consequent adverse effects on the ecosystem represent one of the most crucial challenges of the 21st century for scientists. Humans are primarily responsible for global warming [1-4]. The first indication of an anthropogenic greenhouse effect was given in 1986 by Svante Arrhenius, who was the first to quantify the relationship between the increase in CO_2 concentration in the atmosphere and the Earth surface temperature, suggesting that a doubling of CO_2 concentration would lead to a 4-6°C temperature rise [5].

The exaggerated anthropogenic production has led to an accumulation of CO_2 in the atmosphere with a consequent increase in the amount of the heat retained by the planet and in global average temperatures [6].

Many efforts have been made to identify and implement various strategies to reduce CO_2 emissions [7]. Among the various developed CO_2 capture technologies already in use either in laboratory or on an industrial scale, the chemical absorption using a liquid sorbent has been proposed as the most promising option to reduce CO_2 emission [8].

This technique is based on the ability of a sorbent to react with CO_2 forming a compound characterized by weak bonds which will subsequently be degraded through heat or depressurization, regenerating the original sorbent and obtaining a CO_2 flow at the outlet. Aqueous alkanolamines are used as typical sorbents, due to their high affinity for CO_2 through carbamate/carbonate formation, with the following efficiency trend: monoethanolamine (efficiency over 90%) > diethanolamine > diisopropanolamine > methyldiethanolamine [9].

The use of alkanolamines as liquid sorbents, however, has some disadvantages such as the volatility, the corrosiveness and the thermal degradation to which they undergo at 100 – 150 °C so that the amine regeneration cannot be operated at optimal high values of temperatures and pressure, with consequent high energy consumption and cost increase [10]. Moreover, the amine degradation leads

to a considerable loss of active amine and to the generation of compounds which are potentially toxic for humans and harmful for the environment [11].

To overcome these problems, alternative methods for carbon capture have been explored. Due to their peculiar characteristics, such as wide liquid range, thermal stability, low vapour pressure, non-flammability and good solvating ability for a wide range of solutes, some ionic liquids (ILs), which are molten salts consisting of an organic cation and a polyatomic anion with asymmetric structures and delocalized charges, have attracted considerable interest as CO_2 sorbents[12]. The main advantage of using ionic liquids as sorbents is that there is no loss of the capture agent into the gas stream during the CO_2 capture process, thanks to their negligible vapor pressure. Moreover, ILs can be easily regenerated by heating or bubbling nitrogen through the solution. Many studies have revealed a high CO_2 solubility in ionic liquids, especially alkylimidazolium-based ILs [13]. In the capture process, conventional ILs act as physical solvents with CO_2 solubility depending on several factors, such as free volume available to host CO_2, strength of the interactions between the IL components, type of the constituent anion and cation [14, 15]. A more efficient CO_2 capture has been obtained through a chemical absorption by using a task-specific ionic liquid (TSILs) in which the constituent ions have been functionalized with amine moiety [16-19].

However, despite the fact that ILs have been often considered green solvents, many ionic liquids, especially those with lipophilic cations, have proven to be toxic since they are capable of destroying cell membranes due to the insertion of IL cations among the membrane phospholipids [20]. Moreover, they are poorly biodegradable and water-soluble ionic liquids tend to accumulate in the aqueous environment, manifesting a certain toxicity towards various aquatic organisms [21]. Finally, their synthesis, that requires large amounts of salts and solvents, is really far from being environmentally friendly and the high cost of production and purification renders this method commercially unviable.

Deep Eutectic Solvents (DESs) share with ILs many physicochemical characteristics (thermal stability, low vapour pressure, non-flammability) and, similar to ILs, their properties can be tuned

simply by changing the nature or the ratio of the DES constituents. Unlike ILs, the synthesis of DESs is very simple, it does not require the use of solvents and simply requires mixing the starting materials, a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), in the correct ratio to form eutectics that are liquid at ambient temperatures [22]. Additionally, most of the DES components are nontoxic [23], biodegradable [24] and inexpensive. For these reasons, DESs are considered a valid, truly "green" alternative, not only to conventional organic solvents but also to ionic liquids, overcoming the poor environmental benignity that some of ILs have shown.

DESs have been successfully used as solvents in many organic reactions [25-30] and, recently, they have been proposed as liquid sorbents for gas absorption [31-34].

Nowadays, special DESs made from natural metabolites such as organic acids, amino acids and sugars and commonly referred to as Natural Deep Eutectic Solvents (NADESs), have aroused particular interest from researchers especially in the field of green chemistry [35]. Considering that these components are natural occurring these solvents can be considered completely safe and environmentally friendly. In the present work, we have investigated the CO_2-capture potential of some zwitterionic Natural Deep Eutectic Solvents (NADESs) based on N,N,N-trimethylglycine (TMG), a natural metabolite from choline and constituent of many foods [36], and some carboxylic acids, (oxalic, glycolic and phenylacetic acid, which are common constituents of plants [37]), as the HBA and HBD components, respectively.

The amount of CO_2 absorbed by the NADESs was determined gravimetrically and the effect of different operating conditions (pressure, temperature, exposure time) on the process was assessed. The NADES in which the best CO_2 uptake was observed, was then subjected to subsequent CO_2 absorption cycles to evaluate whether it retains its effectiveness after use and regeneration.

2. Experimental

2.1 Chemicals and materials

Trimethylglycine (TMG), oxalic acid dihydrate, glycolic acid and phenylacetic acid were purchased from Sigma-Aldrich. TMG was dried under vacuum over silica gel and P_2O_5 prior to use. Carboxylic acids were crystallized (if necessary) and dried under vacuum at 60 °C over P_2O_5 for one day before use.

CO_2 was SS-grade (99.8% CO_2) from SOL S.p.A. (Italy).

