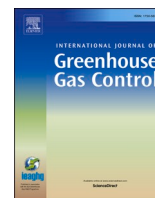




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Signs of alkylcarbonate formation in water-lean solvents: VLE-based understanding of pKa and pKs effects

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ABSTRACT

Water-lean solvents are solvents for CO₂ capture which contain at least one amine and one organic diluent. Carbamate-forming amines in nonaqueous water-lean solvents typically absorb CO₂ through the formation of carbamate species. Conversely, tertiary amines in nonaqueous amino-organic mixtures cannot form carbamate nor undergo bicarbonate formation. However, protic organic diluents might take part in an alkylcarbonate formation pathway: in this route, the diluent is deprotonated by the amine, and its conjugate base is then able to react directly with CO₂ to form an alkylcarbonate. This is an interesting reaction mechanism, as it offers a possibility for formulating solvents that deviate from the two most common reaction pathways for CO₂ absorption (i.e., carbamate and bicarbonate formation). The present study introduces a simple way for evaluating alkylcarbonate-forming water-lean solvents based on the properties of its single constituents, namely the basicity of the amine and the autoprotolysis constant of the organic diluent. Our theoretical framework shows that higher CO₂ absorption capacities can be obtained for solvents containing amines with high pKa and diluents with low pKs. We assess both the challenges and possibilities for alkylcarbonate-forming solvents and propose a framework for their development and utilization in the industry.

1. Introduction

Absorption of CO₂ into aqueous amine solvents is standard practice for carbon capture in the industry (Rochelle, 2016). Amongst typical examples of these solvents, one can find aqueous monoethanolamine (MEA), aqueous piperazine (PZ) (Rochelle et al., 2011), and aqueous blends of piperazine with 2-amino-2-methyl-1-propanol (AMP) (Feron et al., 2020). Following the historical development of aqueous amine solvents is illustrative of the typical issues faced by the industry: issues of solvent volatility, viscosity, stability towards degradation, absorption rates, CO₂ solubility and enthalpy of absorption are all taken into account when researching new absorbents (Kohl et al., 1997a). All of these concerns must be addressed simultaneously to enable proper solvent performance in industrial applications.

Of course, many of these issues are interconnected. More specifically, the mechanism of CO₂ absorption is strongly correlated to solubility, kinetics, and exothermicity of reaction. For a clear example: aqueous MEA absorbs CO₂ mostly through the formation of carbamate (Kortunov et al., 2015). This reaction consumes 2 mols of amine for each mol of CO₂, is fast, and is characteristic of solvents that have a moderately high

enthalpy of absorption (−80 to −90 kJ/mol CO₂) (Svendsen et al., 2011). A tertiary amine such as N-methyldiethanolamine (MDEA) absorbs CO₂ mostly through the formation of bicarbonate, in a reaction that consumes 1 mol of amine for each mol of CO₂, is slow, and is characteristic of solvents that have a moderately low enthalpy of absorption (−55 to −65 kJ/mol CO₂) (Chowdhury et al., 2013). The three aspects of stoichiometry, kinetics and reaction enthalpy are thus intertwined.

The difference between primary amines such as MEA and tertiary amines such as MDEA is that the nitrogen atom of MEA is available for a nucleophilic attack, whereas that of MDEA is not. Though there is nothing preventing MEA from following the bicarbonate pathway, the carbamate pathway is simply thermodynamically more favourable, and thus takes precedence. Absorption of CO₂ in aqueous MEA also forms bicarbonate, just less so than carbamate. Furthermore, the carbamate-to-bicarbonate ratio of speciation in a solvent will depend on how accessible their nitrogen atom is. Secondary amines form relatively more bicarbonate than primary amines, and the absorption enthalpies in aqueous solutions of the former (−70 to −75 kJ/mol CO₂) (Svendsen et al., 2011) reflect this. Sterically hindered amines such as AMP are not

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Table 1
Relevant information regarding chemicals employed in this study.

Name	Abbreviation	CAS	Purity	pKa	pKs
Triethanolamine	TEA	102–71–6	≥ 99.0%	7.85	–
N-methyldiethanolamine	MDEA	105–59–9	≥ 99.0%	8.65	–
N,N-diethylethanolamine	DEEA	100–37–8	≥ 99.5%	9.75	–
Water	H ₂ O	7732–18–5	D.I. water	–	14
Methanol	MeOH	67–56–1	99.8%	–	16.71
Ethanol	EtOH	64–17–5	≥ 99.5%	–	18.9
Ethylene glycol	MEG	107–21–1	≥ 99.0%	–	15.84
N-methyl-2-pyrrolidone	NMP	872–50–4	≥ 96.0%	–	≥ 24.2
Sulfolane	TMS	126–33–0	99.0%	–	24.45
Tetrahydrofurfuryl alcohol	THFA	97–99–4	99.0%	–	?
Formic acid	HCOOH	64–18–6	≥ 95.0%	–	6.2

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so prone to nucleophilic attacks from CO₂, behaving similarly to tertiary amines (Sartori and Savage, 1983). Blending amines of different groups is a convenient way of coupling fast absorption kinetics with high CO₂ solubilities (Astarita et al., 1981), which is the reason behind the success of solvents such as the aqueous AMP + PZ blend (Feron et al., 2020). Moreover, aqueous amine solvents also absorb CO₂ through the formation of carbonate (CO₃²⁻) and the physical solubilization of molecular CO₂, although these two pathways are severely subdued when in comparison to the carbamate and bicarbonate pathways (Kortunov et al., 2015; Wong et al., 2016).

All of this might seem like a deterrent to the development of new solvents. If there is no alternative for breaking the deadlock between capacity, kinetics and enthalpy, this leaves little room for improvement in aqueous amine solvents (at least with regards to these three factors). And yet, once one forgoes the demand that the solvent is *aqueous*, new mechanisms of reaction might be open to research. More interesting to the present study is the alkylcarbonate reaction mechanism, already well known from the works by Barzagli et al. (2019, 2014, 2013) and the development of CO₂BOL solvents (Heldebrant et al., 2010; Rainbolt et al., 2011). This mechanism is particularly pertinent to nonaqueous solutions of tertiary or sterically hindered amines. The growing interest in the alkylcarbonate pathway can be well exemplified by the recent work of Chowdhury et al. (2020), wherein a series of alcohols and tertiary amines were evaluated for their capacity in absorbing CO₂. The proposed advantages of these solvents are their low enthalpy of absorption (Chowdhury et al., 2020; Wanderley et al., 2020b) coupled with the possibility of desorbing CO₂ at lower temperatures (e.g., 80 °C) (Barzagli et al., 2013; Chowdhury et al., 2020; Li et al., 2020).

We are particularly interested in providing a clear theoretical framework for understanding the effect of diluent and amine properties in the resulting water-lean solvent. In Section 2, we will provide a short review of what is known of the alkylcarbonate pathway and lay down the grounds for our theoretical framework. In Section 3, we will briefly explain our empirical methodology. In Section 4, we will provide a series of new experimental vapour-liquid equilibrium (VLE) data to support the theoretical framework. We will also derive chemical equilibrium and enthalpy of absorption estimates from the VLE data as a way of aiding our discussion. Clearly, though, these estimates *cannot* be considered the final word on alkylcarbonate formation data, and we must strongly impress the fact that some of our results are speculative in nature. It is also in Section 4 that we shall point out the limitations of our own initial hypotheses, which are important for assessing knowledge gaps. Most crucially, we will attempt to assess the industrial viability of alkylcarbonate-forming solvents as an alternative to standard aqueous amines. Finally, in Section 5 we will present our conclusions.

Our theoretical approach is quite simple. We will attempt to reduce the myriad of properties regarding both amine and diluent in alkylcarbonate-forming water-lean solvents to two key parameters: the basicity of the amine, represented by its pKa, and the capacity for the diluent to dissociate into its conjugate base, represented by its pKs. Both pKa and pKs can then be used to map the performance of novel solvents.

pirit, this is a similar approach to what we have carried out in Wanderley and Knuutila (2020), where the performances of carbamate-forming water-lean solvents containing MEA were mapped based on the viscosity, dielectric permittivity, and Henry's coefficient of the diluent.

The novelty of this present approach is in providing a novel understanding of the phenomena involved in CO₂ absorption in water-lean solvents containing alkylcarbonate-forming agents. Let us consider the work of Barzagli et al. (2013), for example. In that paper, the authors compared the CO₂ absorption capacity of AMP/DEA blends with the diluents: (i) 1,2-propanediol + ethanol; (ii) ethylene glycol + methanol; (iii) 1-propanol; and (iv) methyl carbitol. The loading capacity of the solvents increased in the order (i) ≈ (iii) < (iv) < (ii). Though these AMP/DEA blends are not strictly bicarbonate-forming or alkylcarbonate-forming (i.e., DEA can and does form a carbamate), quick verification of a table of autoprotolysis constants (e.g., Table 1 Section 3) shows that these increase in the order 1-propanol < ethanol < methanol < ethylene glycol. Hence, it is reasonable that the formation of propyl carbonate is less favoured than that of ethyl carbonate, or of methyl carbonate for that matter. Our framework can shed new light over these results and provide an explanation for this series. Furthermore, though the addition of ethylene glycol to methanol in solvent (ii) was a measure taken by Barzagli et al. (2013) to balance solvent *volatility* and *viscosity*, we might add that it is a wise choice also in terms of solvent *capacity*, as ethylene glycol displays a remarkably low pKs. With this knowledge, one can perhaps carry out a more targeted, focused screening of new solvents for CO₂ absorption.

