Solubility and heat of absorption of CO_2 into diisopropylamine and *N*,*N*-diethylethanolamine mixed with organic solvents

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ABSTRACT: We have evaluated the vapor-liquid equilibrium and heat of absorption of CO_2 over water-lean mixtures of the amines diisopropylamine and *N*,*N*-diethylethanolamine (DEEA). This extends our previous research on water-lean solvents containing ethanolamine. The organic diluents *N*-methyl-2-pyrrolidone (NMP) and ethylene glycol (MEG) have been employed for solvent formulation. Since both diisopropylamine (a hindered amine) and *N*,*N*-diethylethanolamine (a tertiary amine) react with CO_2 to form mainly bicarbonate in aqueous solutions, their behavior in nonaqueous mixtures is quite different from that of monoethanolamine. While MEG seems to maintain the reactivity of both diisopropylamine and DEEA even in nonaqueous mixtures, nonaqueous solvents with NMP act essentially as physical absorbents. This

is an important indication that MEG is able to take part in the reaction mechanism between these amines and CO_2, perhaps through alkylcarbonate formation, a fact that can be traced back to its relatively low autoprotolysis constant (pK_S). This study represents a departure from our previous treatment on loss of CO_2 solubility in water-lean solvents with monoethanolamine based on solvation phenomena alone, as it has become clear that the shift in equilibria in solvents with hindered and tertiary amines must account for Le Chatelier's principle.

1. Introduction

Water-lean solvents for CO_2 absorption are mixtures of amines and organic diluents, which are commonly proposed for addressing some of the issues faced by the standard aqueous amine solvents[1–3]. Seminal works on water-lean solvents include the screenings performed by Woertz[4] and by Rivas and Prausnitz[5] in the 1970s, the kinetic studies performed by Sada et al.[6–9] in the 1980s and the myriad of solubility studies performed by several authors throughout the last decades of the 20th century[10–16]. In recent years, water-lean solvents have been assessed both in terms of their rate of absorption[17–20], heat of regeneration[3,21] and proneness for degradation[22]. Potentially interesting water-lean solvents for industrial applications have been developed by RITE[23,24], RTI International[2,25,26], the University of Florence[27,28] and the Pacific Northwest National Laboratory[29,30]. A good review on the state of the art of water-lean solvents has recently been published by Heldebrant et al.[31].

In a previous study[32], we have assessed the vapor-liquid equilibrium (VLE) behavior and the enthalpy of CO_2 absorption in a series of different water-lean solvents containing ethanolamine (MEA) as the reactant of choice. Following that study, solvents based on organic compounds

with low volatility such as *N*-methyl-2-pyrrolidone (NMP) and ethylene glycol (MEG) deliver particularly interesting performances, as the CO_2 solubility in their mixtures with MEA does not decrease as much as it is observed among some esters and ketones assessed by that same investigation. Nevertheless, a clear deficiency of that analysis was its constraint in dealing with one single amine. The present study intends to address that drawback by introducing two new reactants with vastly different properties than ethanolamine.

From an investigative point of view, the most obvious drawback of choosing MEA instead of other amines for all analyses is the fact that MEA forms a stable carbamate upon reaction with CO_2. This reaction is so thermodynamically favorable that it happens even in the absence of water[33]. Conversely, one would not expect to see the same reaction pathway in hindered amines[34,35] nor in tertiary amines[36,37]. In both these cases, the CO_2 absorption into aqueous solutions follows mostly the bicarbonate formation mechanism. It is a matter of speculation how absorption into nonaqueous solutions of these amines would look like, as the absence of water implies the impossibility of bicarbonate formation. Nevertheless, nonaqueous mixtures of hindered and/or tertiary amines were precisely the solvents investigated by some previous successful researches[2,27,38].

In service of abridging our previous research on VLE and heat of absorption in water-lean solvents[32], we have employed NMP and MEG to formulate nonaqueous solvents with a hindered amine, diisopropylamine, and with a tertiary amine, *N*,*N*-diethylethanolamine (DEEA). We will refrain from abbreviating diisopropylamine as "DIPA" since another chemical commonly employed in CO_2 absorption, diisopropanolamine, is already known as DIPA. However, we might employ the abbreviation "DIPA*" when necessary for reasons of figure plotting.

As a final note, we have decided to employ solvents with 10 %wt. content of amine. This low concentration is perhaps unsuitable for the formulation of industrially interesting solvents[39]. Nevertheless, it has been previously demonstrated[32,40] that the intrinsic peculiarities in behavior when shifting from aqueous to water-lean solvents become more apparent at low amine concentrations. We have taken the conscient choice of employing low concentrations to facilitate our analysis, to the sacrifice of economic interest and industrial viability. As a first step towards proper understanding the system at hand, however, this is the best alternative.

2. Materials and methods

All solvents and amines were purchased from Sigma-Aldrich, with qualities specified on **Table 1**, and employed without further purification. Their structures can be visualized on **Figure 1** together with their IUPAC nomenclatures. We have used deionized water for every experiment involving aqueous solvents. Meanwhile, CO_2 with 99.999% purity was supplied by Yara.

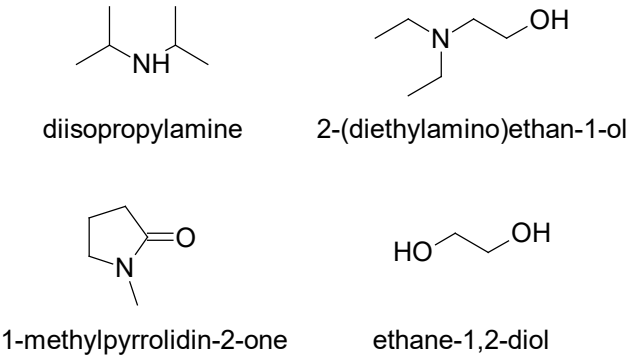

Figure 1. Chemical structures of the compounds analyzed in this study.

Table 1. Practical information regarding the compounds employed in this work.

	Abbreviation	CAS	Purity	pKa

Amines				
Diisopropylamine	–	108-18-19	99.5%	10.57[41]
N,*N*-diethylethanolamine	DEEA	100-37-8	99.5%	9.75[42]
Ethanolamine	MEA	141-43-5	99.0%	9.44[43]
Solvents				
N-methyl-2-pyrrolidone	NMP	872-50-4	99.5%	–
Ethylene glycol	MEG	107-21-1	99.0%	–

The experimental setup for obtaining VLE and heat of absorption data is schematically shown in **Figure 2**. This is precisely the same equipment used by Kim et al.[44,45]. The core of the setup is the calorimeter CPA122 fabricated by ChemiSens AB.

