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From hybrid solvents to water-lean solvents – A critical and historical review

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ABSTRACT

Every year, a plethora of studies focused on developing water-lean solvents for CO_2 capture is published in the scientific literature. More often than not, these studies lack a satisfactory contextualization with the previous body of work. The reasons for this are manyfold, but perhaps the main culprit is the multitude of possible diluent and amine constituents for water-lean solvent formulation. This multitude of options can render a comprehensive analysis of water-lean solvents and their common properties quite a challenging task. However, precisely because there is such a diversity of results and observations, the ordering and categorization of distinct phenomena involving water-lean solvents is the more essential. Although there are some novel sophisticated deployements for the concept of organo-amine mixtures (such as the CO_2BOLs and the NAS for example), many works on water-lean solvents adopt a traditionalistic approach, one that is conceptually based on the mixing of a physical and a chemical absorbent to generate a so-called hybrid solvent. We have demonstrated in this review that this particular class of solvents have more in common than one could be initially led to believe, and set clear guidelines to contextualize past and future results in terms of CO_2 solubility, kinetic rates, mass transfer rates and heat of regeneration analyses. By doing this, we have also identified the main knowledge gaps remaining in the field of water-lean solvents – namely, degradation and corrosion data, as well as pilot plant data. We also believe that our comprehensive categorization and discussion of past literature on water-lean solvents delivers an important trove of references for those willing to carry on working with organo-amine mixtures, traditional or otherwise. With this study, we aim to aid future researchers to have easy access to key concepts for discussing their results.

1. Introduction

The search for plausible solvents for CO_2 absorption covers a wide range of investigations, from the typical ones with benchmark aqueous amines [1] to curious alternatives such as human fat [2]. Along these investigations came water-lean solvents, better known in previous years as hybrid solvents. Somewhere along the line, researchers realized that mixing organic diluents to aqueous amines could enhance the physical absorption capabilities of the solvent without affecting too much their chemical properties. The name 'hybrid solvent' reflects this combinatorial effect.

This emphasis on combination, on aiming for the best of both worlds, has visibly shifted as time went by. Nowadays, many of the most promising water-lean solvents, such as the CO_2BOLs [3,4] or those developed by Barzagli et al. [5,6], rely on alternative mechanisms of reaction other than the ones observed in typical aqueous amines. Together with this shift came the gradual changing of nomenclature. What these solvents have in common is a reduction in water content and substitution by an organic diluent. Therefore, the name 'water-lean solvents' became certainly more descriptive. However, it is also a bit vague. Now that the pretext of physical + chemical absorption seems to be somewhat obscured, what exactly do water-lean solvents have in common? And what do they aim to achieve?

The present review intends to trace the historical development of water-lean solvents discussing their properties and performances from the perspective of hybrid solvents. What we mean by this is that there will be an emphasis on mixtures of amines and organic diluents with the goal of operating a gas scrubbing plant similarly to how one does with aqueous solvents. Therefore, we will not discuss ionic liquids nor mixtures of ionic liquids with amines, even though these mixtures have every right to be called water-lean solvents themselves. These solvents have very particular properties, and one could argue that usually it is amines that are added to ionic liquids with the goal of enhancing their

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Nomenclature

Amines

2FPEA	2-fluorophenetylamine
2PDE	2-piperidineethanol
2MPZ	2-methylpiperazine
AEEA	2-(2-aminoethylamino)ethanol
AEPD	2-amino-2-ethyl-1,3-propanediol
AMP	Aminomethyl propanol
AMPD	2-amino-2-methyl-1,3-propanediol
CHA	Cyclohexylamine
DBA	Dibutylamine
DEA	Diethanolamine
DEEA	Diethylethanolamine
DGA	Diglycolamine
DIPA	Diisopropanolamine
DMA	Dimethylamine
DMHDA	Dimethyl hexanediamine
EDA	Ethylene diamine
EMEA	Ethylethanolamine
HA	Hexamine
LysK	Potassium lysinate
MAPA	3-(methylamino)propylamine
MEA	Ethanolamine
MIPA	Isopropanolamine
MPA	Propanolamine
MDEA	Methyl diethanolamine
ProK	Potassium prolinate
PZ	Piperazine
TBA	Tributylamine
TEA	Triethanolamine
TETA	Triethylenetetramine