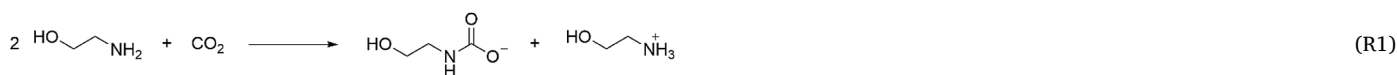
2. Theoretical framework

We will start this Section 2 by doing a quick overview of amine reactions with CO₂ in aqueous solvents (Section 2.1) before discussing the new mechanism that arises once water is shifted to an organic diluent (Section 2.2). Then, we shall provide a very quick mathematical interpretation of alkylcarbonate formation in nonaqueous solvents in Section 2.3. The culmination of this mathematical interpretation is a methodology to map the performance of alkylcarbonate-forming solvents, which is given in Section 2.4. Section 2.4 additionally includes a short historical review of empirical investigations on these novel solvents. Our methodology is then put to test in Sections 3 and 4.

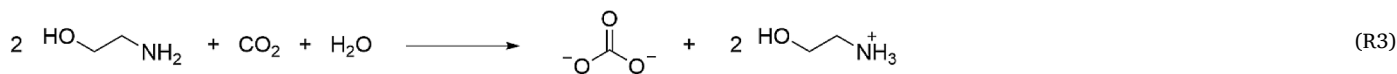
The scope and application of our theoretical framework is made very clear at the end of Section 2.4, where a numbered list of assumptions which *must* be respected for our treatment to be applicable is laid bare to the reader. However, we can start this Section 2 by surveying the two most important assumptions: a solvent that fits our treatment must be nonaqueous and non-carbamate-forming, i.e., either contain a tertiary amine or a heavily hindered secondary/primary amine. That is not to say that an extension of our treatment cannot be imagined for semi-aqueous solvents, or carbamate-forming solvents. However, that is not the scope of the present investigation. Whereof one cannot speak, thereof one must remain silent.

2.1. Amine reactions in aqueous solvents

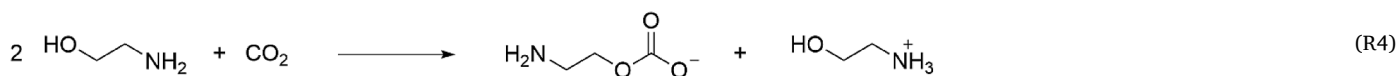
Let us consider an amine such as MEA. The carbamate pathway for CO₂ absorption into MEA is given by Eq. (R1). The bicarbonate pathway is given by Eq. (R2). As mentioned in Section 1, the carbamate pathway follows a 2 MEA:1 CO₂ stoichiometry, whereas the bicarbonate pathway follows 1 MEA:1 CO₂. Additionally, the bicarbonate pathway requires the presence of water in the milieu. This is so crucial that, for many years, researchers have stated the impossibility of any reaction between tertiary amines and CO₂ in nonaqueous solvents (Versteeg and van Swaaij, 1988). Such statement has been somewhat supported by empirical evidence (Li et al., 2014; Pohorecki and Mozeński, 1998).



Besides Eqs. (R1) and (R2), the carbonate pathway Eq. (R3) has been observed to take place to a small extent in aqueous solvents. It is particularly significant in strong basic solutions (Kortunov et al., 2015). In general, however, it is not very significant for CO₂ absorption purposes.



Finally, there is the alkylcarbonate mechanism. This mechanism can be regarded as a counterpart of the bicarbonate formation pathway, where, instead of the water being deprotonated and its conjugate (OH⁻) acting as a base, it is the alcohol group of the amine itself that deprotonates. This can be observed in Eq. (R4).



At a quick glance, this reaction is quite similar to the carbamate formation shown in Eq. (R1). The stoichiometry is once again 2 MEA: 1 CO₂. However, this reaction is heavily disfavoured when compared to that forming carbamate. Only quite recently have studies begun to show empirically that alkylcarbonate formation is present in aqueous solutions of MEA (Behrens et al., 2019; Cieslarova et al., 2018) and MDEA (Behrens et al., 2017). This is perhaps due to an oversimplified reading of the work of Jørgensen et al. (1954), who already in the 1950s proposed that alkylcarbonate formation is not quite relevant in aqueous

triethanolamine (TEA) solutions of pH < 10. Though this is certainly true, it does not follow that the alkylcarbonate reaction is *inexistent*. Nevertheless, it is correct that the amino group of an alkanolamine is a much stronger base than its alcohol group, and thus Eq. (R4) proceeds to a small extent when compared to Eq. (R1).

2.2. Alkylcarbonate formation in water-lean solvents

Another point about the work of Jørgensen et al. (1954) is that, though they approach alkylcarbonate formation within TEA molecules, they do not mention the possibility of alkylcarbonates being formed within the molecules of the *diluent*. They did not have a reason to mention that, since their studies were carried out in aqueous solvents. In

nonaqueous amine solutions, however, if one has a *protic* diluent, then the set of reactions Eqs. (R5)–(R7) can take place. In these reactions, SH denotes a protic diluent whereas HOB denotes an alkanolamine.



This is a very straightforward set of sequential reactions. The overall

balance of this set is given by Eq. (R8). The reader shall notice that if HOB is MEA and SH is water, then Eq. (R8) is just a general case of Eq. (R2). Conversely, if SH is methanol, then SCOO⁻ is simply methyl carbonate (CH₃OCOO⁻). Ethanol forms ethyl carbonate, 1-propanol forms propyl carbonate, and so forth. There is nothing inherently preventing protic solvents other than water from taking place in this mechanism.



And yet, it is safe to say that the formation of methyl carbonate is heavily disfavoured when compared to the formation of bicarbonate in a

corresponding aqueous solution. To explain why, let us consider the chemical equilibrium of Eq. (R5).

2.3. A simplified mathematical treatment

If the chemical equilibrium of Eq. (R5) is given by K_s , then $pK_s = -\log_{10}(K_s)$ is the so-called *autoprotolysis constant* of the diluent. Additionally, the chemical equilibrium of Eq. (R6) can be given by K_b , while the equilibrium of its reverse reaction is given by K_a , such as that $K_b = 1/K_a$. Then $pK_a = -\log_{10}(K_a) = \log_{10}(K_b)$. Finally, we will name the equilibrium constant of Eq. (R7) K_{sc} . With this in place, and calling K the equilibrium constant of the overall reaction Eq. (R8), then Eq. (1) shows how this equilibrium is affected by pK_s and pK_a .

$$K = \frac{K_s \cdot K_{sc}}{K_a} \quad (1a)$$

$$pK = -\log_{10}K = pK_s + pK_{sc} - pK_a \quad (1b)$$

The equilibrium constant K will achieve higher values if pK_s is small and pK_a is large. What this means is quite simply that the alkylcarbonate mechanism relies on having a diluent that is capable of easily letting go of its proton and an amine that can act as a strong base. With regards to K_{sc} , or pK_{sc} , there is not much that can be said at this moment. Nevertheless, since Eq. (R7) is an acid-base reaction where the base is the conjugate of SH, a strong base S^- will require a weak acid SH, which paradoxically might imply that pK_{sc} is *inversely proportional* to pK_s . For now, however, we will focus on pK_s and pK_a .

It is simple to find tables of pK_s and pK_a in literature. A comprehensive table of pK_s is given by Izutsu (2002) and by Rondinini et al. (1987). A comprehensive table of pK_a of typical amines employed for CO₂ capture is given by Bernhardsen and Knuutila (2017). It is important to notice that the pK_s of a diluent must be measured in pure solutions of that diluent, and that the pK_a of a base is measured in infinitely diluted aqueous solutions of that base, which critically means that neither the pK_s nor the pK_a found in chemical tables is strictly applicable to Eq. (1). However, these tabled values are a good indication of *patterns* that one might observe in real water-lean solvents.

In general, the pK_s of diluents increase in the order water < methanol < ethanol and so forth (Izutsu, 2002). Water is a typical amphiprotic substance, meaning it can act simultaneously as a Brønsted base and as a Brønsted acid, just as demanded by Eq. (R5). This probably has to do both with the electronegativity of its oxygen atom and with its excellent solvation properties, since any OH⁻ and H₃O⁺ species must be stabilized after being formed. Conversely, the basicity of an alkanolamine increases with the size of its carbon chains and decreases with the proximity between its amino group(s) and its alcohol group(s) (and also with the number of alcohol groups) (Kohl et al., 1997a). It is thus that propanolamine has a larger pK_a than ethanolamine and that TEA (3 alcohol groups) has a lower pK_a than MDEA (2 alcohol groups), which has a lower pK_a than N,N-diethylethanolamine (DEEA, 1 alcohol group) (Bernhardsen and Knuutila, 2017).

Therefore, it is not surprising that neither Pohorecki and Možeński (1998) nor Li et al. (2014) have observed alkylcarbonate formation in their solvents: the former worked with mixtures of TEA and propylene carbonate, whereas the latter worked with mixtures of MDEA and polyethylene glycol, neither diluent having a particularly low pK_s (Izutsu, 2002).