2.2 Synthesis of NADESs

The NADESs used in this work, are shown in Figure 1. They have been synthetized in the molar ratio HBA:HBD 1:2, following a procedure reported in the literature. [38]

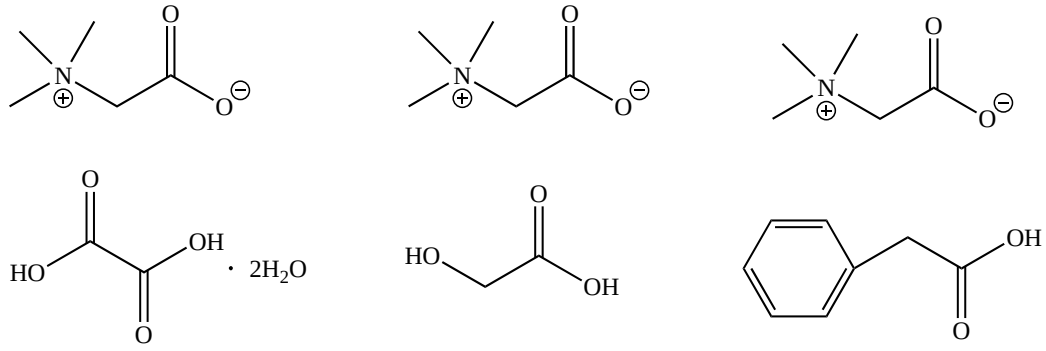

Figure 1. Structures of the components of the selected NADESs

TMG and the carboxylic acid were directly weighed in a flask fitted with a stopper. The solid mixture was stirred and heated at 90 °C until a colourless liquid was formed, typically in 20–30 minutes.

2.3 Determination of CO_2 capture

The solubility of CO_2 in the NADESs was measured gravimetrically at different temperatures (range: 298.15 - 333.15 K) and pressures (range: 0.1 - 4 MPa). Approximately 2 g of NADES were used for each experiment. Before each determination, the NADES was heated to 343.15 K for 1 hour under stirring (100 rpm) and under vacuum to remove any traces of moisture.

Experiments were conducted in a pressure-resistant (up to 10 MPa) AISI 316L stainless steel reactor having an internal volume of 250 ml. The reactor was equipped with a Swagelok Quick fit inlet for gases, and a pressure gauge.

The vial containing the sample was weighed and then introduced into the reactor chamber. The reactor was then connected to the cylinder containing CO_2 from which the gas was introduced into the reactor at the desired pressure. The reactor was heated indirectly via a thermal chamber with flowing water maintaining a constant stable temperature. During gas loading the sample was agitated continuously.

After introduction of the gas, a measurements were conducted after one hour. The vial containing the sample was then removed from the reactor, transferred to a small thermostated bath of Vaseline oil in order to maintain the temperature at the desired value, and weighed again.

For high weighing precision, a Mettler Toledo AG265 Analytical Balance with Fully Automatic Calibration Technology (FACT) was used, resulting in a typical weighing uncertainty of less than 0.005%.

No change in the physical appearance and colour of the NADES samples were observed after the experiment.

To evaluate the effect of the exposure time to CO_2 on the ability of NADES to act as sorbent, in some cases experiments were carried out allowing the CO_2/NADES system to equilibrate for 2 h. Finally, three absorption / desorption cycles have been carried out to evaluate the possibility of recycling the

solvent. The CO_2 desorption has been executed obtained by heating the sample at 343.15 K for 1 hour under vacuum and with a constant stirring rate of 100 rpm.

2.4 FTIR measurements

The IR spectra were recorded on a Varian Scimitar 1000 FT-IR spectrometer (Varian Inc., Palo Alto, California) by placing a thin film of the sample on a KBr tablet. All spectra were collected at 2 cm^{-1} resolution in the range of 4000−400 cm^{-1}. The obtained FTIR spectra were corrected for background spectra using pure NADES loaded-KBr tablet registered at the same parameter setup and were processed using Varian Resolutions software version 4.0.5.009 (Varian Inc., Palo Alto, California).

3. Results and discussion

3.1 Effect of temperature and pressure on CO_2 capture

The ability of the NADESs to absorb CO_2 has been tested, gravimetrically, at three different temperatures and, for each selected temperature, at three different pressure values. Only in the NADES **3**, which has proven to be the most effective sorbent for CO_2, experiments were carried out even at P = 2.5 MPa.

The experimental results are collected in Table 1 as a function of temperature and pressure. The amount of absorbed CO_2 (1 hour after initial exposure to the gas) has been expressed in terms of mg absorbed CO_2/ g NADES. As the three NADESs have different molecular weight, the amount of absorbed CO_2 has been also reported in brackets as percentage of the ratio between the number of moles of absorbed CO_2 (n_{CO2}) and the number of moles of the sorbent (n_{NADES}), for the sake of comparison.

Data in Table 1 clearly show that NADES **1** is the solvent with the lowest absorption capacity while NADES **3** proves to be the best CO_2 sorbent among the three tested NADESs.

Since the HBA component in the studied NADESs is the same, the different observed behaviour is assigned to the different characteristics of the HBD component. In our particular case, the HBD components are all carboxylic acids and therefore the acidic nature of the DESs is obviously due to the presence of the carboxylic functional group.

Table 1. mg of CO_2 absorbed per g of NADES at different temperatures and pressures. Measurements were carried out after a 1-hour interval following introduction of the gas. The percentages of the ratio n_{CO2}/n_{NADES} are reported in brackets

T (K)	mg absorbed CO_2/g NADES ($\% n_{CO2}/n_{NADES}$)									
	0.1 MPa			1 MPa			2.5 MPa	4 MPa		
	1	**2**	**3**	**1**	**2**	**3**	**3**	**1**	**2**	**3**
298.15	0 (0)	0.85 ±0.06 (0.6)	1.15±0.07 (1.1)	0.48±0.03 (0.3)	7.64±0.31 (4.7)	9.92±0.43 (8.8)	13.6±0.5 (12.0)	0.24±0.03 (0.1)	9.15±0.55 (5.5)	14.5±0.5 (12.8)
313.15	0.35±0.02 (0.2)	0.54±0.04 (0.3)	1.18±0.07 (1.1)	0.45±0.03 (0.3)	2.91±0.18 (1.8)	13.1±0.5 (11.8)	21.6±0.9 (19.1)	0.52±0.04 (0.3)	2.84±0.19 (1.7)	38.1±1.2 (33.7)
333.15	0.32±0.02 (0.2)	0.24±0.03 (0.1)	1.15±0.07 (1.1)	0.18±0.03 (0.1)	3.10±0.15 (1.8)	12.3±0.6 (10.9)	20.5±0.8 (18.1)	1.72±0.11 (1.1)	1.68±0.11 (1.0)	32.0 ±1.1 (28.3)