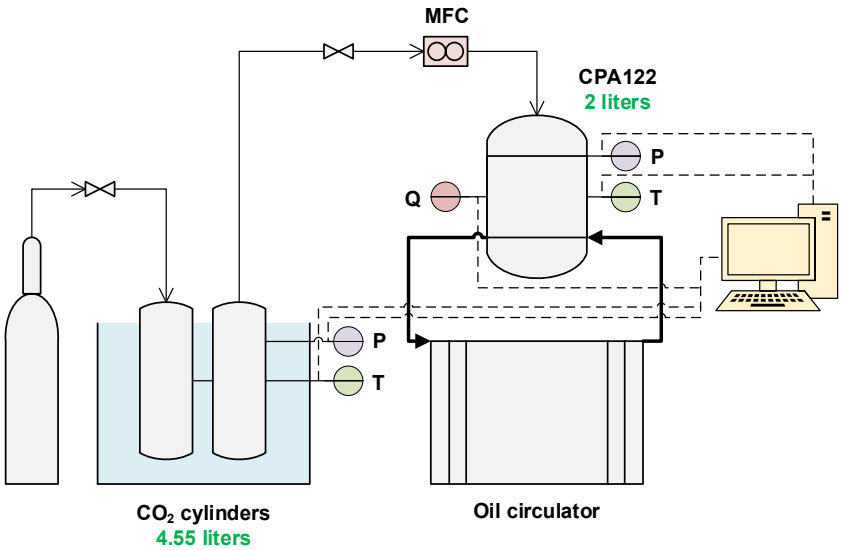

Figure 2. Schematic view of the calorimeter CPA122 setup.

Initially, vacuum is made into the stirred cell reactor so that the solvent can be easily inserted through differential pressure (i.e. "sucked" into the cell). A certain measured amount of lean solvent, typically around 1.2 liters, is fed to the reactor (2 liters) through an upper inlet. This inlet is coupled with a valve, and closing this valve seals the reactor with the solvent therein. Once sealed, the reactor is vacuumed 2–3 times so that only the solvent and its equilibrium vapor remain inside the stirred cell. Enough time under vacuum conditions is given so that one can verify that the system is airtight. A temperature setpoint is chosen and the stirrer is set to rotate at about 500 rpm. In the meantime, while operating the experiment, CO_2 5.0 is stored in a pair of cylinders (4.55 liters total) submerged in a water bath so as to keep their temperature constant. Pressure and temperature are measured at each moment, and the number of mols of CO_2 stored in the cylinders can be calculated by means of the Peng-Robinson equation of state (EOS). When injecting CO_2 into the reactor, this EOS is employed to calculate the mass of CO_2 before and after the gas leaves the cylinders, so that one can find precisely how much CO_2 has been injected. Simultaneously, and differently from the setup employed in our previous publication[32], this setup includes a mass-flow controller (MFC) through which one has a second evaluation of how much CO_2 is injected at each moment. In our experiments, we have checked both values in order to have an extra degree of confidence in our data, although only the values obtained through mass balance are reported in Section 3. To supplement this information, we are also reporting the AARDs between the loadings measured with either methodology for each experimental run. The AARD is given by Eq. (1), where α^{MB} is the loading calculated by mass balance, α^{MFC} is the loading calculated through use of the mass-flow controller and N is the number of datapoints in each experiment. The importance of this AARD calculation is that it allows us to be more confident of our results, since we are able to employ two very distinct

methodologies for treating our datasets and, through the consistency of the values obtained, cross-validate each one of these methodologies.

$$AARD = \frac{1}{N} \cdot \sum \frac{\left(\alpha_i^{MB} - \alpha_i^{MFC}\right)^2}{\alpha_i^{MB} \cdot \alpha_i^{MFC}} \quad (1)$$

Pressure and temperature are also measured in the stirred cell vapor phase. At each CO_2 injection, both pressure and temperature go up. The temperature eventually returns to its setpoint following the controller actions. As the amount of heat exchanged by the reactor is also measured at each instant, one is able to, through integration of the heat profile, essentially obtain the CO_2 heat of absorption (more details on this calculation are given in the appendix to our previous paper[32]). This heat of absorption refers to that of a small injection of CO_2, being approximately a *differential* heat of absorption. We report this data in kJ·mol CO_2 absorbed^{-1} in the Supporting Information. Conversely, one could also calculate the total heat employed to absorb CO_2 through the sum of all injections up to the current loading, obtaining the *integral* heat of absorption. These values, also in kJ·mol CO_2 absorbed^{-1}, are also reported in the Supporting Information.

Finally, the Peng-Robinson EOS can be applied to the vapor phase of the stirred cell itself. This calculation of mass, performed before and after each CO_2 injection, results in the amount of CO_2 that has been added to the vapor phase. By subtracting this amount from the total CO_2 that left the cylinders, we calculate the amount of CO_2 that has been transferred to the liquid phase. We report these values in terms of the loading α, which is mols of CO_2 absorbed per mols of amine in the solvent.

All of our datapoints are reported together with their experimental uncertainties. An in-depth description of how these uncertainties are calculated is given in the Appendix to our previous paper[32]. Furthermore, both the apparatus and the procedure have been validated by performing an experiment with aqueous MEA 30 %wt. at 40 °C, a solvent for which there is an abundance of published data. Results for the validation experiment are given in the Supporting Information to this study.

Finally, NMR experiments were carried with a Bruker 600 MHz Avance III HD spectrometer employing a 5 mm cryogenic CP-TCI z-gradient probe, and the resulting spectra was processed with the software Bruker TopSpin 4.0.7. This procedure was used to identify the species formed upon CO_2 absorption in the nonaqueous solvents between diluents *N*-methyl-2-pyrrolidone and ethylene glycol and the amine *N*,*N*-diethylethanolamine. The loaded samples were not diluted before being added to the NMR tubes. A coaxial insert containing deuterated water as "lock" solvent and TMSP (trimethylsilylpropanoic acid) as internal reference standard was used for the spectrometry analysis. The results of these investigations are briefly discussed in Section 3.2, whereas a more detailed discussion is carried in the Supporting Information.

3. Results and discussion

The dielectric permittivities of NMP and MEG are slightly different, with NMP having $\varepsilon = 32.55$ and MEG having $\varepsilon = 41.4$ at 20 °C[46]. In our previous efforts[19,32], we have made a point of using the dielectric permittivity as a placeholder for electrostatic/solvation properties, like many others in literature before us[8,13,47]. Still, NMP has proved to be an excellent diluent for MEA regardless of its lower ε when compared to MEG[20,32]. In other words, we had not anticipated to see a big difference in performance between NMP and MEG with regards to their solvation capacities.