Additionally, alkylcarbonates might be formed internally amongst the alkanolamine molecules. Eqs. (R9) and (R10) present this sequence of reactions, which can be condensed in the overall reaction Eq. (R11). This is merely the mechanism discussed by Jørgensen et al. (1954). Eq. (R9) shows indeed the autoprotolysis of the alkanolamine, and its equilibrium constant might thus be called K_s' . Eq. (10) is an alkylcarbonate-forming reaction similar to Eq. (R7), and its equilibrium constant is K_{sc}' .



If the equilibrium constant of Eq. (R11) is named K' , then Eq. (2) can be used to estimate how K' varies with pK_s' and pK_{sc}' .

$$pK' = pK_s' + pK_{sc}' \quad (2)$$

In summary, nonaqueous solutions of tertiary amines are theoretically capable of chemically absorbing CO₂ either by forming an alkylcarbonate between CO₂ and the diluent, following Eq. (R8), or by forming an alkylcarbonate between CO₂ and the amine itself, following Eq. (R11). In reality, both mechanisms are possibly happening at the same time. We would suggest that the second mechanism is less important than the first, as one would expect a less amphiprotic behaviour from an alkanolamine than from an alcohol. However, this is up to discussion. Indeed, NMR analyses presented in Skylogianni et al. (2020) and in Wanderley et al. (2020b), both on solvents containing a tertiary amine mixed into ethylene glycol (MEG), show the formation of alkylcarbonates *both* amidst tertiary amine and glycol molecules. Finally, molecular CO₂ is certainly solubilized in these nonaqueous solutions. This is also particularly nonsignificant – Wong et al. (2016) demonstrate how physical solubilization of CO₂ in aqueous amine solvents happens on a small scale, and Yuan and Rochelle (2018) show how that solubility decreases in water-lean solvents.

2.4. Mapping amines and diluents for alkylcarbonate-forming solvents

It is perhaps fitting to introduce a brief history of empirical investigations on alkylcarbonate formation in nonaqueous solutions of hindered/tertiary amines. Sada et al. (1989) proposed alkylcarbonate formation between diluent and amine to explain their kinetics data in solvents containing TEA plus methanol, ethanol, and 2-propanol and treated their data accordingly. They were followed by Park et al. (2006a), who adopted the same approach to explain absorption data in solvents containing TEA plus a series of alcohols (and propylene carbonate). These authors later returned to the same array of diluents, only this time mixed with MDEA (Park et al., 2006b). In none of these three publications were the researchers able to prove the existence of alkylcarbonate formation, but merely to infer it based on kinetic data. To our knowledge, Barzagli et al. (2019, 2014, 2013) were amongst the first to use NMR spectroscopy in order to determine alkylcarbonate formation between CO₂ and alcohols in solvents containing AMP. Shortly thereafter, alkylcarbonate formation was identified by Chen et al. (2015) in mixtures of MDEA and ethanol. From the start of 2020 up to the present date alone, NMR studies showed alkylcarbonate formation in mixtures of MDEA and MEG (Skylogianni et al., 2020), DEEA and MEG (Wanderley et al., 2020b), 2-(tert-butylamino)ethanol (TBAE) and MEG (Li et al., 2020), and TEA and glycerol (Furtado et al., 2021). Quite recently, Chowdhury et al. (2020) published a very comprehensive report on their screening of alcohols and amines for elaborating a solvent that absorbs CO₂ via alkylcarbonate formation. At around the same time, a study by Sen et al. (2020) evaluated the utilization of a series of tertiary amines in ethylene glycol for a joint separation and conversion to methanol process. In other words, to say that studies focused on this particular mechanism of reaction have ramped up lately is an understatement.

Our discussion so far suggests that the pK_s of the diluent and the pK_a of the amine may be good indicators of the viability of alkylcarbonate formation in a nonaqueous solvent. However, very few of the publications referred in the last paragraph even mention the autoprotolysis constant. The idea that the autoprotolysis constant might be the key to explaining alkylcarbonate formation was proposed in the dissertation of Eimer (1994) 27 years ago. If our thought process can be trusted, the

implications of considering pK_a and pK_s as parameters for alkylcarbonate formation in nonaqueous solutions of tertiary amines may be summarized by the schematic representation shown in Fig. 1.

Fig. 1 is a simple consequence of Eq. (1), if and only if the equilibrium of Eq. (R7) pK_{sc} is not so inversely proportional to pK_s so as to shift the trend entirely. Essentially, it acknowledges that the capacity for alkylcarbonate formation in a nonaqueous tertiary amine solvent will depend on its diluent's capacity for auto-ionization and its amine's basicity. We hypothesize that CO_2 capacity in these solvents, measured by simple VLE studies, can give a measure of how strongly pK_a and pK_s are correlated to solubility phenomena. More specifically, it relies on a series of assumptions already discussed in the text:

- Carbamate formation is impossible (Sada et al., 1989; Versteeg and van Swaaij, 1988);
- Bicarbonate formation is irrelevant, i.e., the water content in these nonaqueous solutions can be deemed to be negligible;
- Physical solubility of CO_2 is not significant when compared to chemical solubility (Wong et al., 2016; Yuan and Rochelle, 2018);
- Alkylcarbonate formation within amine molecules is less significant than within diluent molecules (Jørgensen et al., 1954) (otherwise some difficult considerations with regards to Eq. (2) would have to be made);
- The values of pK_s and pK_{sc} are not so inversely proportional to the point that increases in pK_s provoke steeper decreases in pK_{sc} ;
- The values of pK_s and pK_a obtained in chemical tables can be extended to the context of CO_2 absorption in nonaqueous solvents, even though these do not refer to exactly equal conditions.

Of these assumptions, the most problematic ones are (ii), (v) and (vi). Since we have had no possibility of performing analytical characterisations of our samples, such as the Karl Fischer method for measuring water content, we cannot be completely sure that our solutions are entirely water-free. In fact, an NMR analysis of our nonaqueous DEEA + MEG solvent in a previous paper (Wanderley et al., 2020b) did identify trace amounts of HCO_3^- after CO_2 absorption. However, these trace amounts were not substantial enough to significantly affect the quality of our measurements back then, nor do we believe they should do so in the present case. Regarding issue (v), the relationship between pK_s and pK_{sc} is complex. The autoprotolysis constant reflects the equilibrium of a reaction wherein the diluent acts both as an acid and as a base.

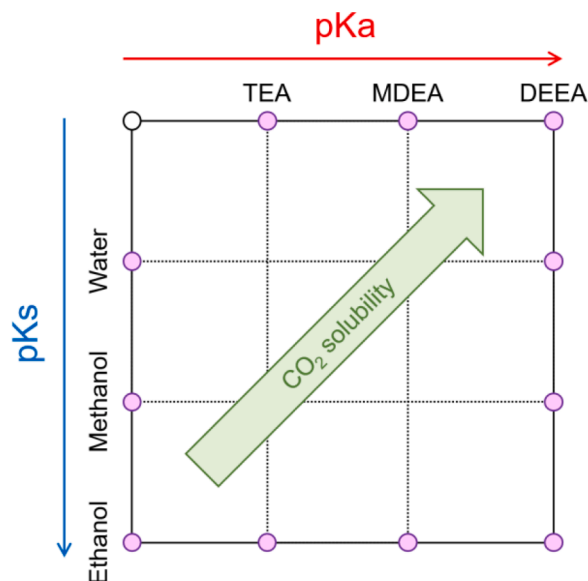


Fig. 1. Schematic representation of the $pK_a \times pK_s \times CO_2$ solubility hypothesis.

Meanwhile, the pK_{sc} reflects the equilibrium of a reaction where the conjugate of the diluent acts as a base, and thus this reaction is favoured if the diluent is a weak acid. Therefore, one might expect that a small pK_{sc} would imply a large pK_s and vice-versa. However, the autoprotolysis constant is a far more complicated affair than a simple balance between acidic/alkaline behaviour, and it also accounts for solvation phenomena and electrostatic forces (Farajtabar and Gharib, 2009; Ohtaki, 1973; Rondinini et al., 1987) amongst other aspects. We shall discuss this issue a bit further in Section 4. Finally, regarding the issue (vi), we might dismiss this problem by restating that we are not interested in obtaining quantitative data so much as in identifying patterns and trends, which should not be heavily affected by variations in pK_a and pK_s in real loaded amine solvents.

The advantage of this theoretical framework, assuming it works properly, is that one might thus be able to start designing an alkylcarbonate-forming solvent of moderately high CO_2 capacity simply by perusing pK_a and pK_s tables. The reasons for doing that can be more properly gaged by discussing the VLE data of these nonaqueous solvents, and we shall withhold this discussion for Section 4.

3. Experimental methodology

The experimental procedure for obtaining VLE data is similar to the one described by Skylogianni et al. (2020) and by Buvik et al. (2021). Fig. 2 shows a schematic representation of the apparatus.

The apparatus consists essentially of a CO_2 tank and a stirred cell reactor, both of which have pressure and temperature measured at every 5 s and logged into a computer. The maximum pressure in both is at around 600 kPa. The stirred cell reactor has its temperature controlled with a glycol bath supplied by Julabo GmbH, so that experiments can be carried at fixed setpoints between 20 °C and 120 °C. Pressures are measured with accuracies of ± 0.15 kPa, and temperatures are measured with accuracies of ± 0.1 °C. The volume of the CO_2 cylinder is 1158 ± 3 cm^3 , while that of the stirred cell is 1031 ± 16 cm^3 .