Diluents

1BuIMI	1-butylimidazole
1BuOH	1-butanol
1MIMI	1-methylimidazole
1HeOH	1-hexanol
1PeOH	1-pentanol
1PrOH	1-propanol
1OcOH	1-octanol
2EE	2-ethoxyethanol
2EHeOH	2-ethylhexanol
2ME	2-methoxyethanol
2PrOH	2-propanol
3DMAPN	3-(dimethylamino)propionitrile
4H	4-heptanone
ACE	Acetone
ACEA	Acetoacetamide
BP	Benzyl alcohol
CARB	Carbitol
CC5	Cyclopentanone
CCL4	Carbon tetrachloride
CH	Cyclohexanol
CHCL3	Chloroform
DACE	Diacetyl
DEG	Diethylene glycol
DEGDME	Diethylene glycol dimethyl ether
DMC	Dimethyl carbonate
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
EC	Ethylene carbonate
EtOH	Ethanol
FA	Furfuryl alcohol
GBL	Gamma butyrolactone
GLY	Glycerol
L92	Liquid crystal $(EO)_8(PO)_{47}(EO)_8$
MEG	Ethylene glycol
MEK	Methyl ethyl ketone
MeOH	Methanol
NFM	N-formyl morpholine
NMF	N-methyl formamide
NMP	N-methyl-2-pyrrolidone
OFP	Octafluoropentanol
PC	Propylene carbonate
PG	Propylene glycol
PEG	Polyethylene glycol
TEG	Triethylene glycol
TEGDME	Triethylene glycol dimethyl ether
TEGMME	Triethylene glycol monomethyl ether
THFA	Tetrahydrofurfuryl alcohol
TMS	Tetramethylene sulfone, or sulfolane
TOL	Toluene
TOU	2,5,7,10-tetraoxaundecane

performance, and not the opposite. Similarly, though we shall mention biphasic solvents as a way of registering which combinations result in phase separation, we will not focus on their peculiarities nor on how one is supposed to operate a CO_2 absorption plant with solvent demixing. Rather than restricting this review, we believe that such delimitation of content will enable a more insightful and meaningful discussion. For a different perspective, the reader could perhaps refer to the excellent review on CO_2BOLs and alternative reaction mechanisms carried by Heldebrant et al. [7], or to the review on biphasic solvents carried by Zhuang et al. [8].

Being a critical review, this text intends to present overaching ideas regarding a diverse, sometimes contradictory set of experimental data. This is a risky endeavor, as one might point out that the available body of work on water-lean solvents is not conclusive enough to warrant general statements on chemical kinetics or CO_2 solubility. We have tried to present and digest a vast of sources, pointing out the ones that follow a clear pattern, but also highlighting the ones that come off as outliers.

Nearly all of the data discussed in this review has been obtained in lab-scale experiments, since these make the bulk of the available published literature on water-lean solvents. On one hand, lab-scale experiments are the most appropriate procedure for delivering fundamental data such as CO_2 solubility and kinetic rates, which can then be employed for project design and modelling applications. On the other hand, bench and pilot-scale operations are ideal for producing insights into real industrial challenges. This is the more relevant in at least three particular areas: CO_2 absorption rates, energy performance, and solvent degradation phenomena. Bench and pilot plant data obtained for solvents containing methanol and monoethanolamine has been produced by a series of authors [9–14] and is discussed briefly in Section 6.3 regarding CO_2 absorption rates. Also in the topic of absorption rates, pilot plant data for the Sulfinol-D® solvent was obtained by Yih and Lai [15], and bench scale data for mixtures of N-methyl-2-pyrrolidone and monoethanolamine have been obtained by Tan et al. [16]. Section 8.4 deals explicitly with pilot plant data obtained by Semenova and Leites [17] in the context of energy performance. This is currently the extent of bench and pilot plant data found in this literature review. With respect to issues such as solvent degradation, solvent emissions, and equipment corrosion, there is unfortunately a lack of published information.