This is the reason why we will discuss the huge discrepancies observed in the current study not in terms of solvation effects (i.e. differences in ε), but instead in terms of the reactivities of the diluents themselves, which are clearly demonstrated by the different autoprotolysis constants (pKs) of MEG and NMP.

This Section 3 is divided into Section 3.1, dealing with diisopropylamine solvents, and Section 3.2, dealing with *N*,*N*-diethylethanolamine solvents. A third part, Section 3.3, will analyze the properties of solvents with *N*-methyl-2-pyrrolidone a bit more deeply. All of the data obtained in the course of this research can be found in the Supporting Information.

3.1. Nonaqueous 10 %wt. diisopropylamine

Figure 3 shows the vapor-liquid equilibrium results obtained for solutions containing mixtures of different diluents and 10 %wt. of diisopropylamine, both at 40 °C and at 80 °C. This data can also be found on the Supporting Information together with its uncertainties.

The blue-colored datapoints refer to values obtained under operation at 40 °C, and clearly indicate heavy depression of chemical reaction in the NMP–diisopropylamine blend (◇ markers). This is evidenced by the almost entirely linearly dependent set of VLE data obtained both at 40 °C and 80 °C, typical of physical absorption behavior (i.e. Henry's law). Conversely, H_2O–diisopropylamine and MEG–diisopropylamine have VLE curves commonly observed for chemical solvents, hallmarks of which are little dependence of CO_2 solubility on partial pressure up to near the stoichiometric limit (α = 1 mol CO_2·mol amine^{-1}) and, afterwards, a sharp dependency of solubility on pressure.

We have not been able to obtain reliable data with aqueous diisopropylamine 10 %wt. at 80 °C due to excessive volatilization of the solvent. This volatilization led to the formation of rock-solid white precipitate in some key parts of the calorimeter apparatus, including around the pressure transducer. Consequentially, the pressure readings of these experiments had to be completely discarded. In fact, aqueous diisopropylamine 10 %wt. presents issues even before loading began. Close inspection of the unloaded solution inside a transparent bottle reveals separation between a light organic phase and a heavy aqueous phase.

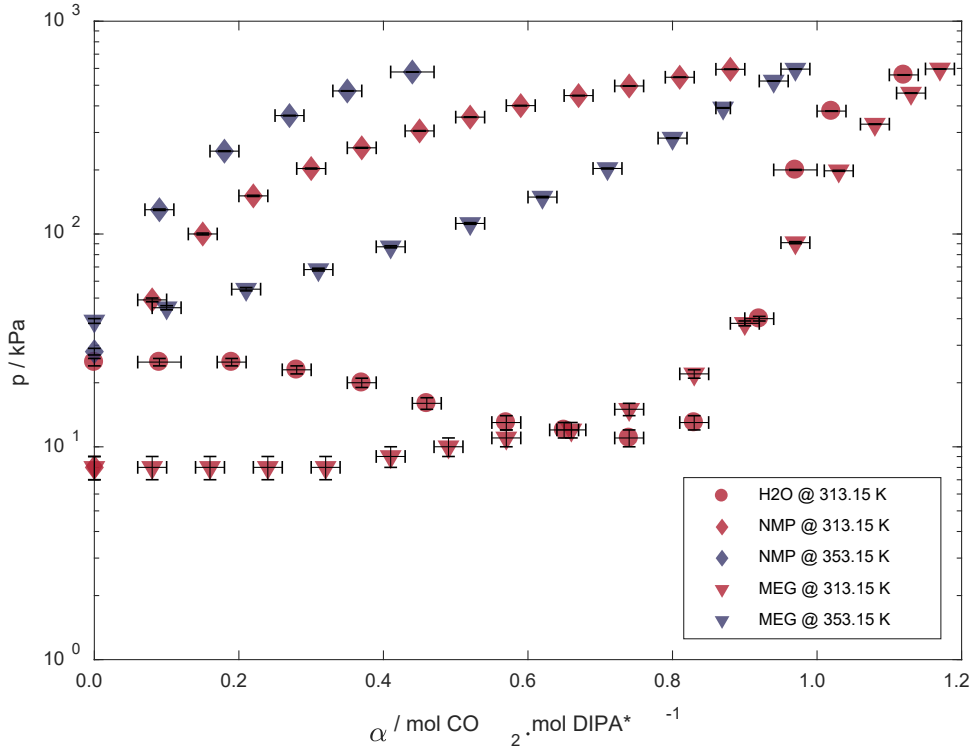

Figure 3. Vapor-liquid equilibrium data for solvents containing 10 %wt. diisopropylamine.

Conversely, phase separation has not been observed for mixtures of diisopropylamine either with *N*-methyl-2-pyrrolidone nor with ethylene glycol. As a preliminary result, this indicates that shifting from water to an organic diluent enables the utilization of diisopropylamine for CO_2 absorption/desorption in conditions otherwise impractical in aqueous solvents.

Figure 4 shows the integral heat of absorption obtained for solutions containing mixtures of different diluents and 10 %wt. diisopropylamine only at 40 °C. Data for the heat of absorption at both 40 °C and 80 °C can be found on the Supporting Information together with its uncertainties.

The heat of absorption in aqueous diisopropylamine is surprisingly high, perhaps due to unaccounted phase transition phenomena, e.g. a biphasic solvent endothermically becoming single phase upon loading, or maybe sublimation of products over cold spots inside the equipment as also experienced at 80 °C. For ethylene glycol + diisopropylamine, the heat of absorption is that typical of secondary and/or hindered amines such as aqueous DEA or aqueous AMP[48], $\Delta H \approx 65–70$ kJ·mol CO_2^{-1} for loadings below $\alpha = 1$ mol CO_2·mol amine^{-1} both at 40 °C and 80 °C (ΔH does seem to decrease slightly from 40 °C to 80 °C, but given the uncertainties of the experiment this reduction is most certainly negligible). More interestingly, the heat of absorption in NMP–diisopropylamine is of about 20 kJ·mol CO_2^{-1} at 40 °C and 13 kJ·mol CO_2^{-1} at 80 °C. These results are congruent with physical absorption heat[38], and are further indication of the severe abatement of chemical reaction caused by using *N*-methyl-2-pyrrolidone as a solvent.