It is known that the solubility of CO_2 in DESs is influenced by the pH value, with the CO_2 showing a greater affinity towards basic solvent rather than acidic ones [39]. Taysun et al. have measured the pH of three DESs containing benzyl triethylammonium chloride as HBA and *p*-toluene sulfonic acid (PTSA), oxalic acid (OX) and citric acid (CA) as HBD [40]. They found pH values of −1.5, −0.8 and 1 for the three DESs, respectively. As the pK_a values of the acids follow the same trend (PTSA is the strongest acid followed by OX and CA), pK_a can be considered representative of the acidity of the medium. In a recent paper it was shown that small differences in the pK_a values of the components of the DESs do not linearly correlate with the acidic properties of the resulting liquids [41]. However,

in the current NADESs, the carboxylic acids used as HBD components are: oxalic acid (pK_a = 1.46), glycolic acid (pK_a = 3.6) and phenylacetic acid (pK_a = 4.31); their differences in the pK_a values are large, so their acidic behaviours are different. Indeed, the solubility of CO_2 follows the different acidity of the HBD components: the lower pK_a value of oxalic acid corresponds to the lower solubility of CO_2; the higher pK_a value of the phenylacetic acid corresponds to the higher CO_2 uptake. This result agrees with that reported by Mirza et al. who showed that CO_2 solubility decreases in the order: ethaline (HBD = ethylene glycol; pK_a = 14.22) > reline (HBD = urea; pK_a = 13.82) > malinine (HBD = malic acid; pK_a = 3.40) [42].

NADESs used in the present work are conventional DES, i.e. they do not have functional groups that can chemically react with CO_2, such as for example, amino groups. Therefore, they can interact with CO_2 only as physical solvents through weak forces (electrostatic interactions and/or dispersion interactions), without a chemical reaction taking place. In general, carbonyl groups are CO_2-philes thanks to the interaction between the Lewis-basic carbonyl oxygen and the Lewis-acidic central carbon of CO_2 as well as the possibility of forming a hydrogen bond between the -OH group of the carboxylic acid and one of the electronegative oxygen atoms of CO_2 [43, 44]. However, in the case of dicarboxylic oxalic acid and of glycolic acid, the presence of the extra carbonyl group and of the alcoholic group, respectively, allows the formation of a complex and strong intra- and inter-molecular H bond network between acids which results in a lower CO_2 physisorption. Self-association of oxalic acid in choline chloride/ oxalic acid DES has been observed by Gilmore et. al. in a neutron scattering study [45]. Moreover, in NADES **1** the structural water molecules contribute to the H-bonding network and compete with CO_2 molecules for the same interaction sites further reducing CO_2 absorption.

Regarding the role of the HBA component of the NADES in the absorption of CO_2, HBA could act as a basic site for CO_2 so that the CO_2 uptake could be obtained through the formation of a Lewis acid–base complex between HBA and CO_2, in analogy to what has been demonstrated for the anionic

component of ionic liquids. Several studies have shown that the solubility of CO_2 in ionic liquids is more influenced by the nature of the anion rather than that of the cation [13, 46-48]. However, the ability of the anion to interact with CO_2 depends not only on its basicity but also on the strength of the anion-cation interactions. Weak anion-cation interactions would contribute to high CO_2 absorption capacity, while strong interactions would quench the ability of the anion to interact with CO_2 thus reducing the CO_2 uptake [49]. Different association constants between the two constituents of some NADESs have been observed [50]. Recently, Shukla et al. have compared the CO_2 uptake in two DES both having ethylenediamine (EDA) as HBD and 1-methylimidazolium chloride (HMIM·Cl) or monoethanolammonium chloride (MEA·Cl) as HBA. They found lower CO_2 absorption in [HMIM·Cl] [EDA] than in [MEA·Cl] [EDA] and interpreted this result in terms of stronger H-bonding interactions in the former DES rather than in the latter [39].

In the current selection of NADESs the strength of the H-bond can be correlated to the pK_a values of the carboxylic acids used as HBDs as it was also observed in Walden plot determination for these liquids [38]. Indeed, a lower pK_a value corresponds to a higher partial positive charge density on the -OH oxygen of the carboxylic acid and, consequently, to a larger dipolar contribution to the H-bond. This makes the H-bond stronger, especially when the HBA has a formal negative charge [51], as in the case of TMG. On this basis, the strength of the H-bonding interaction between HBA and HBD in the present NADESs increases in the order: phenylacetic acid < glycolic acid < oxalic acid, which is the reverse order of effectiveness of NADESs as CO_2 sorbents.

It is interesting to note that NADES **3**, which has shown the greatest CO_2 uptake, is the only one in which the carboxylic acid used as HBD has an aromatic ring. It has been demonstrated that the π–π interactions between aromatic and non-aromatic monomers may be stronger than that between two aromatic molecules [52, 53] and several authors have highlighted that the non-covalent stacking interaction between CO_2 and a phenyl group, leading to a site-selective solvation of CO_2 around the aromatic ring, significantly contributes to the absorption of CO_2 [43, 54]. As NADES **1** and **2**, in

which only electrostatic interactions such as hydrogen bonding can contribute to the physical absorption of CO_2, turned out to be less efficient as CO_2 sorbents than NADES **3**, it can be suggested that π–π interactions play a dominant role so that NADESs with π delocalized systems could be considered the best candidates for CO_2 physisorption.

Beside solute-solvent interactions, a free volume mechanism for the dissolution of CO_2, both in ionic liquids [48] and in DESs [55, 56], has been proposed according to which the CO_2 molecules are hosted into the available void space between the solvent components.

For ionic liquids, molecular dynamic simulation and quantum chemical calculation [57, 58] have suggested that empty vacancies, or holes, lie in the interionic space between cation and anion. In analogy, it can be supposed that, in DES, they lie in the space between the HBA and the HBD components so that weak HBA−HBD interaction, as in NADES **3**, favour the CO_2 uptake.