At the start of each experiment, a known amount of fresh solvent (around 500 cm^3) is loaded into the reactor. The mass of the solvent is measured accurately, so that one can be sure of how many mols of amine are inside the stirred cell. A vacuum pump is employed to degas the solvent, and at the end of three cycles of vacuuming we are left only with the vapour pressure of the pure solution in the vapour phase. The stirrer is then set to 500 rpm while a temperature setpoint is chosen. Most of the experiments described in this work were carried at a setpoint of 40 °C.

Each injection consists of opening the valve connecting the CO_2 cylinder to the stirred cell reactor for a certain amount of time and then closing it. With this, pressure in the cylinder goes down and pressure in the stirred cell goes up. Since we know temperatures, pressures and volumes of both the cylinder and the vapour phase of the reactor, we are able to calculate their CO_2 mol number with an equation of state. In this work, we have employed the Peng-Robinson equation of state for such calculations. Notice that this implies subtracting the partial pressure of pure solvent inside the stirred cell, which requires the underlying

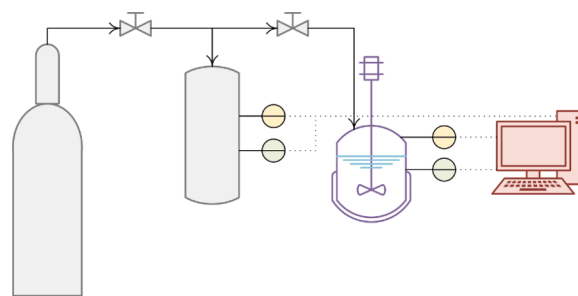


Fig. 2. Schematic representation of VLE apparatus. Adapted from Buvik et al. (2021).

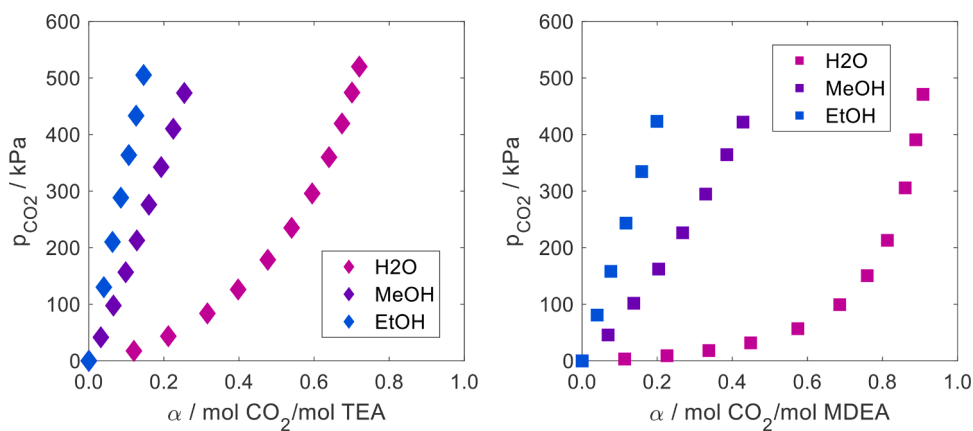


Fig. 3. Vapour-liquid equilibrium at 40 °C for solvents containing water, methanol or ethanol as diluents. On the left, solvents based on 7 molal TEA. On the right, solvents based on 7 molal MDEA.

assumption that solvent partial pressure does not change with CO₂ loading. Finally, the CO₂ that has left the cylinder and that cannot be accounted for in the vapour phase of the stirred cell must have been absorbed by the liquid. The CO₂ loading after each injection is calculated by this procedure. Since each injection requires pressure and temperature stabilities in order for us to obtain accurate data, the period between each injection is of 4–8 h and experiments might easily take up to 5 days to be completed. This apparatus is well trustable, and VLE results of its experiments have been validated repeatedly by Skylogianni et al. (2020) for example.

We often report that this experiment produces total pressure (p) \times CO₂ loading (α) data, and not partial pressure (p_{CO_2}) \times CO₂ loading (α) data. This is because one must subtract the partial pressure of the solvent from p to obtain p_{CO_2} , which requires the assumption of constant solvent partial pressure. However, we must highlight that even the calculation of α requires the assumption of constant solvent partial pressure, otherwise one would not be able to perform the mass balance in the vapour phase. This can be problematic if there are low pressure increases after each injection, something typical of very reactive amines, because then fluctuations in solvent partial pressure might significantly affect the resulting VLE data. Fortunately for us, the tertiary amines employed in this study are often not very reactive, and the pressure increases after each injection are usually quite meaningful.

Table 1 shows relevant information on the amines and diluents employed in this study. All chemicals, with the exception of deionized water, have been supplied by Sigma-Aldrich. The pKa in Table 1 were obtained in Bernhardsen and Knuutila (2017), and the pKs were obtained in Izutsu (2002). The pKs of tetrahydrofurfuryl alcohol was not found anywhere in the literature, but we still felt inclined to test this particular organic diluent due to its interesting properties for water-lean solvent formulations (Wanderley et al., 2020a).

As discussed in Section 2, most of the organic diluents employed in our experiments are known to be hygroscopic, which means that they might contain trace amounts of water at the end of the experiments. We have tried to minimize this factor by opening new bottles of diluents for each solvent preparation, and by keeping solvent bottles insulated with a plastic film. As previously mentioned, we do not believe these trace amounts to have a significant effect on the VLE patterns obtained in this study.

4. Results and discussion

4.1. VLE data correlating pKa, pKs and CO₂ solubility

All VLE results provided in this section via graphical form are also presented in the Appendix, together with their uncertainties, as data tables. We will only present $p_{\text{CO}_2} \times \alpha$ in these figures, with the caveat

that CO₂ partial pressure is not directly measured (as already mentioned in Section 3), in order to facilitate the discussion. Total pressure data can also be found in the Appendix.

Following our hypothesis, it is appropriate to investigate a series of solvents based on tertiary amines of very distinct pKa and diluents of very distinct pKs. Let us begin with the series first suggested in Fig. 1. The amines TEA, MDEA and DEEA have pKa of respectively 7.85, 8.65 and 9.75 (Bernhardsen and Knuutila, 2017). Meanwhile, water, methanol and ethanol have pKs of respectively 14, 16.71 and 18.9 (Izutsu, 2002). If our hypothesis is on the right track, it should be possible to observe the CO₂ solubility prediction shown in Fig. 1 empirically.

Fig. 3 illustrates the VLE results obtained at 40 °C with solvents based on 7 molal TEA and MDEA (i.e., 7 mols of amine in 1 kilogram of pure diluent) with water, methanol and ethanol. The axes of both graphs are fixed at the same proportions, so that CO₂ solubility can be visually gaged by how much each VLE curve leans to the right side of the graph. Each graph contains the datapoints for solvents with different diluents and a single amine. Clearly, in both cases, CO₂ solubility in the aqueous solvent surpasses that of the methanolic solvent, which surpasses that of the ethanolic one. This is consistent with our hypothesis that lower values of pKs mean higher CO₂ solubilities. Additionally, a comparison between the graphs shows that, for any given diluent, the CO₂ solubility when the amine is MDEA is higher than that when the amine is TEA. This is consistent with our hypothesis that higher values of pKa mean higher CO₂ solubilities. A corollary of this is that, for aqueous solutions of tertiary amines, CO₂ solubility is merely a function of amine basicity. This is a well-known fact that has been previously discussed by

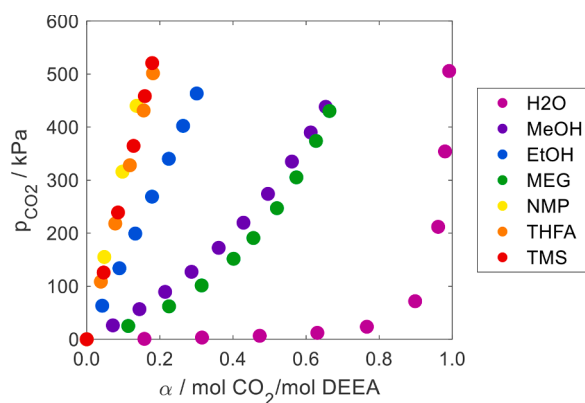


Fig. 4. Vapour-liquid equilibrium at 40 °C for solvents containing 7 molal DEEA in water, methanol, ethanol, ethylene glycol, N-methyl-2-pyrrolidone, tetrahydrofurfuryl alcohol or sulfolane.

Bernhardsen and Knuutila (2017), amongst others.