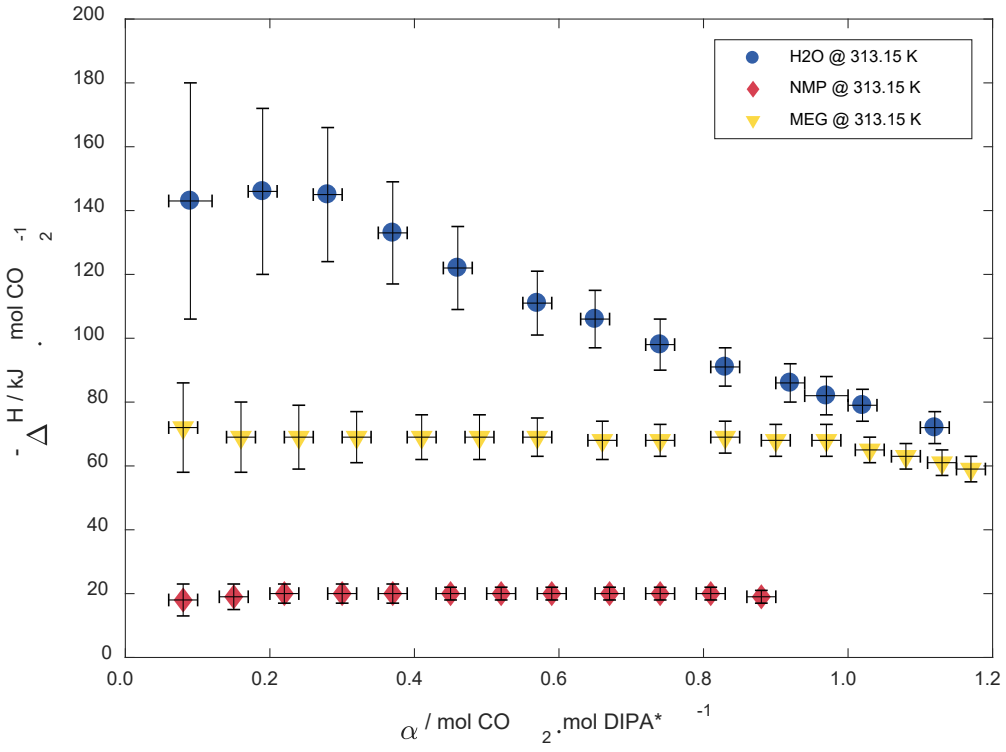

Figure 4. Integral heat of absorption data for solvents containing 10 %wt. diisopropylamine.

The failure of diisopropylamine to adequately react with CO_2 in *N*-methyl-2-pyrrolidone poses some interesting questions. The big difference between NMP and MEG is that NMP is an aprotic solvent, whereas MEG is not only protic but also has a significatively low autoprotolysis constant. If the reaction mechanism between diisopropylamine and CO_2 were to be primordially one of direct reaction forming carbamate, the solvent being protic or aprotic would hardly be an issue. Instead, hindered amines consume CO_2 through a mix of carbamate and bicarbonate formation in aqueous solvents[34]. In nonaqueous solvents with ethylene glycol, no bicarbonate can be formed at all, and the only options left are carbamate and MEG-carbonate (diisopropylamine cannot form an alkylcarbonate itself since it lacks a hydroxy group). These are shown in **Figure 5**. Conversely, in nonaqueous solvents with *N*-methyl-2-pyrrolidone, only carbamate formation should be observed. If no carbamate formation is observed in NMP, this

perhaps implies that the carbamate route is subdued in solvents with diisopropylamine, making the bicarbonate/alkylcarbonate one the main responsible for CO_2 absorption. This being the case, the similarity of the VLE curves between MEG–diisopropylamine and H_2O–diisopropylamine is all the more remarkable, as it signifies that ethylene glycol has an incredible capacity of forming alkylcarbonates. More on this will be addressed regarding the results for ethylene glycol + 10 %wt. *N*,*N*-diethylethanolamine.

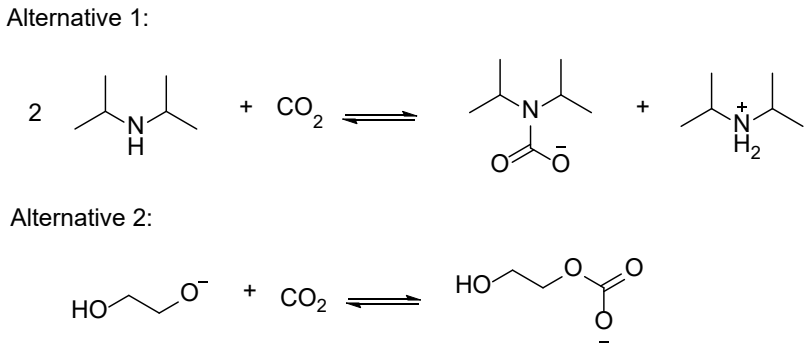

Figure 5. Two possible reaction pathways for nonaqueous ethylene glycol + 10 %wt. diisopropylamine.

Another interesting aspect of the experiments with diisopropylamine comes from its comparison with DIPA, i.e. diisopropanolamine. Between the two, DIPA has lower pKa (8.84[43] against 10.57 from diisopropylamine[41]), and there are no reasons to suppose it should be less sterically hindered than diisopropylamine. Nevertheless, DIPA reacts with CO_2 in aprotic diluents such as tetramethylene sulfone[49] (sulfolane or TMS), a mixture that is indeed the basis of the Sulfinol-D® process[50]. Granted, the Sulfinol-D® solvent contains a certain percentage of water, which perhaps is enough to justify its reactivity with CO_2. Or perhaps the alcohol group of DIPA can directly react with CO_2, forming DIPA-carbonate. Hwang et al.[51] were able to measure the kinetics of CO_2 absorption into nonaqueous solutions of DIPA in propylene carbonate, another aprotic solvent, which might indicate a carbonate-forming pathway involving the alkanolamine

itself. This discussion puts into perspective much of the data obtained for DIPA in nonaqueous protic solvents such as alcohols[51] and polypropylene glycols[52]. However, discussing solvents with DIPA is beyond the scope of this study.

3.2. Nonaqueous 10 %wt. *N*,*N*-diethylethanolamine

Figure 6 shows the vapor-liquid equilibrium results obtained for solutions containing mixtures of different diluents and 10 %wt. of *N*,*N*-diethylethanolamine, both at 40 °C and at 80 °C. This data, together with its uncertainties, can also be found on the Supporting Information.