There is also a lack of data referring to water balance in plants operating with water-lean solvents, which might become an issue due to the hygroscopicity of organic diluents such as ethylene glycol and N-methyl-2-pyrrolidone. In lab-scale experiments, water solubility in the solvent is often not a problem: pure CO_2 is commonly used in solubility measurements, and even when water-saturated streams are used in, for example, mass transfer rate studies (such as those of Yuan and Rochelle [18]), the experiments are not carried out long enough for water balance to become an issue.

Finally, to facilitate our discussion, a list of abbreviations for amines and diluents can be found at the end of this study.

2. A history of shifting perspectives

Water-lean solvents, or rather hybrid solvents, have experienced a history of shifting interests loosely guided by two distinct factors. The first of these factors, in a pretty straightforward fashion, is the conditions of the raw gas that one wants to treat and the quality of the product one wants to generate. The second, a bit more abstract, is what one perceives as being the ideal properties of a solvent for CO_2 absorption.

Regarding the first factor, one could consider Fig. 1 adapted from the book Fundamentals of Natural Gas Processing [19]. In Fig. 1, one can identify the locus for hybrid solvents in the context of gas qualities. Hybrid solvents are indicated for absorbing CO_2 from gases with high impurity content and, more importantly, high pressures, adding up to CO_2 partial pressures above 700 kPa (7 bars).

In this conception, hybrid solvents are viewed in light of their double-absorption qualities. The keyword for them is capacity. The performance of these solvents is seen to override that of aqueous amines at high pressures due to the crossing-over factor (which we will discuss in detail in Section 4). This is perhaps too restrictive. The demand of 700 kPa of CO_2 partial pressure essentially bars the utilization of hybrid solvents in any post-combustion capture applications, as it does with biogas upgrading applications. This means that hybrid solvents should only be suitable for very particular pre-combustion capture scenarios. In the 1960s and 1970s, industrial processes such as the Amisol® process [20], the Sulfinol® process and the Selefining® process gained territory in pre-combustion capture [21], all operating with hybrid solvents.

One important remark is that it was often not the intention of these treating processes to generate a CO_2 stream that was pure enough for CSS (carbon capture and storage, i.e. either geological storage, enhanced oil recovery or selling as a product). Their goal was producing natural gas with high heating value. With the aim shifting in the past few decades towards climate change mitigation technologies, the CO_2 purity obtained by most physical solvent treatments starts to become a problem [21]. Standing on the edge between physical and chemical absorption, hybrid solvents developed then might not be as interesting now. Another interesting factor is the higher selectivity that hybrid solvents have for H_2S instead of CO_2 absorption, a feature often perceived as a positive point of these technologies in the context of natural gas treatment [21]. Many early investigations measure both H_2S and CO_2 solubilities in hybrid solvents [22–24]. Isaacs et al. [25], for example, clearly show that the Sulfinol-D® solvent excels in H_2S absorption at acid gas partial pressures way below those for the crossing-over with CO_2 when compared with aqueous DIPA.