Fig. 4 shows the VLE results for solvents based on 7 molal DEEA. Since DEEA is a stronger base than TEA and MDEA, its effect on CO₂ solubility is strong enough for us to feel confident in trying a larger set of diluents. These diluents are water, methanol, ethanol, ethylene glycol (pKs = 15.84), N-methyl-2-pyrrolidone (pKs ≥ 24.2), sulfolane (pKs = 24.45) (Izutsu, 2002) and tetrahydrofurfuryl alcohol. If ethylene glycol has a low pKs, even below that of methanol, the three last diluents have very high values of pKs. N-methyl-2-pyrrolidone and sulfolane are considered *aprotic* compounds due to the fact that they do not possess a hydrogen atom attached to an electronegative atom, and thus auto-ionization is quite disfavoured. Meanwhile, though tetrahydrofurfuryl alcohol does have a hydrogen atom attached to an oxygen atom, and although one can find sources in literature defining this compound as *protic*, we have been unable to find a value for its pKs. However, one might expect that the bulkiness of its furan ring reduces the electronegativity of the oxygen atom, which could mean its pKs is not particularly low. And indeed, the CO₂ solubilities in the solvents presented in Fig. 4 follows the order water > MEG > MeOH > EtOH > NMP ≈ TMS ≈ THFA. Not only this, but for water, methanol and ethanol as diluents, it can be observed that solvents with 7 molal DEEA absorb more CO₂ than their counterparts with MDEA and TEA (Fig. 3). Therefore, the pattern expected from Fig. 1 is observed empirically.

Any suspicions that what one is observing in Fig. 4 is merely the physical solubility of CO₂ in a series of different diluents should be quickly dismissed for several reasons. A first reason is that the VLE curves in Fig. 4 do not always follow the Henry's law approach to physical absorption, according to which CO₂ solubility should increase linearly with CO₂ partial pressure. Although this linear behaviour can be somewhat observed for all aprotic diluents, the curves of methanolic (purple circles) and glycolic (green circles) solvents present a clear positive inflection typical of chemical absorption phenomena. A second reason is that the order of solubilities in Fig. 4 does not follow the order of solubilities for pure organic diluents: the solubility of CO₂ in pure methanol and in pure N-methyl-2-pyrrolidone should be above that of CO₂ in pure ethylene glycol (Williams, 2007), and yet the glycolic solvent outperforms most mixtures in Fig. 4. Finally, comparison between Figs. 3 and Fig. 4 shows that the solubility of CO₂ in a certain alcohol + alkanolamine is quite diverse depending on whether the amine is TEA, MDEA or DEEA. Since molalities are kept constant in our experiments and these amines have similar molar weight (TEA = 149.2 g/mol, MDEA = 119.2 g/mol, DEEA = 117.2 g/mol), one would expect solubilities to be similar in case there was no chemical reaction. Their stark differences is a strong evidence of the fact that the tertiary amines are reacting in nonaqueous media. A more direct comparison between the physical solubility of CO₂ in ethylene glycol and in N-methyl-2-pyrrolidone with that in nonaqueous amine solvents containing these

diluents is given in our previous work (Wanderley et al., 2020b).

For all solvents in Figs 3 and 4, what we call CO₂ solubility is not a single value but a function of p_{CO2}. Once we fix p_{CO2} = 100 kPa, however, we can determine single values for all CO₂ solubilities. These values are shown in Fig. 5 for all previous solvents shown in Figs. 3 and 4, with the exceptions of DEEA + TMS and DEEA + THFA so as not to render the image excessively confusing.

Fig. 5 is a collection of empirically obtained data that supports the hypothesis presented on Fig. 1. This is a good indication that our hypothesis is at least acceptable in explaining the real phenomena of alkylcarbonate formation in nonaqueous solutions of tertiary amines. It also shows that pKa and pKs do not have the same influence in CO₂ solubility. It seems that pKs is almost entirely dominant in enabling CO₂ absorption in the solvent. Once we screen all different organic diluents and arrive at water, which has the lowest pKs amongst the ones tested so far, then the pKa of the amine acquires a huge influence on CO₂ absorption capacity.

4.2. Temperature dependence of CO₂ solubility and enthalpy of absorption

Many researchers presently studying alkylcarbonate-forming nonaqueous mixtures mention the possibility of regenerating their solvents at low temperatures. To assess this possibility, we have chosen the solvent MEG + 7 molal DEEA to evaluate its VLE performance at 60 °C, 80 °C and 100 °C. We have done the same for aqueous 7 molal DEEA. This gives us an opportunity to estimate its cyclic loading (i.e., Δα = the difference between rich and lean loadings) and also its enthalpy of absorption via the van 't Hoff equation. This is because the van 't Hoff equation allows us to approximate the enthalpy of absorption in a solvent by Eq. (3).

$$\frac{d \ln p_{CO_2}}{dT} = \frac{\Delta H}{R \cdot T^2} \quad (3)$$

The differential in Eq. (3) must be calculated at constant speciation conditions, meaning that the variation of CO₂ partial pressure with temperature must be evaluated while all chemical species in the solvent are fixed. The chemical activities should also be kept fixed. An explanation of the necessary assumptions is given by Sherwood and Prausnitz (1962) and also by Svendsen et al. (2011), as well as an explanation on the shortcomings of the van 't Hoff equation. However, this procedure will serve us as a preliminary estimation.

In order to employ the van 't Hoff equation, we require an expression that correlates p_{CO2} with temperature and speciation (or with α, if one assumes that same loadings imply same speciation). This is provided by the *soft-model* (Aronu et al., 2014), Eq. (4).

$$\ln p_{CO_2} = A \cdot \ln \alpha + k_1 + \frac{B}{1 + k_2 \cdot \exp(-k_3 \cdot \ln \alpha)} \quad (4a)$$

$$k_1 = \frac{k_{1,1}}{T} + k_{1,2} \quad (4b)$$

$$k_2 = \exp\left(\frac{k_{2,1}}{T} + k_{2,2}\right) \quad (4c)$$

$$k_3 = \frac{k_{3,1}}{T} + k_{3,2} \quad (4d)$$

In Eq. (4), the parameters A, B, k_{1,1}, k_{1,2}, k_{2,1}, k_{2,2}, k_{3,1} and k_{3,2} must be obtained by fitting of the available solubility data. This requires a fair amount of empirical data. Once this data is obtained, however, the fitting can be simply carried out through a *particle swarm optimization* (PSO) algorithm much like the one employed in our previous works (Evjen et al., 2019; Skylogianni et al., 2019). Finally, differentiation of Eq. (4) with temperature and fixed α yields Eq. (5).

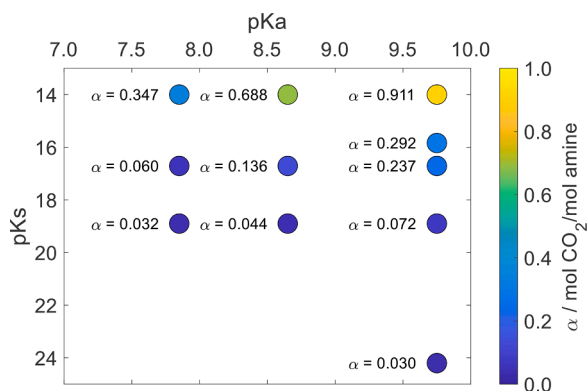


Fig. 5. Solubilities of CO₂ at 40 °C and p_{CO2} = 100 kPa in solvents containing 7 molal amines with distinct pKa and diluents with distinct pKs.

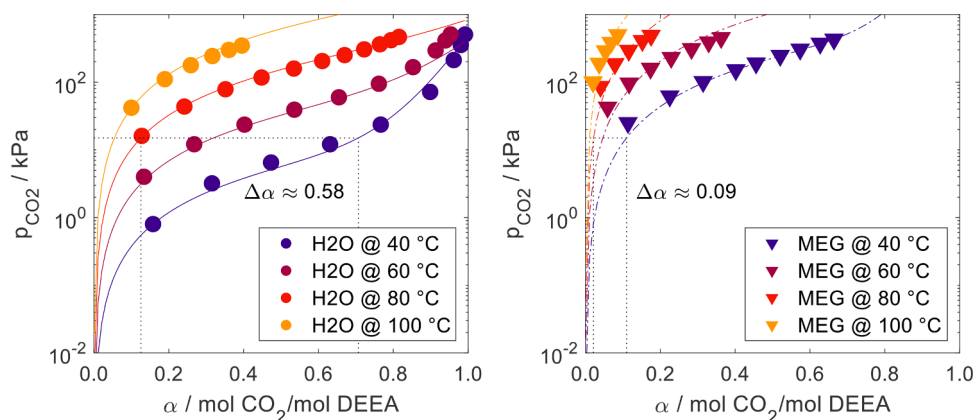


Fig. 6. Vapour-liquid equilibrium at 40, 60, 80 and 100 °C for solvents based on 7 molal DEEA. On the left, solvents containing water. On the right, solvents containing ethylene glycol. Estimations via the soft-model Eq. (4) based on the parameters presented in Table 2 are also shown in the plots. The cyclic capacity defined by Eq. (6) is sketched by dotted lines.

$$\frac{d \ln p_{CO_2}}{dT} = \frac{dk_1}{dT} + \frac{B \cdot \exp(-k_3 \cdot \ln \alpha)}{(1 + k_2 \cdot \exp(-k_3 \cdot \ln \alpha))^2} \cdot \left(k_2 \cdot \ln \alpha \frac{dk_3}{dT} - \frac{dk_2}{dT} \right) \quad (5a)$$

$$\frac{dk_1}{dT} = -\frac{k_{1,1}}{T^2} \quad (5b)$$

$$\frac{dk_2}{dT} = -\frac{k_{2,1}}{T^2} \exp\left(\frac{k_{2,1}}{T} + k_{2,2}\right) \quad (5c)$$

$$\frac{dk_3}{dT} = -\frac{k_{3,1}}{T^2} \quad (5d)$$

Therefore, Eqs. (3)–(5) will be henceforth employed for evaluating the enthalpy of absorption in our two solvents. The data obtained experimentally, together with the soft-model fitting, is shown in Fig. 6. The fitting of parameters was performed by minimization via PSO of the average absolute relative deviation (AARD) between empirical and estimated p_{CO_2} for both the aqueous and the glycolic solvent. Values of AARD thus obtained are 12.3% for aqueous 7 m DEEA and 17.6% for MEG + 7 m DEEA, which indicates a moderately good fitting. The soft-model parameters are given in Table 2.