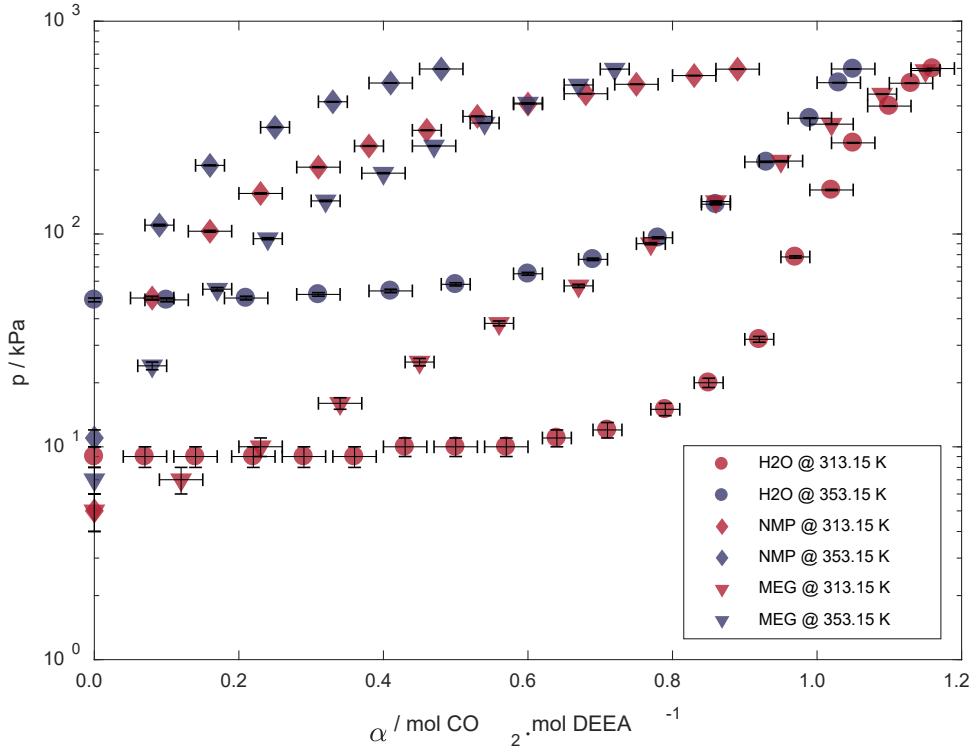

Figure 6. Vapor-liquid equilibrium data for solvents containing 10 %wt. *N*,*N*-diethylethanolamine.

This time, it is possible to draw a direct comparison between the water-lean solvents and H_2O–DEEA both at 40 °C and at 80 °C, as no volatility issues nor phase separation were observed in

the aqueous solution. Naturally, this lower volatility is direct consequence of the alcohol group of DEEA, which is the reason alkanolamines are favored over organic amines for CO_2 absorption purposes in the first place[53].

Once again, the NMP-based solvents show performances typical of a physical absorbent, with blue and red ◇ markers in **Figure 6** presenting an almost linearly dependent correlation consistent with the Henry's law approach. The integral heat of absorption of NMP + DEEA 10 %wt. at 40 °C shown on **Figure 7** is also comparable to that of physical solvents ($\Delta H \approx 15$ kJ·mol CO_2^{-1}).

On the other hand, MEG + DEEA 10 %wt. again shows a typical chemical absorption profile both at 40 °C and at 80 °C, and its heat of absorption shown on **Figure 7** supports the assumption of a reactive fixation of CO_2 ($\Delta H \approx 58–60$ kJ·mol CO_2^{-1}, typical of tertiary amines[48]).

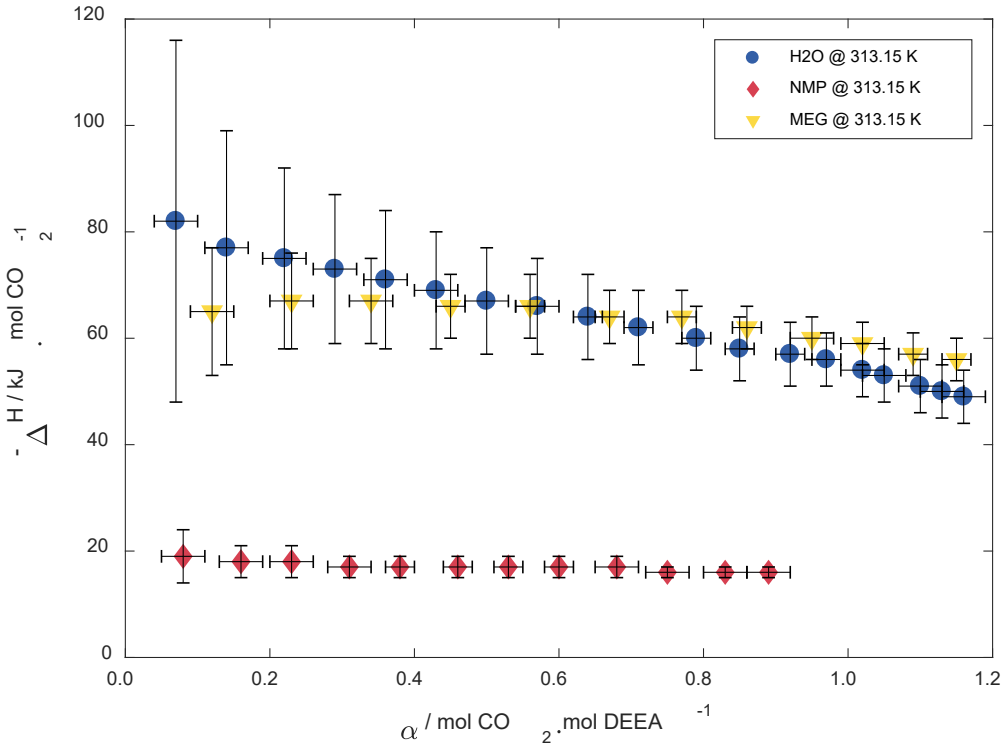

Figure 7. Integral heat of absorption data for solvents containing 10 %wt. *N*,*N*-diethylethanolamine.

The addition of diisopropylamine or *N*,*N*-diethylethanolamine unequivocally increases the absorption capacity of ethylene glycol. **Figure 8** provides a comparison between the VLE data gathered in this work with previously published solubility data of CO_2 in pure organic diluent[54,55]. This enhancement of CO_2 solubility is clear indication of chemical reaction phenomena.