Indeed, free volume is inversely related to fluid density [59, 60], i.e. a lower density corresponds to a larger free volume and, consequently, more space in the bulk of the liquid is available to host the CO_2 molecules [55, 56]. For the current NADESs, density follows the trend: NADES **1**> NADES **2** > NADES **3** [38] which can justify the observed different CO_2 solubility, according to the free volume mechanism.

Cardellini et al. have also determined the energies for activation of the viscous flow, E_η, for the current NADESs and values of 34.2 KJ/mol, 42.6 KJ/mol and 41.6 KJ/mol have been calculated for NADES **1**, NADES **2** and NADES **3**, respectively [38]. E_η values inversely correlate with the radius of the vacancies in the liquid: high values indicate that molecules move with difficulty, due to the small dimensions of the vacancies [61, 62]. Even if a linear correlation between the viscosity-based calculated E_η and the ability of NADESs to act as CO_2 sorbent cannot be found, it appears, however, that vacancy size should be as well considered because small vacancies may promote CO_2 embedding when specific interactions, such as π–π interactions, are effective.

In NADES **3**, the amount of the absorbed CO_2 is rather poor at the lowest value of the operating pressure, while the efficiency of NADES as sorbent increases as the operating pressure increases, for each constant temperature.

This result is not surprising and validates what has been reported in several previous studies. For example, Li et al. have determined the solubility of CO_2 in choline chloride – urea DES at 313.15, 323,15 and 333,15 K and pressures up to 13 MPa, showing that the solubility increases as pressure increases, at constant temperature [63]. The same trend had been reported a few years later by Leron et al. with a larger range of temperature (from 303.15K to 343.15 K in 10 K intervals) [64].

Considering the amount of absorbed CO_2 as a function of temperature, at constant pressure, it is evident that the increase in temperature has no influence on the absorbing capacity of the NADES at the lowest pressure value (P = 0.1 MPa) while, for each considered pressure ≥ 1 MPa, an increase in temperature from 298.15 to 313.15 K, corresponds to an increase in the amount of absorbed CO_2 (1.3 times at P = 1 MPa; 1.6 times at P = 2.5 MPa; 2.6 times at P = 4 MPa). This result may seem in conflict with those obtained in the previous cited studies, which have shown, as a typical trend in DESs, a decrease in the solubility of CO_2 with increasing temperature, at all pressure values. However, it should be noted that the NADES is highly viscous at 298.15 K and the viscosity represents an important obstacle to the mass transfer of the gas into the solvent. Indeed, on increasing the temperature from 298.15 to 313.15 K, the viscosity of NADES decreases [38] allowing the capture of greater amounts of CO_2. A further increase in temperature up to 333.15 K leads, as expected, to a decrease in the absorption capacity of the NADES because of the weakening of the forces that restrain the gas into the liquids.

For T = 313.15 K and 333.15 K a direct proportionality between the mg of absorbed CO_2 and pressure values exists (Figure 2).

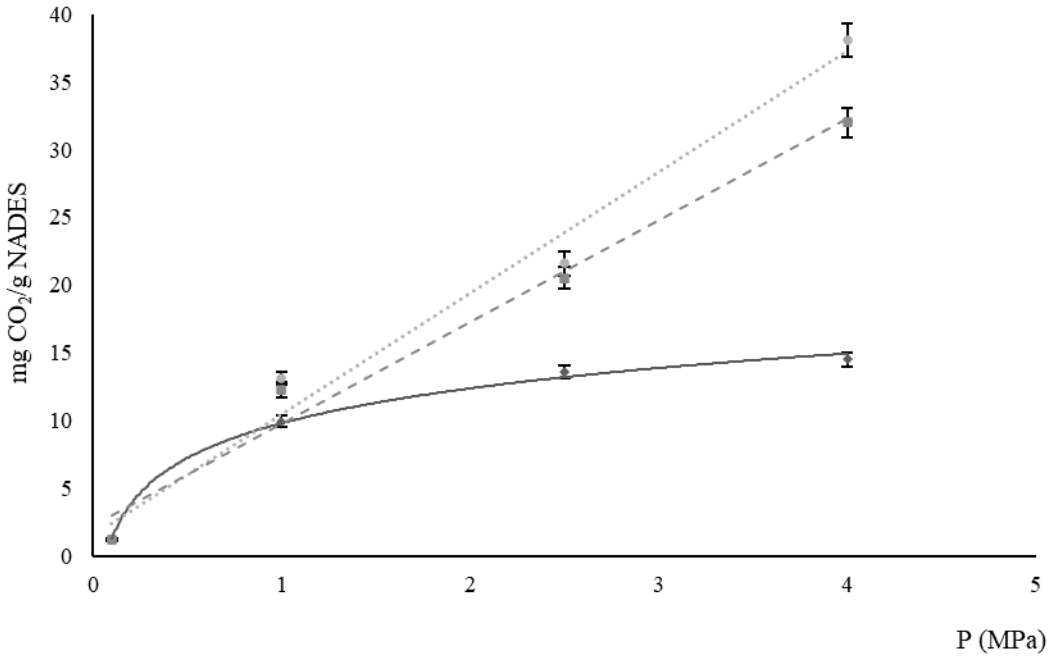

Figure 2. CO_2 solubility as a function of pressure in NADES **3** (TMG-phenylacetic acid 1 : 2) at 298.15 K (♦), 313.15 K (● R^2 = 0.98), and 329 K (■ R^2 = 0.98).

At T = 298.15 K, a linear trend is not observed: initially the solubility increases with increasing pressure until a plateau is reached at P = 2.5 MPa. This behaviour could confirm the free volume mechanism of CO_2 absorption. In fact, when the pressure increases the free volume available to host the CO_2 molecules decreases until, at a certain pressure value, further CO_2 molecules do not find space available to be accommodated. The plateau was not reached at higher temperatures because the NADES density decreases proportionally to the increase in temperature [38] so it is presumed that higher operating pressures have to be applied to reduce the vacancies in the fluid and reach the plateau, at these temperature values.