There are different ways of estimating the cyclic loading of a solvent. Amongst others, Bernhardsen and Knuutila (2017) suggest the Eq. (6). This expression defines the lean loading as the loading in equilibrium with 15 kPa of CO_2 at 80 °C and the rich loading as that in equilibrium with 15 kPa of CO_2 at 40 °C.

$$\Delta \alpha = \alpha_{40^\circ C, 15kPaCO_2} - \alpha_{80^\circ C, 15kPaCO_2} \quad (6)$$

The lean and rich loadings defined by Eq. (6) are sketched in Fig. 6. In aqueous 7 m DEEA, lean loading is evaluated at $\alpha = 0.1257$ and rich loading at $\alpha = 0.7065$ mol CO_2 /mol DEEA. In the mixture of ethylene glycol, lean loading is evaluated at $\alpha = 0.0214$ and rich loading at $\alpha = 0.1098$ mol CO_2 /mol DEEA. With this, the cyclic capacity $\Delta \alpha$ of the aqueous solvent is about six times higher than that of the glycolic solvent.

Table 2
Soft-model parameters for solvents evaluated in this study.

	H2O + 7 m DEEA	MEG + 7 m DEEA
A	1.665	1.783
B	7.901	11.307
$k_{1,1}$	-9154.06	-8058.10
$k_{1,2}$	32.082	32.378
$k_{2,1}$	-6144.47	-6142.91
$k_{2,2}$	19.939	20.218
$k_{3,1}$	7527.59	7529.45
$k_{3,2}$	-17.779	-14.958

By looking at Fig. 6, one can see that the distance between the VLE curves of the MEG + DEEA solvent becomes large at higher CO_2 partial pressures, but is comparatively very small for low CO_2 partial pressures (e.g., compare blue and orange curves in the right-side plot). If Eq. (6) was evaluated at a higher p_{CO_2} , for example $p_{CO_2} = 500$ kPa, then MEG + DEEA could have fared better than aqueous DEEA. However, it would only make sense to evaluate a lean loading in equilibrium with 500 kPa of CO_2 if absorption were to be carried under high pressures. What this means is that the alkylcarbonate-forming solvent might have a higher cyclic capacity than the aqueous solvent if one considers pre-combustion CO_2 capture of natural gas (where pressures can be quite high, see Arinelli et al. (2017)) or if the CO_2 capture system were to operate under a pressure swing loop typical of physical solvents (Hochgesand, 1970).

The enthalpy of absorption of MEG + DEEA was projected with Eq. (5) and compared to that of aqueous DEEA. These projections are shown in Fig. 7. The aqueous solvent was evaluated as having $-\Delta H \approx 76.1$ kJ/mol CO_2 , whereas the glycolic solvent was evaluated as having $-\Delta H \approx 67.0$ kJ/mol CO_2 . This is a small difference, and it must be noted that authors such as Lee et al. (1974) estimate that enthalpies of absorption obtained through the van 't Hoff equation might have uncertainties upwards of $\pm 20\%$ depending on the accuracy of the VLE data, meaning that the results shown in Fig. 7 could be quite inconclusive. However, we should mention that our previous calorimetric experiments also pointed towards MEG + DEEA having a lower enthalpy of absorption than aqueous DEEA (though amine concentrations in those experiments were below 7 molal) (Wanderley et al., 2020b). Therefore, predictions of Eq. (6) and empirical calorimetric data are at least qualitatively consistent.

Therefore, it can be concluded that this particular alkylcarbonate-forming mixture has, comparatively with regards to the corresponding aqueous solvent:

- Lower cyclic capacity $\Delta \alpha$ at low CO_2 partial pressures;
- Higher or equivalent cyclic capacity $\Delta \alpha$ at high CO_2 partial pressures;
- Lower enthalpy of absorption.

It is unknown if these points apply to every other alkylcarbonate-forming solvent addressed in this work, but we have no reasons to believe that the DEEA-glycol formulation would behave particularly differently from the other mixtures. These three points taken in conjunction indicate that the development of alkylcarbonate-forming solvents that would perform better than benchmark aqueous amine solvents will be very challenging for post-combustion CO_2 -capture with low CO_2 partial pressure in the gas. Accordingly, in this work, to explore the advantages of an alkylcarbonate-forming solvent, we shall treat it as a variant of a physical solvent.

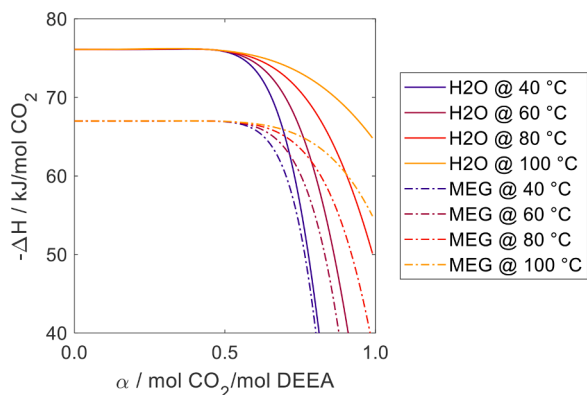


Fig. 7. Enthalpy of absorption obtained for 7 molal DEEA in water and in ethylene glycol following soft-model approximation Eq. (5) with parameters presented in Table 2.

4.3. Possible industrial applications

Fig. 8 shows an interpretation of the work of Hochgesand (1970) regarding the configuration of a physical solvent-based CO₂ capture plant. The absorption-desorption cycle is performed by pressure swing, meaning that absorption is carried out at high CO₂ partial pressures and desorption is carried out by reduction of pressure (plus addition of moderate levels of low-grade heat). The main distinctions between this process configuration, when compared to the standard aqueous amine solvent process configuration, are:

- i. The absorber operates at *high pressures* (e.g., above 8 bars (Bucklin and Schendel, 1985));
- ii. Depending on the delivery pressure of the acid gas, this requires *pre-compression* of the gas;
- iii. Due to absorption at high pressures, not only CO₂ will be solubilized in the solvent, which will commonly require *one or more levels of flashing* for reducing slip-gas levels;
- iv. Desorption is carried out with low-grade heat in a *flash vessel*, not in a desorber column, as the lack of solvent vaporization would not warrant the installation of a stripping column. The flash vessel operates at low pressures and moderately high temperatures (e.g., 1 bar and 80 °C).

A good review on physical solvents and techniques for operating pressure-swing absorption is given by Bucklin and Schendel (1985) and by Hochgesand (1970) respectively. Bauer et al. (2013) shows that physical absorption plants incur in more usage of electrical energy (to drive pumps and compressors) though less usage of thermal energy (to

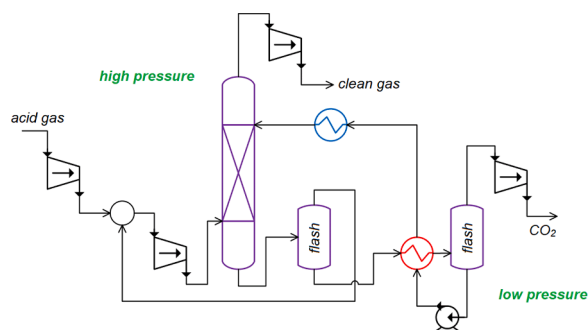


Fig. 8. Suggested process configuration from a physical solvent/alkylcarbonate-forming solvent.

regenerate the solvent) when compared to chemical absorption plants.

As mentioned previously, the configuration shown in Fig. 8 can be particularly advantageous for CO₂ removal of natural gas, since the acid gas is then delivered already at high pressures. This point is supported by Kidnay and Parrish (2006) for example. Additionally, Carranza-Abaid et al. (2021) have recently demonstrated that the configuration shown in Fig. 8 might also be appropriate for the case of biogas upgrading to biomethane, because in this scenario the “clean gas” (i.e., biomethane) must often be delivered at high pressures, so that the energy for pre-compression of the acid gas is not completely wasted.

Alkylcarbonate-forming solvents, at least to the extent of the example of MEG + 7 molal DEEA, should be treated similarly to physical solvents inasmuch as they present high cyclic capacity when operating between high CO₂ partial pressures and require comparatively low heat input at low temperatures for solvent regeneration. Therefore, we suggest that, if this brand of water-lean solvents is to have a future in CO₂ capture applications, this will probably exist in the context of natural gas treating or biogas upgrading. Meanwhile, comparison with aqueous amine solvents in the context of post-combustion CO₂ capture will most likely not fare well for alkylcarbonate-forming solvents.

Moreover, it must be noted that Fig. 8 might apply for the MEG + 7 molal DEEA solvent due to its low volatility. Conversely, if the solvent volatility is high, e.g., if the absorbent is prepared using alcohols such as methanol or ethanol, then additional stages of cooling and recovering of solvent carry-overs might be required. This will undoubtedly increase the complexity of the process.