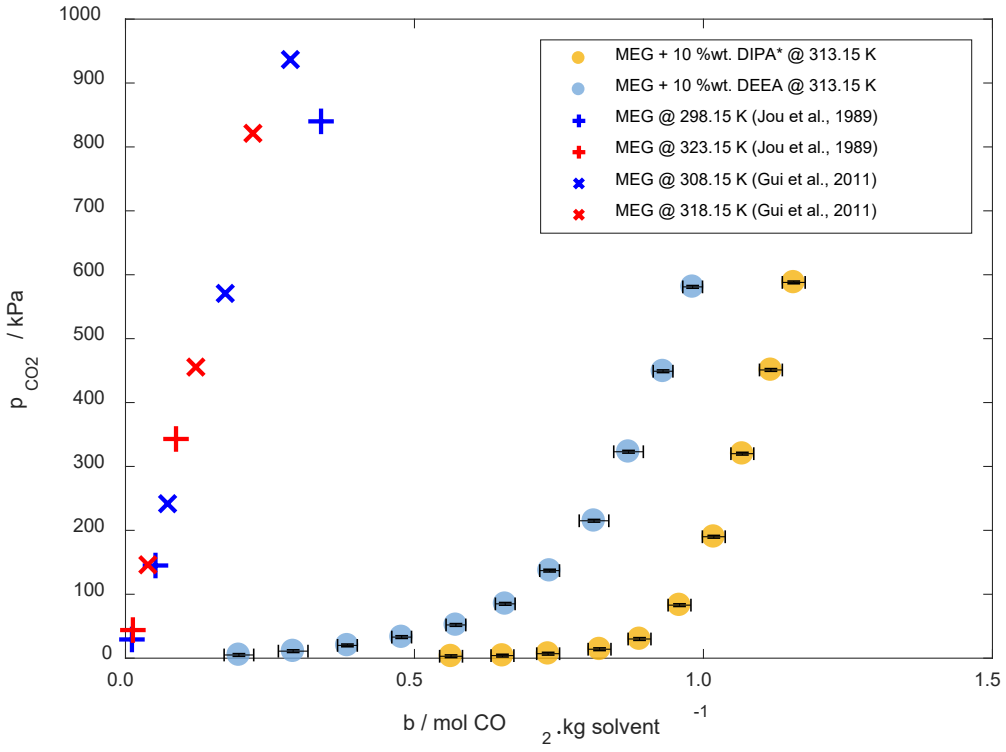

Figure 8. Solubility of CO_2 in water-lean solvents containing 10 %wt. diisopropylamine and *N*,*N*-diethylethanolamine when compared to pure ethylene glycol. Data from literature[54,55].

It has been a point of contention in the last decades whether chemical absorption of CO_2 can happen with tertiary amines in nonaqueous solvents or not. While many authors support that there is no direct reaction between the amine and CO_2 itself and suggest that water is needed for the conversion to take place[56–58], others propose an alkylcarbonate mechanism where the tertiary amine can react with CO_2 even in the absence of water[6,59]. In recent years, NMR spectroscopy has shown that alkylcarbonates are indeed formed upon absorption with tertiary amines, validating the latter point of view[60,61]. Still, the depression of the reactive absorption of CO_2 when shifting from aqueous to nonaqueous tertiary amine solvents has been experimentally observed to be strong enough to support both viewpoints. Conversely, to the best of our

knowledge, the absorption profiles shown on **Figure 6** are the strongest VLE examples of a tertiary amine behaving in a nonaqueous solvent as closely as it would in pure water, with a singularly small loss of capacity when compared to aqueous DEEA.

We suggest that this remarkably unabated absorption capacity of MEG + DEEA 10 %wt. is due to two distinct factors. The first factor is related to ethylene glycol. The autoprotolysis constant of this dialcohol is 15.84, while that of water is 14 and that of *N*-methyl-2-pyrrolidone is above 24.2[62]. For a diluent with generic composition SH, the autoprotolysis constant is defined as in Eq. (2), where a_{SH} is the activity of SH and so on.

$$pK_S = -log_{10}\left(\frac{a_{S^-} \cdot a_{H^+}}{a_{SH}}\right) \quad (2)$$

Eq. (2) indicates that, the lower the pK_S of a solvent, the higher is its self-ionization potential. If one considers that the self-ionization of the solvent is an important step in enabling the alkylcarbonate formation, the fact that ethylene glycol has one of the lowest pK_S among all organic solvents helps understanding its surprising performance. Since the pK_S scale is logarithmic, it might be slightly deceitful to look at its values directly. With a bit of algebra, however, we can reformulate it like this: assuming that the activity coefficients of all species are the same so that one can work with concentrations directly, there are about 8 times more molecules of OH^- in one mol of water than molecules of deprotonated MEG in one mol of ethylene glycol, while there are 15,000 times more molecules of deprotonated MEG in one mol of ethylene glycol than molecules of deprotonated NMP in one mol of *N*-methyl-2-pyrrolidone.

The second factor is the high basicity of DEEA. With pKa = 9.75, *N*,*N*-diethylethanolamine is more basic than TEA (pKa = 7.85) and MDEA (pKa = 8.65)[63]; in fact, it is more basic than MEA

itself. Such high basicity, especially when compared to the other tertiary amines tested previously (precisely TEA[56,57] and MDEA[58,64]), also explains why high absorption capacity in nonaqueous tertiary amines has not been observed before.

We have carried NMR analyses in unloaded and loaded solutions of ethylene glycol and *N*-methyl-2-pyrrolidone with *N*,*N*-diethylethanolamine to verify if one is able to qualitatively identify peaks relating to alkylcarbonate formation. The results of these studies are in the Supporting Information to this manuscript. In short, both alkylcarbonates of ethylene glycol and *N*,*N*-diethylethanolamine could be observed in the loaded MEG + DEEA solvent, but no alkylcarbonate whatsoever has been observed in the NMP + DEEA solvent. Meanwhile, molecular carbon dioxide can be observed experimentally in loaded NMP + DEEA, accounting for physical absorption of CO_2 in that formulation.

Figure 9 shows the two possible alkylcarbonate formation pathways for nonaqueous solutions of MEG and DEEA, where either the deprotonated solvent or the deprotonated amine itself can react directly with CO_2 to form carbonate species. For the first pathway to be viable, the solvent must be capable of being deprotonated, which ties in directly with its self-ionization constant. At the same time, both alternatives benefit from having a strong base in solution, so that the deprotonation step can be taken to its maximum extent. Therefore, having a mixture of a diluent with low pK_S and an amine with high pKa is the best possible combination for enabling CO_2 absorption in tertiary amines.