3.2 Effect of exposure time on CO_2 capture

To evaluate whether the ability of the NADES to absorb CO_2 may also depend on the exposure time of the sorbent to the gas, experiments were performed keeping the system NADES/CO_2 inside the reactor, at the desired pressure (P ≥ 1MPa) and at constant stirring, for two hours, at 313.15 and 333.15 K. The results of gravimetric determinations are reported in Table 2. The comparison of the data in Table 2 with those reported in Table 1 shows that the absorption capacity of the NADES increases with increasing exposure time, at T = 313.15 K while no differences are evident for the absorption at 333.15 K. We can therefore conclude that at lower operating temperatures a longer equilibrium time is required for the system. .

Table 2. mg of CO_2 absorbed per g of NADES **3** at different temperatures and pressures. Measurements performed at a two-hour interval after introduction of gas

T (K)	**mg absorbed CO_2/g NADES**		
	0.1 MPa	**1 MPa**	**4 MPa**
313.15	15.9±0.7	28.3±0.7	45.5±1.7
333.15	12.0±0.4	20.5±0.6	33.7±1.1

3.3 FTIR measurements

FTIR spectroscopy is a useful qualitative technique to assess the absorption of CO_2 by a solvent. For example, by means of FTIR spectroscopy, Gurkan et al. have been able to distinguish between the

physical dissolved and the chemically reacted CO_2 into the phosphonium- based amino acid ionic liquid, trihexyl(tetradecyl)phosphonium methioninate ([P66614][Met]) [65]. In fact, the physically absorbed CO_2 can be easily detected by the appearance of the band due to the asymmetric stretching of CO_2 between 2370 and 2310 cm^{-1} and to the active bending at around 670 cm^{-1} [65, 66]. In our work, we used FTIR spectroscopy to provide further information about the interactions between CO_2 and NADES **3**. The spectra have been collected before and after a 2 hours-exposure of the NADES to CO_2 at 313.15 K and 4 MPa and are reported in Figure 3.

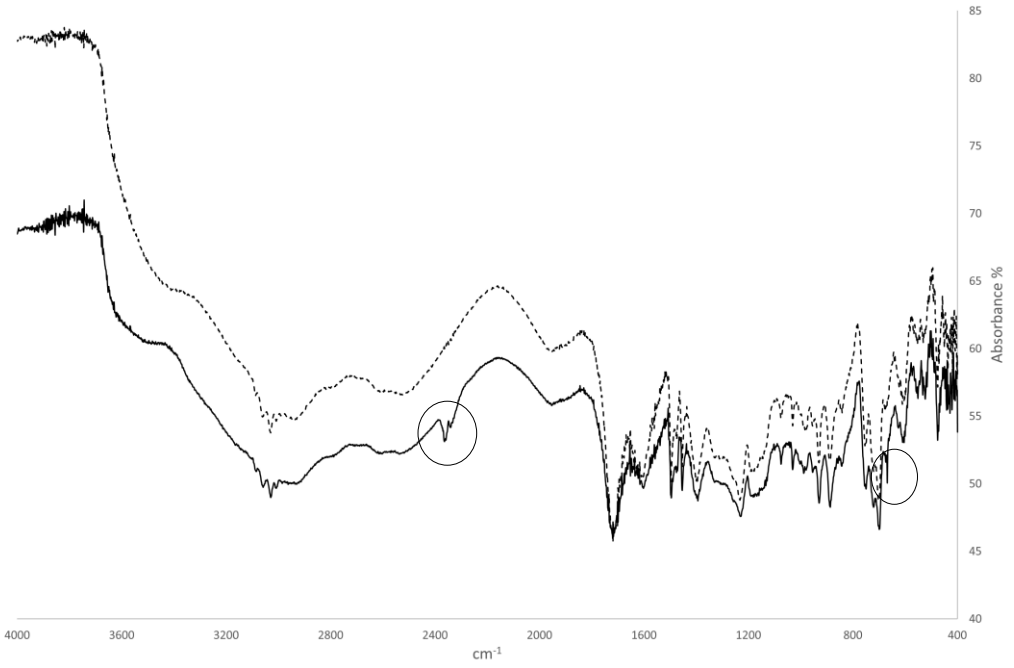

Figure 3. FTIR spectra of NADES **3** before (dashed line) and after exposure to CO_2 (full line). The circles highlight the bands at 2350 cm^{-1} and at 668 cm^{-1} that confirm the physical absorption of CO_2.

As expected, there is no evidence of chemical interaction between the components of the NADES and CO_2 while the physical absorption of the gas is proven by the appearance, in the spectrum recorded after the exposure of NADES to the gas, of the CO_2 asymmetric stretching band at 2350 cm^{-1} and of the band at 668 cm^{-1} due to the active bending of the CO_2 molecule. The band at 668 cm^{-1} is very weak because the groups of the NADES components strongly absorb in the same region.

3.4 Recyclability of NADES

The possibility of a low-energy required purification of the sorbent as well as its recycling are fundamental in the economics of the CO_2 capture process. Beside the disadvantage of physisorption, compared to chemisorption, of a lower quantity of absorbed CO_2, physical sorbents have the advantage of being easily purified in a non-destructive manner, generally by heating. We recycled the process of CO_2 uptake by repeating sorption/desorption cycles three times and the desorption has been obtained simply by heating the sample at 343.15 K under vacuum and stirring for 1 hour. The absorption cycles were performed at 313.15 K and 4 MPa and gravimetric measurements were carried out at 2 hours of exposure to the gas. The obtained results (2nd cycle: 43.3±1.2 mg absorbed CO_2/g NADES; 3rd cycle: 37.5±1.5 mg absorbed CO_2/g NADES) show a slight loss of the absorption capacity for subsequent cycles (Fig.4).