It is difficult for us to forecast how the real performance and stability of a nonaqueous alkylcarbonate-forming solvent would appear in an industrial facility. However, we must point out that (i) knowledge of practical operations with water-lean solvents is currently on the rise (Gupta et al., 2021; Rabindran et al., 2021) and (ii) knowledge of practical operations with organic physical solvents is well-established (Kohl et al., 1997b; Palla and Leppin, 2003). Additionally, the stability of most amines mentioned in this study is already well understood in aqueous systems (Lepaumier et al., 2009a, 2009b), whereas their stability in nonaqueous systems is currently under investigation (Høisæter and Knuutila, 2019; Shoukat et al., 2019). Again, we must remark that only practical, empirical investigations will enable the use of alkylcarbonate-forming solvents in real-world applications.

As a final note, one should mention that the development of alkylcarbonate-forming solvents coupling a strong base with an alcohol is precisely what led to the development of the ‘switchable solvents’ by the Pacific Northwest National Laboratory (PNNL) (Jessop et al., 2005; Phan et al., 2008). These were originally mixtures of guanidines or amidines, i.e., extremely strong bases, with alcohols such as hexanol. In a later development, the group from the PNNL decided to condense the alcohol and the base into a same molecule, thus creating the 2nd generation of CO₂BOLs (Heldebrant et al., 2011, 2010). This brand of solvents has recently struggled with high viscosity issues (Cantu et al., 2017; Zheng et al., 2016). It is likely that alkylcarbonate-forming solvents such as those described in the present study would also have high viscosities when compared to aqueous amine solvents.

4.4. Limitations of the pKa × pKs framework

The theoretical framework presented in Section 2 adheres pretty well for diluents with pKs above that of water (pKs = 14) as shown in Section 4.1. However, it begins to fail when one considers solvents with pKs below that of water. Pure formic acid, for example, has pKs ≈ 6 (Izutsu, 2002; Rondinini et al., 1987). Meanwhile, while mixtures of water with alcohols tend to have autoprotolysis constants with values between those of pure water and pure alcohol (Åkerlöf, 1932; Rondinini et al., 1987), the same does not apply to water + ethylene glycol mixtures, which have a clear minimum of pKs between pKs ≈ 13–14 at low MEG concentrations (Banerjee et al., 1967; Izutsu, 2002). Following our framework, a mixture of ethylene glycol, water and a tertiary amine

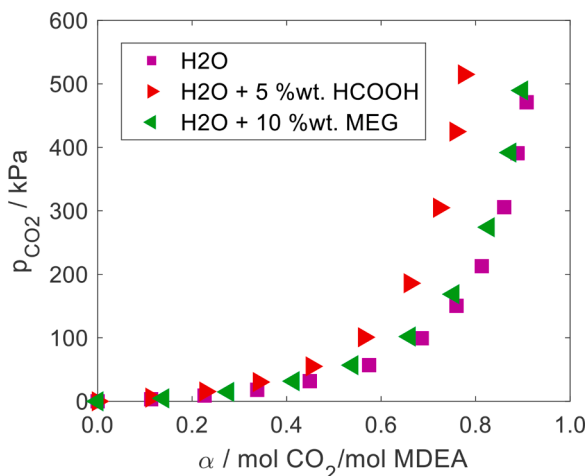


Fig. 9. Vapour-liquid equilibrium at 40 °C for solvents containing 7 molal MDEA in water, water + 5%wt. of formic acid and water + 10%wt. of ethylene glycol.

should have *more* capacity for CO₂ absorption than the corresponding aqueous amine. However, this is not observed in practice.

Fig. 9 shows the VLE behaviour of solvents containing 7 molal MDEA and different diluents at 40 °C. These diluents are water, then water + 5%wt. formic acid and water + 10%wt. ethylene glycol, these latter supposedly having a pKs above that of pure water. (In hindsight, we have no clear knowledge on whether mixtures of formic acid and water have a low pKs, and it is perhaps a stretch to assume that the pKs of this solvent should fall in between that of pure water and that of pure formic acid.) In all of these mixtures, the addition of a co-solvent to the mixture engendered a *reduction* of CO₂ solubility. This could be due to chemical equilibrium issues or due to solvation issues, as discussed in our previous papers (Wanderley et al., 2021, 2020a). What is clear, however, is that these counterexamples contradict the pKa × pKs approach shown in Section 2.

To discuss the reasons behind this limitation, we can perhaps focus on the example of water + formic acid + MDEA since it is the most extravagant one. Clearly, no one would expect that adding an acid to an amine solvent would increase its capacity for CO₂ capture. What is happening is that the formic acid undergoes an acid-base reaction with MDEA and the resulting formate anion, which is the basic conjugate of formic acid, is simply not basic enough to react with CO₂ at any considerable rate. This plays back to what has been mentioned with regards to pKsc in Section 2: the equilibrium of the reaction between S⁻ and CO₂ is favoured if S⁻ is a strong base, meaning SH is a weak acid.

Our whole focus on the autoprotolysis constant is a consequence of the demand that the diluent be somewhat amphiprotic, since (i) it must be acidic enough to deprotonate and (ii) it must be not-acidic enough so that the resulting conjugate base is a strong base. That is to say, *even if Eqs. (R5)–(R6) do not take place*, and instead the diluent SH reacts directly with the base HOB, the pKs of the diluent is a better measure of its reactivity than its acidity (i.e., pKa), since there is a duality between it being an acid in the first half of the alkylcarbonate mechanism and its conjugate being a base in the second half. However, it seems that even the autoprotolysis constant is not enough to explain the behaviour of the diluent in cases where its pKs is below that of water.

We might point out, however, that there are a couple of patents from C-Capture Ltd. that mention the use of carboxylate anions as bases for CO₂ capture (Barnes et al., 2019; Rayner et al., 2017). Nevertheless, in both these patents the basicity of the carboxylates is increased either by the use of organic co-solvents (Rayner et al., 2017) or particularly high

carboxylate concentrations in aqueous media (Barnes et al., 2019).

Banerjee et al. (1967) show that the measured autoprotolysis of the ethylene glycol + water solvent is actually the product of a series of parallel reactions. It is not unexpected that this increase in complexity of the reacting milieu might push the theoretical framework presented in Section 2 beyond its reach. Meanwhile, one could argue that aqueous mixtures of formic acid have no amphiprotic behaviour whatsoever – instead, they quite clearly have an *acidic* behaviour. Therefore, we cannot affirm that the results shown in this section invalidate the pKa × pKs approach. However, they certainly show that this approach should be taken with nuance. The pKa × pKs correlation can be applied to binary mixtures of protic solvents and tertiary amines for quick evaluation purposes, but its application to ternary mixtures is questionable and should be further verified.

5. Conclusion

Alkylcarbonate formation is an alternative mechanism of reaction to carbamate and bicarbonate formation. It is most easily observed in nonaqueous solvents of tertiary or hindered amines, and requires a reaction between the amine and a protic diluent followed by the reaction between the conjugate base of the diluent with CO₂. As such, the enthalpy of absorption following this mechanism is diverse from that following other mechanisms. Our studies so far suggest that this enthalpy of absorption is possibly lower in alkylcarbonate-forming nonaqueous solvents than in their corresponding aqueous solvents. This comes at the price of a lower solvent cyclic capacity at low CO₂ partial pressures. For this reason, nonaqueous solvents that follow the alkylcarbonate pathway might be more suitable for processes akin to that of physical solvents, i.e., absorption at high CO₂ partial pressures and desorption at low pressures with moderate input of low-grade heat. This might be promising for biogas upgrading and natural gas sweetening purposes, though an in-depth assessment is required.

The CO₂ capture capacity of a nonaqueous alkylcarbonate-forming solvent can be correlated with the amphiproticity of its diluent (represented by its pKs) and by the basicity of the amine (represented by its pKa), insofar as CO₂ solubility increases with pKa and decreases with pKs. This trend can be used to estimate the behaviour of theoretical alkylcarbonate-forming solvents in the absence of experimental data, though experimental data is ultimately essential for assessing the performance of any new formulation.

In summary:

- One should pay attention to amine basicity and diluent autoprotolysis when designing an alkylcarbonate-forming water-lean solvent with reasonable CO₂ capture capacity.
- The resulting solvent will quite probably never have the same capacity for CO₂ capture as its aqueous solvent counterpart; one can simply hope for a reduction in the enthalpy of absorption.
- Following van 't Hoff, a reduction in enthalpy of absorption will probably mean a reduction in cyclic capacity in the traditional temperature swing process.
- As a consequence of the point above, a pressure swing is perhaps suggested for operating with these solvents. That is to say, they could be considered variants of physical solvents (e.g., Genosorb™, Purisol™) for scrubbing operations.

The theoretical framework developed in this study is not complete, but it gives important hints towards the understanding and development of novel water-lean solvents for CO₂ capture.