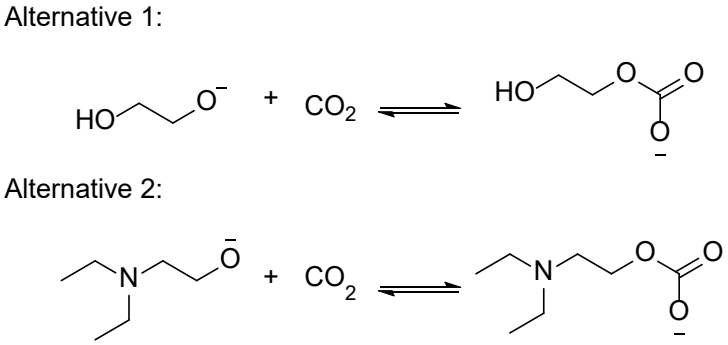

Figure 9. Two possible alkylcarbonate formation mechanisms for nonaqueous ethylene glycol + 10 %wt. *N*,*N*-diethylethanolamine.

Interestingly, the solubility of CO_2 in the MEG–DEEA solvent decreases more with temperature than that of H_2O–DEEA. Looking back at **Figure 6**, the distance between the blue and red scattered ▽ curves is significatively larger than the distance between the blue and red scattered ○ curves. Bernhardsen and Knuutila[66] offer Eq. (3) as a definition of cyclic capacity in order to describe the potential of a solvent for treating flue gas when only VLE data at 40 °C and 80 °C is available.

$$\Delta\alpha = \alpha_{40°C,15kPaCO_2} - \alpha_{80°C,15kPaCO_2} \quad (3)$$

By this token, the cyclic capacity of aqueous 10 %wt. DEEA would be $\Delta\alpha \approx 0.29$ mol CO_2·mol DEEA^{-1} while that of MEG–DEEA would be $\Delta\alpha \approx 0.32$ mol CO_2·mol DEEA^{-1} (with the caveat that we are interpolating values of loadings and CO_2 partial pressures indirectly calculated from the total pressure data presented in the Supporting Information). On a molecular level, one could perhaps attribute the high reaction reversibility in MEG to the inherent instability of the carbonate species shown in **Figure 9** when compared to that of bicarbonate, the main product formed in aqueous solutions. Such thermodynamic potential for more easily desorbing CO_2 in

water-lean solvents has been commonly acknowledged since Rivas and Prausnitz[5]. This potential does not apply to the case of NMP–DEEA, a solvent that overall experiences very little chemical reaction, and in which $\Delta\alpha \approx 0.02$ mol CO_2·mol $DEEA^{-1}$ following Eq. (3).

3.3. Some extra insight on the *N*-methyl-2-pyrrolidone issue

To better understand the role of *N*-methyl-2-pyrrolidone in depressing the CO_2 absorption capacity of solvents based on diisopropylamine and DEEA, we have assessed the VLE and heat of absorption for water-lean mixtures with different water–NMP proportions plus 10 %wt. of each of the amines. This procedure allows for a smooth evaluation of the shift from aqueous to nonaqueous amine. Solvents with 60 %wt. water to 30 %wt. NMP and 30 %wt. water to 60 %wt. NMP (or 2:1 and 1:2 water-to-NMP mass ratios) were investigated at 40 °C, and the resulting data can be seen on the Supporting Information and on **Figure 10**.

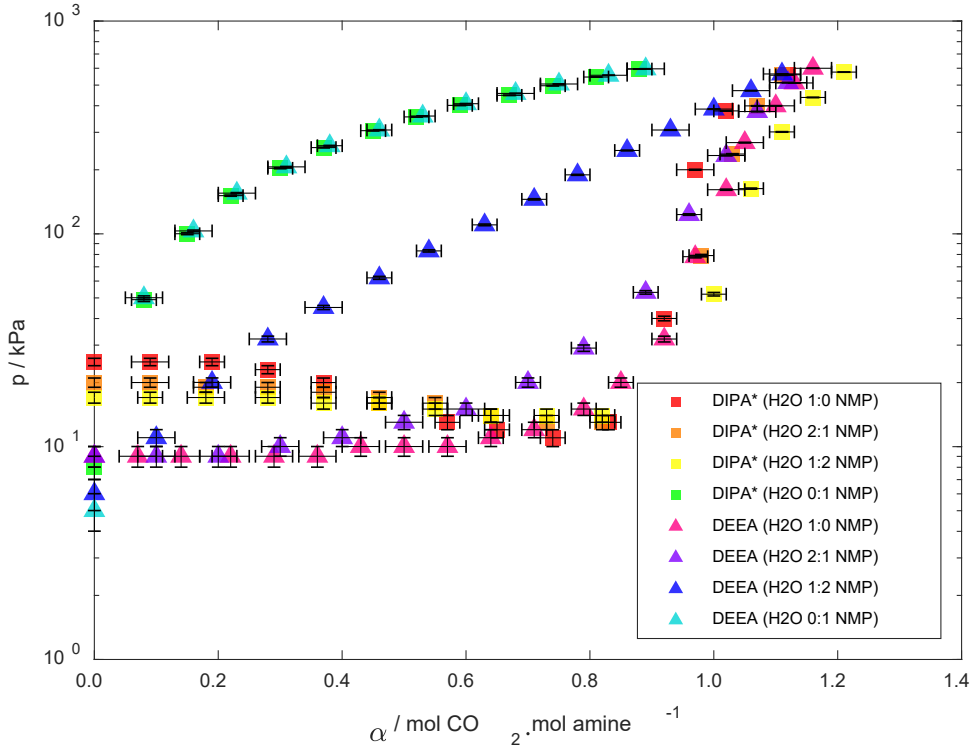

Figure 10. Vapor-liquid equilibrium data for solvents containing different proportions of water and *N*-methyl-2-pyrrolidone plus 10 %wt. amine at 40 °C.

On **Figure 10** one can see that the shift from aqueous to nonaqueous DEEA 10 %wt. is indeed gradual and monotonical. The highest CO_2 solubility is observed for the aqueous solvent (pink △). Then, as more water is exchanged by NMP, the CO_2 solubility steadily decreases while the VLE curve experiences what in **Figure 10** can be translated as a "*shift to the left*". In this case, the solvent with 2:1 water–NMP mass ratio (purple △) shows a VLE very similar to the aqueous amine, while the solvent with 1:2 water–NMP mass ratio (dark blue △) shows a huge decrease in capacity. This time, and differently from our previous researches[19,32], nothing indicates that the VLE curves are somewhat parallel – indeed, they visibly are not. The culmination of this shift to the left process is that, in nonaqueous DEEA in NMP, the behavior of the solvent is similar to that of a physical absorbent.