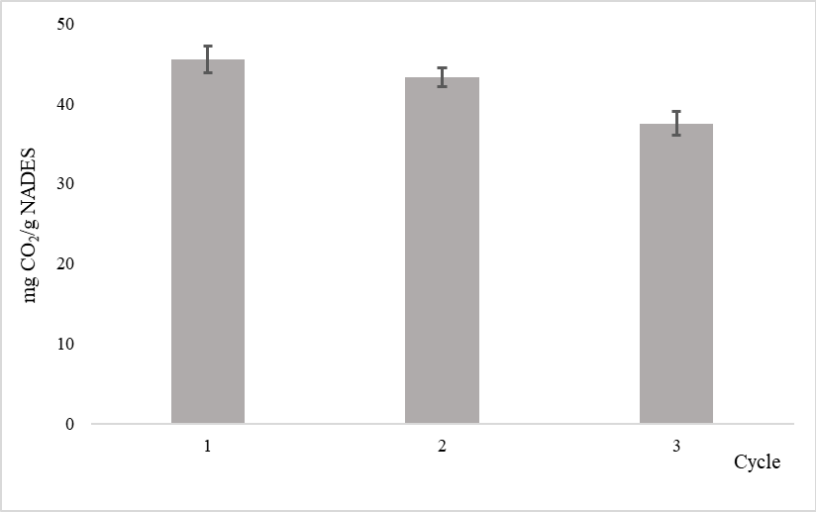

Figure 4. mg of CO_2 absorbed per g of NADES **3** in three subsequent absorption/desorption cycles.

4. Conclusions

The properties of three carboxylic acid-based NADESs as environmentally friendly solvents for the CO_2 capture have been evaluated. The highest uptake has been obtained when phenylacetic acid is

used as the HBD component while glycolic acid- and oxalic acid-based NADESs showed slight CO_2 absorption. The suggested physisorption process, confirmed by FTIR measurements, turned out to be dependent on several factors such as the acidity of the HBD component, the strength of the interactions between HBA and HBD, the presence of water molecules and the molecular structure of the carboxylic acid. Indeed, the π-π interactions between the aromatic ring of the phenylacetic acid and CO_2 seem to play a fundamental role in the ability of the NADES to absorb the gas. It is noteworthy that the CO_2 absorption capacity is inversely related to the density of NADES and this result suggests the involvement of the free volume mechanism in which the CO_2 molecules are accommodated into the intermolecular spaces between the NADES components. The occurrence of the free volume mechanism is also supported by the fact that an absorption plateau is reached at the highest pressure values, at a fixed temperature.

The amount of absorbed CO_2 increases with increasing gas pressure and exposure time, with the maximum absorption occurring at P = 4 MPa, T = 313,15 K and t =2 h, for NADES **3**. Finally, it has been demonstrated that NADES is still able to absorb CO_2 after three absorption/desorption cycles even if its efficiency slightly decreases. This study provides a valuable insight for the design of the optimal NADES to act as physical sorbent for the capture of CO_2.

Notes

There are no conflicts of interest to declare.

References

[1] D. Rapp, Anthropogenic Influences on Climate Change. In: Assessing Climate Change, Springer Praxis Books. Springer, Cham (2014) 533-595.

[2] P. P. Reddy, Causes of Climate Change In: Climate Resilient Agriculture for Ensuring Food Security; Springer India: New Delhi, (2015) 17−26.

[3] B. Metz and Intergovernmental Panel on Climate Change. Working Group III., IPCC special report on carbon dioxide capture and storage, Cambridge University Press, for the Intergovernmental Panel on Climate Change, Cambridge (2005).

[4] M. R. Raupach, G. Marland, P. Ciais, C. Le Quere, J. G. Canadell, G. Klepper and C. B. Field, Proc. Natl. Acad. Sci. U. S. A., 104 (2007) 10288–10293.

[5] S. Arrhenius, On the Influence of Carbon Acid in the Air upon the Temperature of the Ground, Philosophical Magazine and Journal of Science Series 5, 41 (1896) 237-276.

[6] NOAA Global Monitoring Laboratory, Trends in Atmospheric Carbon Dioxide https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html Last updated: April 6, 2020.

[7] D.Y.C. Leung, G. Caramanna, M. M. Maroto-Valer, An overview of current status of carbon dioxide capture and storage technologies, Renew. Sust. Energ. Rev. 39 (2014) 426–443.

[8] I. P. Koronaki, L. Prentza, V. Papaefthimiou, Modeling of CO_2 capture via chemical absorption processes − An extensive literature review, Renew. Sust. Energ. Rev. 50 (2015) 547-566.

[9] A. Veawab, A. Aroomwilas, P. Tontiwachwuthiku, CO_2 absorption performance of aqueous alkanolamines in packed columns, Fuel Chem. Div. P Repr. 47 (2002) 49-50.

[10] G. T. Rochelle, Thermal degradation of amines for CO_2 capture, Curr. Opin. Chem. Eng., 1 (2012) 183–190.

[11] S.B. Fredriksen, K.-J. Jens, Oxidative degradation of aqueous amine solutions of MEA, AMP, MDEA, Pz: a review, Energy Procedia 37 (2013) 1770–1777.

[12] S. Zeng, X. Zhang, L. Bai, X. Zhang, H. Wang, Ji. Wang, D. Bao, M. Li, X. Liu, S. Zhang, Ionic-Liquid-Based CO_2 Capture Systems: Structure, Interaction and Process, Chem. Rev. 117 (2017) 9625−9673.

[13] C. Cadena, J. L. Anthony, J. K. Shah, T. I. Morrow, J. F. Brennecke, E. J. Maginn, Why is CO_2 so soluble in imidazolium-based ionic liquids?, J. Am. Chem. Soc. 126 (2004) 5300-5308.

[14] E. I. Izgorodina, J. L. Hodgson, D. C. Weis, S. J. Pas, D. R. MacFarlane, Physical Absorption of CO_2 in Protic and Aprotic Ionic Liquids: An Interaction Perspective, J. Phys. Chem. B 119 (2015) 11748−1175.

[15] J. Palomar, M. Gonzalez-Miquel, A. Polo, F. Rodriguez, Understanding the Physical Absorption of CO_2 in Ionic Liquids Using the COSMO-RS, 50 Method Ind. Eng. Chem. Res. (2011) 3452–3463.

[16] E. D. Bates, R. D. Mayton, I. Ntai, J. H. Davis, Jr., CO_2 Capture by a Task-Specific Ionic Liquid J. Am. Chem. Soc. 124 (2002) 926-927.

[17] Y. S. Sistla, A. Khanna, CO_2 absorption studies in amino acid-anion based ionic liquids, Chem. Eng. J. 273 (2015) 268–276.