CRedit authorship contribution statement

Ricardo R. Wanderley: Conceptualization, Methodology, Validation, Investigation, Writing – original draft, Writing – review & editing.
Karen K. Høisæter: Conceptualization, Writing – review & editing.
Hanna K. Knuutila: Methodology, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix

This Appendix presents [Table A.1](#), [Table A.2](#), [Table A.3](#) and [Table A.4](#) with vapour-liquid equilibrium data obtained in this research. Total pressures are directly measured via pressure transducers and have uncertainties of ± 0.15 kPa. On the other hand, CO₂ partial pressures are obtained through a subtraction operation involving two total pressure values, having thus uncertainties of ± 0.21 kPa. Loadings have expanded uncertainties with 95% level of confidence of around 10% (i.e., $\pm 5\%$ of their given value). This uncertainty estimate is obtained through a mixed calculation of inherent inaccuracies and repeatability studies described in detail in a previous paper ([Dawass et al., 2020](#)).

Table A.1

Vapour-liquid equilibrium data for TEA-based solvents at 40 °C.

Water + 7 molal TEA at 40 °C		
α / mol CO ₂ /mol TEA	p / kPa	p _{CO2} / kPa
0	7.2	–
0.12	24.8	17.6
0.21	50.7	43.5
0.32	91.0	83.9
0.40	133.3	126.2
0.48	185.8	178.7
0.54	242.3	235.1
0.59	303.1	295.9
0.64	367.1	359.9
0.67	426.7	419.6
0.70	481.4	474.3
0.72	527.3	520.1
Methanol + 7 molal TEA at 40 °C		
α / mol CO ₂ /mol TEA	p / kPa	p _{CO2} / kPa
0	30.2	–
0.032	71.9	41.6
0.066	128.0	97.7
0.098	186.9	156.6
0.13	243.1	212.9
0.16	306.3	276.0
0.19	372.7	342.5
0.22	440.5	410.3
0.25	503.8	473.5
Ethanol + 7 molal TEA at 40 °C		
α / mol CO ₂ /mol TEA	p / kPa	p _{CO2} / kPa
0	15.4	–
0.040	145.6	130.2
0.063	225.5	210.2
0.085	303.7	288.4
0.11	379.1	363.7
0.13	448.7	433.3
0.15	520.6	505.2

Table A.2

Vapour-liquid equilibrium data for MDEA-based solvents at 40 °C.

Water + 7 molal MDEA at 40 °C		
α / mol CO ₂ /mol MDEA	p / kPa	p _{CO2} / kPa
0	7.3	–
0.11	10.5	3.2
0.23	16.3	9.1
0.34	25.4	18.2
0.45	39.0	31.8
0.57	64.2	56.9
0.69	106.6	99.3
0.76	157.7	150.5
0.81	220.2	213.0
0.86	313.0	305.7
0.89	398.0	390.8
0.91	478.3	471.0
Methanol + 7 molal MDEA at 40 °C		
α / mol CO ₂ /mol MDEA	p / kPa	p _{CO2} / kPa
0	29.8	–
0.069	75.6	45.8
0.14	131.6	101.8
0.20	192.0	162.2
0.27	256.1	226.3
0.33	324.7	294.8
0.39	394.1	364.3
0.43	451.8	422.0
Ethanol + 7 molal MDEA at 40 °C		
α / mol CO ₂ /mol MDEA	p / kPa	p _{CO2} / kPa
0	15.0	–
0.040	95.8	80.8
0.077	173.1	158.2
0.12	258.3	243.4
0.16	349.5	334.5
0.20	438.3	423.3
95%wt. water + 5%wt. formic acid + 7 molal MDEA at 40 °C		
α / mol CO ₂ /mol MDEA	p / kPa	p _{CO2} / kPa
0	7.0	–
0.11	12.8	5.8
0.23	22.4	15.4
0.34	37.3	30.3
0.45	62.0	55.0
0.56	107.9	100.9
0.66	193.0	186.0
0.72	311.9	304.9
0.76	431.8	424.8
0.77	521.9	514.9
90%wt. water + 10%wt. ethylene glycol + 7 molal MDEA at 40 °C		
α / mol CO ₂ /mol MDEA	p / kPa	p _{CO2} / kPa
0	7.0	–
0.14	11.7	4.7
0.28	21.8	14.8
0.41	38.7	31.7
0.54	63.8	56.9
0.66	109.0	102.0
0.75	175.7	168.7
0.83	281.2	274.2
0.87	398.8	391.8
0.90	496.6	489.6

Table A.3

Vapour-liquid equilibrium data for DEEA-based solvents at 40 °C.

Water + 7 molal DEEA at 40 °C		
α / mol CO ₂ /mol DEEA	p / kPa	p _{CO2} / kPa
0	7.9	–
0.16	8.6	0.8
0.32	11.1	3.2
0.47	14.4	6.5
0.63	20.0	12.1
0.77	31.5	23.6
0.90	79.6	71.7
0.96	219.8	212.0
0.98	362.0	354.1
0.99	513.6	505.7
Methanol + 7 molal DEEA at 40 °C		
α / mol CO ₂ /mol DEEA	p / kPa	p _{CO2} / kPa
0	29.7	–
0.072	55.8	26.2
0.14	86.4	56.8
0.21	119.0	89.4
0.29	156.8	127.2
0.36	202.0	172.4
0.43	249.4	219.7
0.50	303.8	274.1
0.56	364.6	335.0
0.61	419.5	389.9
0.65	467.9	438.2
Ethanol + 7 molal DEEA at 40 °C		
α / mol CO ₂ /mol DEEA	p / kPa	p _{CO2} / kPa
0	14.8	–
0.042	78.0	63.2
0.089	148.6	133.9
0.13	214.0	199.2
0.18	283.6	268.8
0.22	355.0	340.2
0.26	417.1	402.3
0.30	478.1	463.3
Ethylene glycol + 7 molal DEEA at 40 °C		
α / mol CO ₂ /mol DEEA	p / kPa	p _{CO2} / kPa
0	2.1	–
0.11	27.1	25.1
0.23	64.1	62.1
0.31	103.5	101.4
0.40	153.8	151.7
0.46	193.0	190.9
0.52	249.2	247.1
0.57	307.3	305.2
0.63	376.0	373.9
0.66	432.4	430.3
N-methyl-2-pyrrolidone + 7 molal DEEA at 40 °C		
α / mol CO ₂ /mol DEEA	p / kPa	p _{CO2} / kPa
0	1.9	–
0.048	157.0	155.1
0.098	317.8	315.9
0.14	441.9	440.0
Sulfolane + 7 molal DEEA at 40 °C		
α / mol CO ₂ /mol DEEA	p / kPa	p _{CO2} / kPa
0	1.6	–
0.046	127.4	125.8
0.086	240.6	239.0
0.13	366.1	364.6
0.16	459.9	458.4
0.18	522.3	520.7
Tetrahydrofurfuryl alcohol + 7 molal DEEA at 40 °C		
α / mol CO ₂ /mol DEEA	p / kPa	p _{CO2} / kPa
0	2.4	–
0.039	111.0	108.6
0.078	220.6	218.2
0.12	330.5	328.0
0.16	433.8	431.3
0.18	503.9	501.4

Table A.4

Vapour-liquid equilibrium data for DEEA-based solvents at temperatures above 40 °C.

Water + 7 molal DEEA at 60 °C		
α / mol CO ₂ /mol DEEA	p / kPa	p _{CO2} / kPa
0	20.5	–
0.14	24.5	4.0
0.27	32.5	12.1
0.40	44.1	23.6
0.54	59.7	39.2
0.65	80.3	59.8
0.76	115.2	94.7
0.85	187.2	166.7
0.91	314.2	293.8
0.94	433.5	413.0
0.95	528.2	507.8
Water + 7 molal DEEA at 80 °C		
α / mol CO ₂ /mol DEEA	p / kPa	p _{CO2} / kPa
0	49.1	–
0.13	65.2	16.1
0.24	92.6	43.6
0.35	127.6	78.5
0.45	166.2	117.1
0.53	208.0	158.9
0.61	254.3	205.2
0.67	300.2	251.2
0.72	354.2	305.1
0.76	411.5	362.4
0.79	466.0	416.9
0.82	514.6	465.6
Water + 7 molal DEEA at 100 °C		
α / mol CO ₂ /mol DEEA	p / kPa	p _{CO2} / kPa
0	105.6	–
0.10	147.5	41.9
0.19	216.4	110.7
0.26	283.7	178.1
0.32	348.7	243.0
0.36	405.2	299.6
0.40	453.1	347.4
Ethylene glycol + 7 molal DEEA at 60 °C		
α / mol CO ₂ /mol DEEA	p / kPa	p _{CO2} / kPa
0	2.7	–
0.059	45.1	42.4
0.12	99.0	96.3
0.17	162.3	159.5
0.23	233.1	230.4
0.28	314.3	311.6
0.33	392.4	389.7
0.36	455.1	452.4
Ethylene glycol + 7 molal DEEA at 80 °C		
α / mol CO ₂ /mol DEEA	p / kPa	p _{CO2} / kPa
0	5.5	–
0.040	91.5	86.0
0.079	192.0	186.5
0.12	298.9	293.4
0.15	414.3	408.8
0.18	493.6	488.1
Ethylene glycol + 7 molal DEEA at 100 °C		
α / mol CO ₂ /mol DEEA	p / kPa	p _{CO2} / kPa
0	10.5	–
0.020	110.8	100.4
0.037	199.3	188.8
0.053	300.1	289.6
0.069	395.0	384.5
0.086	509.7	499.2

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