In our previous studies[19,32], we have observed a distinct monotonical decrease in CO_2 solubility as one moves from aqueous to water-lean amine mixtures. Many other authors have observed the same phenomenon[5,20,67]. This reduction in capacity is often correlated to the distinct solvation properties of each different chemical, typically complicated by the issue of organic solvents having lower dielectric permittivities than water (thus being worse solvents for electrolytes). Effectively, Macgregor and Mather[13] argue that, due to the secondary medium effect, water-lean solvents are bound to experience a shift in reaction equilibrium towards less conversion from CO_2 to electrolytic species. This is one possible interpretation for the loss of CO_2 solubility, and one that disregards any reaction mechanism involving the solvent and the amine itself. However, if one considers that there are such reaction mechanisms, then the explanation becomes one guided by Le Chatelier's principle: the addition of more reactant will shift the equilibrium towards increased conversion of CO_2. In the case where this reactant is water, since water plays a role in bicarbonate formation (i.e. the tertiary amine reaction mechanism proposed by Donaldson and Nguyen[68] and the hindered amine reaction mechanism proposed by Sartori and Savage[34]), then the shifting from aqueous to nonaqueous solvent will also bring a reduction in CO_2 solubility.

In both interpretations, either via secondary medium effect or Le Chatelier's principle, one would expect a monotonic shift to the left as observed for DEEA in **Figure 10**. We would like to suggest that both explanations are valid and complementary. Therefore, if in this work we have decided to interpret shifts of solubility in terms of pK_S and reaction pathways, we do not imply that solvation properties are irrelevant. Nevertheless, considering that one is dealing precisely with a tertiary amine that requires the solvent to play an active role in the reaction mechanism,

we believe that a good explanation for the behavior of the VLE of semi-aqueous NMP–DEEA solutions is that of shifting chemical equilibria through Le Chatelier's principle.

The situation is less clear for the data regarding diisopropylamine. From aqueous diisopropylamine (red □), to the solvent with 2:1 water–NMP ratio (orange □) and ending in the solvent with 1:2 water–NMP ratio (yellow □), what one observes in reality is a *shift to the right*. This increase in capacity with the addition of NMP to aqueous diisopropylamine is unlike anything experienced in our previous analyzes. An assessment of the heat of absorption data shown in the Supporting Information, plus of the previous discussion on the phase-changing behavior of aqueous diisopropylamine (Section 3.1), indicates that phase-transition and volatilization phenomena might be responsible for these unexpected results. Perhaps the addition of some quantity of NMP is enough to keep diisopropylamine in one single phase in the solvent, preventing its volatilization upon heating and thus endowing more CO_2 solubility than in the aqueous amine. Since the CPA122 apparatus consists of a closed stirred cell, we are unfortunately unable to visually inspect the reacting medium to see what happens after each injection. However, as with nonaqueous DEEA, nonaqueous diisopropylamine behaves much like a physical solvent.

From a previous study[32] we have yet unpublished measurements of vapor-liquid equilibrium and heat of absorption of CO_2 in pure *N*-methyl-2-pyrrolidone at different temperatures. We have employed this data to regress the Henry's coefficient of CO_2 in NMP both at 40 °C and 80 °C by using Eq. (4), through which Henry's coefficient is obtained with units of pressure (kPa). Notice that, in this formulation, the Henry's coefficient is inversely proportional to the CO_2 solubility. The results have been compared to those regarding CO_2 absorption into the nonaqueous mixtures evaluated in this work. On **Table 2**, one can see that the Henry's coefficients for the water-lean

solvents containing NMP are statistically indistinct from that of the pure organic solvent. This indicates either a complete absence of chemical reaction or the fact that such reaction should be negligible for practical purposes, as one would expect chemical interactions to increase the solubility of CO_2 in these solvents. In other words, **Table 2** reinforces our conclusion that there is negligible enhancement in CO_2 absorption when mixing NMP with 10 %wt. DEEA or diisopropylamine.

$$H_{CO2} = \frac{p_{CO2}}{x_{CO2}} \tag{4}$$

Table 2. Data for absorption of CO_2 into pure *N*-methyl-2-pyrrolidone and its mixtures with 10 %wt. diisopropylamine and 10 %wt. *N*,*N*-diethylethanolamine.

	H_{CO2} / kPa	ΔH / kJ·mol CO_2^{-1}
Pure NMP		
T = 40 °C	10,000 ± 100	18 ± 2
T = 80 °C	18,100 ± 140	18 ± 3
NMP + 10%wt. diisopropylamine		
T = 40 °C	9,060 ± 90	19.7 ± 0.8
T = 80 °C	17,500 ± 210	11.8 ± 0.6
NMP + 10%wt. DEEA		
T = 40 °C	10,760 ± 90	14.9 ± 0.7

T = 80 °C	18,700 ± 190	12.7 ± 0.6

4. Conclusions

Summarizing the results obtained for water-lean solvents based on diisopropylamine:

1. Shifting from water to NMP and MEG enables the utilization of 10 %wt. diisopropylamine while avoiding phase separation in the unloaded solvent and excessive volatilization of the amine.
2. MEG + diisopropylamine 10 %wt. results in a solution that behaves like a typical chemical solvent, promoting a CO_2 absorption capacity much similar to that of aqueous diisopropylamine at 40 °C.
3. NMP + diisopropylamine 10 %wt. results in a solution that behaves like a typical physical solvent, following Henry's law. This is not to imply a complete absence of chemical reactions; however, if there are any, they are severely depressed.
4. Semi-aqueous solutions of NMP–diisopropylamine have a VLE pattern that unexpectedly indicates an increase of CO_2 solubility when removing water and adding NMP to the solvent. This is perhaps because NMP plays a role in avoiding liquid-liquid phase separation and/or the volatilization of the amine, though we cannot be sure.

Summarizing the results obtained for water-lean solvents based on *N*,*N*-diethylethanolamine:

1. Shifting from water to NMP again results in a solution that behaves like a typical physical solvent, perhaps due to its low potential for undergoing self-ionization and, therefore, chemical interaction with the amine.

2. Semi-aqueous solutions of NMP–DEEA follow the known pattern of loss of CO_2 solubility as one moves from aqueous to nonaqueous solvents. This phenomenon can be easily explained through Le Chatelier's principle, although the secondary medium effect could also be meaningful.
3. MEG + DEEA 10 %wt. results in a water-lean solvent with similar properties to that of aqueous DEEA, with very interesting implications towards our understanding of chemical absorption in nonaqueous tertiary amines.
4. Furthermore, the dependency of VLE on temperature is more pronounced in MEG–DEEA than on H_2O–DEEA, likely reflecting the instability of the reaction products between DEEA and CO_2 in the absence of water.

We have no wish to defend the viability of the solvents analyzed in this paper as candidates for industrial CO_2 absorbents. Nevertheless, we are confident that the results presented here have furthered the understanding of reaction pathways and chemical properties of nonaqueous solvents based on hindered and tertiary amines.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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