[18] X. Luo, Y. Guo, F. Ding, H. Zhao, G. Cui, H. Li, C. Wang, Significant Improvements in CO_2 Capture by Pyridine-Containing Anion-Functionalized Ionic Liquids through Multiple-Site Cooperative Interactions, Angew. Chem. Int. Ed. 53 (2014) 7053 –7057.

[19] T. R. Gohndrone, T. Bum Lee, M. A. DeSilva, M. Quiroz-Guzman, W. F. Schneider, J. F. Brennecke, Competing Reactions of CO_2 with Cations and Anions in Azolide Ionic Liquids, ChemSusChem 7 (2014) 1970 – 1975.

[20] J. Ranke, A. Müller, U. Bottin-Weber, F. Stock, S. Stolte, J. Arning, R. Störmann, B. Jastorff, Lipophilicity parameters for ionic liquid cations and their correlation to in vitro cytotoxicity. Ecotoxicol. Environ. Saf. 67 (2007) 430–438.

[21] T. P. T. Pham, C.-W. Cho, Y.-S. Yun, Environmental fate and toxicity of ionic liquids: A review, Water Res. 44 (2010) 352–372.

[22] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, Vasuki Tambyrajah, Novel solvent properties of choline chloride/urea mixtures, Chem. Commun., 2003, 70-71.

[23] F. Ilgen, D. Ott, D. Kralish, C. Reil, A. Palmberger, B. König, Conversion of carbohydrates into 5-hydroxymethylfurfural in highly concentrated low melting mixtures, Green Chem. 11 (2009) 1948–1954.

[24] Y. Yu, X. Lu, Q. Zhou, K. Dong, H. Yao, S. Zhang, Biodegradable naphthenic acid ionic liquids: synthesis, characterization, and quantitative structure–biodegradation relationship, Chem. Eur. J. 14 (2008) 11174–11182.

[25] E.L. Smith, A.P. Abbott, K.S. Ryder, Deep eutectic solvents (DESs) and their applications, Chem. Rev. 114 (2014) 11060–11082.

[26] M. Tiecco, R. Germani, F. Cardellini, Carbon–carbon bond formation in acid deep eutectic solvent: chalcones synthesis via Claisen–Schmidt reaction, RSC Adv. 6 (2016) 43740–43747.

[27] W.-H. Zhang, M.-N. Chen, Y. Hao, X. Jiang, X.-L. Zhou, Z.-H. Zhang, Choline chloride and lactic acid: A natural deep eutectic solvent for one-pot rapid construction of spiro[indoline-3,4′-pyrazolo[3,4-b]pyridines], J. Mol. Liq. 278 (2019) 124-129.

[28] P. Liu, J.-W. Hao, L.-P. Mo, Z.-H. Zhang, Recent advances in the application of deep eutectic solvents as sustainable media as well as catalysts in organic reactions, RSC Adv. 5 (2015) 48675-48704.

[29] M. Zhang, Y.-H. Liu, Z.-R. Shang, H.-C. Hu, Z.-H. Zhang, Supported molybdenum on graphene oxide/Fe_3O_4: An efficient, magnetically separable catalyst for one-pot construction of spiro-oxindole dihydropyridines in deep eutectic solvent under microwave irradiation, Catal. Commun. 88 (2017) 39-44.

[30] C. -T. Ma, P. Liu, W. Wu, Z.-H. Zhang, Low melting oxalic acid/proline mixture as dual solvent/catalyst for efficient synthesis of 13-aryl-13H-benzo[g]benzothiazolo[2,3-b]buinazoline-5,4-diones under microwave irradiation, J. Mol. Liq. 242 (2017) 606-611.

[31] T. J. Trivedi, J. Hoon Lee, H. Jeong Lee, Y. Kyeong Jeong, J. Wook Choi, Deep eutectic solvents as attractive media for CO_2 capture, Green Chem. 18 (2016) 2834-2842.

[32] R. J. Isaifan, A. Amhamed, Review on Carbon Dioxide Absorption by Choline Chloride/Urea Deep Eutectic Solvents, Adv. Chem. (2018) 1-6.

[33] C. Ma, S. Sarmad, J.-. Mikkola, X. Ji, Development of Low-Cost Deep Eutectic Solvents for CO_2 Capture, Energy Procedia 142 (2017) 3320–3325.

[34] G. Cui, M. Lv, D. Yang, Efficient CO_2 absorption by azolide-based deep eutectic solvents, Chem. Commun. 55 (2019) 1426-1429.

[35] Y. Daia, J. van Spronsen, G.-J. Witkampb, R. Verpoortea, Y.H. Choi, Natural deep eu- tectic solvents as new potential media for green technology, Anal. Chim. Acta 766 (2013) 61–68.

[36] S.A.S. Craig, Betaine in human nutrition, Am. J. Clin. Nutr. 80 (2004) 539–549.

[37] V. Vranova, K. Rejsec, P. Formanek, Aliphatic, cyclic, and aromatic organic acids, vitamins, and carbohydrates in soil: a review, Sci. World J. 2013 (2013), 524239.

[38] F. Cardellini, M. Tiecco, R. Germani, G. Cardinali, L. Corte, L. Roscini, N. Spreti, Novel zwitterionic deep eutectic solvents from trimethylglycine and carboxylic acids: characterization of their properties and their toxicity, RSC Adv. 4 (2014) 55990-56002.

[39] S. K. Shukla, J.-P. Mikkola, Intermolecular interactions upon carbon dioxide capture in deep-eutectic solvents, Phys.Chem.Chem.Phys. 20 (2018) 24591-24601.

[40] M. B. Taysun, E. Ser, F. S. Atalay, Effect of Hydrogen Bond Donor on the Physical Properties of Benzyltriethylammonium Chloride Based Deep Eutectic Solvents and Their Usage in 2-Ethyl-Hexyl Acetate Synthesis as a Catalyst, J. Chem. Eng. Data 62 (2017) 1173−1181.

[41] S. Nejrotti, M. Iannicelli, S.S. Jamil, D. Arnodo, M. Blangetti, C. Prandi, Natural deep eutectic solvents as an efficient and reusable active system for the Nazarov cyclization, Green Chem. 22 (2020) 110–117.

[42] N. R. Mirza, N. J. Nicholas, Y. Wu, K. A. Mumford, S. E. Kentish, G. W. Stevens, Experiments and Thermodynamic Modeling of the Solubility of Carbon Dioxide in Three Different Deep Eutectic Solvents (DESs), J. Chem. Eng. Data 60 (2015) 3246-3252.

[43] M. J. Muldoon, S. N. V. K. Aki, J. L. Anderson, J. K. Dixon, J. F. Brennecke, Improving Carbon Dioxide Solubility in Ionic Liquids, J. Phys. Chem. B 111 (2007) 9001-9009.

[44] H. M. Lee, I. S. Youn, M. Saleh, J. Woo Lee and K. S. Kim, Interactions of CO_2 with various functional molecules, Phys.Chem.Chem.Phys. 17 (2015) 10925-10933.

[45] M. Gilmore, L. M. Moura, A. H. Turner, M. Swadźba-Kwaśny, S. K. Callear, J. A. McCune, O. A. Scherman, J. D. Holbrey, A comparison of choline:urea and choline:oxalic acid deep eutectic solvents at 338 K, J. Chem. Phys. 148 (2018) 193823.

[46] S. G. Kazarian, B. J. Briscoe, Thomas Welton, Combining ionic liquids and supercritical fluids: in situ ATR-IR study of CO_2 dissolved in two ionic liquids at high pressures, Chem. Commun. (2000) 2047-2048.

[47] J. L. Anthony, J. L. Anderson, E. J. Maginn, J. F. Brennecke, Anion Effects on Gas Solubility in Ionic Liquids, J. Phys. Chem. B 109 (2005) 6366-6374.

[48] M. Ramdin, T. W. de Loos, T. J.H. Vlugt, State-of-the-Art of CO_2 Capture with Ionic Liquids, Ind. Eng. Chem. Res. 51 (2012) 8149-8177.

[49] X.-Y. Luo, X.-Y. Chen, R.-X. Qiu, B.-Y. Pei, Y. Wei, M. Hu, J.-Q. Lin, J.-Y. Zhanga G.-Ge. Luo, Enhanced CO_2 capture by reducing cation–anion interactions in hydroxyl-pyridine anion-based ionic liquids, Dalton Trans. 48 (2019) 2300–2307.

[50] T. Palomba, G. Ciancaleoni, T. Del Giacco, R. Germani, F. Ianni, M. Tiecco, Deep Eutectic Solvents formed by chiral components as chiral reaction media and studies of their structural properties, J. Mol. Liq. 262 (2018) 285-294.

[51] J. Lin, E. Pozharski, M. A. Wilson, Short Carboxylic Acid–Carboxylate Hydrogen Bonds Can Have Fully Localized Protons, Biochemistry 56 (2017) 391-402.

[52] J. W. G. Bloom, S. E. Wheeler, Taking the Aromaticity out of Aromatic Interactions, Angew. Chem. Int. Ed. 50 (2011) 7847-7849.

[53] S. E. Wheeler, Local Nature of Substituent Effects in Stacking Interactions, J. Am. Chem. Soc. 133 (2011) 10262-10274.

[54] L. Chen, F. Cao, H. Sun, Ab initio study of the π–π interactions between CO_2 and benzene, pyridine, and pyrrole, Int. J. Quantum Chem. 113 (2013) 2261–2266.

[55] S. Sarmad, Y. Xie, J.-P. Mikkola, X. Ji, Screening of deep eutectic solvents (DESs) as green CO_2 sorbents: from solubility to viscosity, New J. Chem. 41 (2017) 290-301.

[56] L. F. Zubeir, D. J. G. P. van Osch, M. A. A. Rocha, F. Banat, M. C. Kroon, Carbon Dioxide Solubilities in Decanoic Acid-Based Hydrophobic Deep Eutectic Solvents, J. Chem. Eng. Data 63 (2018) 913-919.

[57] R. Babarao, S. Dai, D. Jiang, Understanding the High Solubility of CO_2 in an Ionic Liquid with the Tetracyanoborate Anion, J. Phys. Chem. B 115 (2011) 9789-9794.

[58] X. Zhang, X. Liu, X. Yao, S. Zhang, Microscopic Structure, Interaction, and Properties of a Guanidinium-Based Ionic Liquid and Its Mixture with CO_2, Ind. Eng. Chem. Res. 50 (2011) 8323-8332.

[59] A. P. Abbott, J. C. Barron, K. S. Ryder, D. Wilson, Eutectic-Based Ionic Liquids with Metal-Containing Anions and Cations, Chem. Eur. J. 13 (2007) 6495 – 6501.

[60] Y. Yu, D. Bejan, R. Krause-Rehberg, Free volume investigation of imidazolium ionic liquids from positron lifetime spectroscopy, Fluid Phase Equilibria 363 (2014) 48–54.

[61] A. P. Abbott, J. C. Barron, K. S. Ryder, D. Wilson, Eutectic-Based Ionic Liquids with Metal-Containing Anions and Cations, Chem. Eur. J. 13 (2007) 6495 – 6501.

[62] A. P. Abbott, G. Capper, S. Gray, Design of Improved Deep Eutectic Solvents Using Hole Theory, Chem. Phys. Chem. 7 (2006) 803 – 806.

[63] X. Li, M. Hou, B. Han, X. Wang, and L. Zou, Solubility of CO_2 in a choline chloride + urea eutectic mixture, J. Chem. Eng. Data 53 (2008) 548–550.

[64] R. B. Leron, A. Caparanga, M.-H. Li, Carbon dioxide solubility in a deep eutectic solvent based on choline chloride and urea at T = 303.15-343.15K and moderate pressures, J. Taiwan Inst. Chem. Eng. 44 (2013) 879–885.

[65] B. E. Gurkan, J. C. de la Fuente, E. M. Mindrup, L. E. Ficke, B. F. Goodrich, E. A. Price, W. F. Schneider, J. F. Brennecke, Equimolar CO_2 Absorption by Anion-Functionalized Ionic Liquids, J. Am. Chem. Soc. 132 (2010) 2116-2117.

[66] J. Wanga, C. Petit, X. Zhanga, A.-H. A. Park, Simultaneous measurement of CO_2 sorption and swelling of phosphate-based ionic liquid, Green Energy Environ. 1 (2016) 258-265.