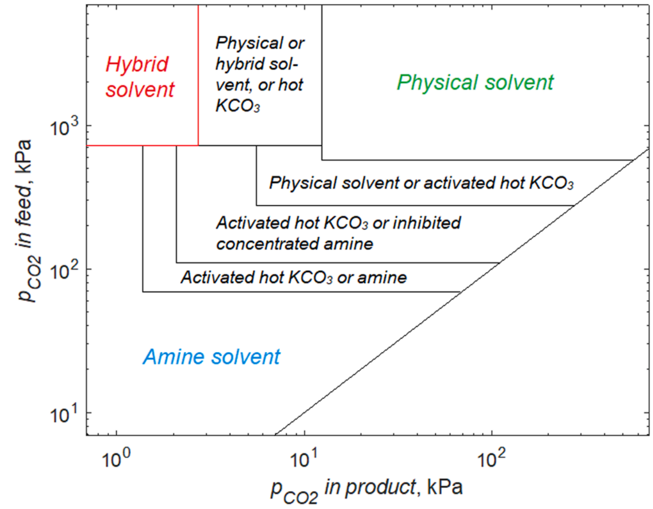


Fig. 1. Recommended conditions for the employement of different CO_2 absorption alternatives in natural gas. Adapted from Kidnay and Parrish [19].

The 1980s and 1990s saw some publications on hybrid solvents highlighting their vapor–liquid equilibria and CO_2 capacities. And then, in the new millennium, more researches started to focus on a different aspect: volatility. According to a number of investigations, the potential for low volatilities in water-lean solvents renders them attractive due to the possibility of recovering the loaded amine while incurring in less latent heat expenditures (i.e. less heat is directed towards the vaporization of the solvent). Studies that propose mixing MEA with diluents such as glycerol [26] and coconut oil [27] are very clear in highlighting this aspect of water-lean solvents. In fact, low volatilities have also been a driving force in the popularization of ionic liquids [28], and Shamiri et al. [26] have explicitly declared their intent in developing an inexpensive green ionic liquid-inspired solvent when mixing MEA with glycerol.

Some other researchers are also optimistic about the huge potential for diversity in water-lean solvent formulation. Given this diversity they can, for example, resort to computational techniques to quickly evaluate the best combination of chemicals to obtain just the right mixture for an hypothetical solvent based on a set of key properties [29,30]. With water-lean solvents, the possibilities could be endless. This clearly shows the shifting of purposes observed for water-lean solvents from the 1970s to the 2010s.

The formation of a secondary phase upon CO_2 absorption, either through liquid–liquid separation or solid precipitation, had been usually seen as an undesirable aspect of some water-lean mixtures. As an example, Leites [31] mentions having screened more than 130 possible diluents for solvent formulation, promptly rejecting all which lead to phase separation. Conversely, the arrival of biphasic systems as possible advantageous CO_2 absorption techniques [8] has recently lead researchers such as Karlsson et al. [32] to specifically target diluents that brought forth carbamate precipitation. Many recent studies focus solely on phase separation in water-lean solvents.

Shifting perspectives have brought a renewal of interest in water-lean solvents. And yet, careful reading of past literature would do well to many of the newcomers. The slow absorption rates in mixtures containing very viscous compounds can be foreseen in the seminal work of Woertz in 1972 [33] and keeps being rediscovered. The benefits of low volatilities in water-lean blends, with the caveat that solvent regeneration should perhaps require stripping with an inert gas, is demonstrated by Rivas and Prausnitz in 1979 [34]. Right now, water-lean solvents are being considered for CCS applications. These applications require that CO_2 is produced with a high degree of purity, something that is not convenient if desorption must be performed with a stripping gas. Or perhaps an application for water-lean solvents other than CCS will become attractive again. One is left to wonder if the extremely high CO_2 content (more than 40 %v/v) typical of natural gas extracted from recently discovered oil fields such as the Brazilian Pre-Salt [35,36] could provide a renewal of interest in hybrid solvents.

This short historical introduction shall motivate the reader interested in working with water-lean solvents to spend more time getting acquitted with the literature. This is especially true if one wants to focus on solvent development. There are plenty of publications regarding very different mixtures between amines and organic diluents, dealing with a wide range of chemicals, but often identifying the same patterns and behaviors. In the present review, some of these patterns will be discussed in depth. However, we believe that the most important thing that we can offer is guiding the reader to the right source literature.

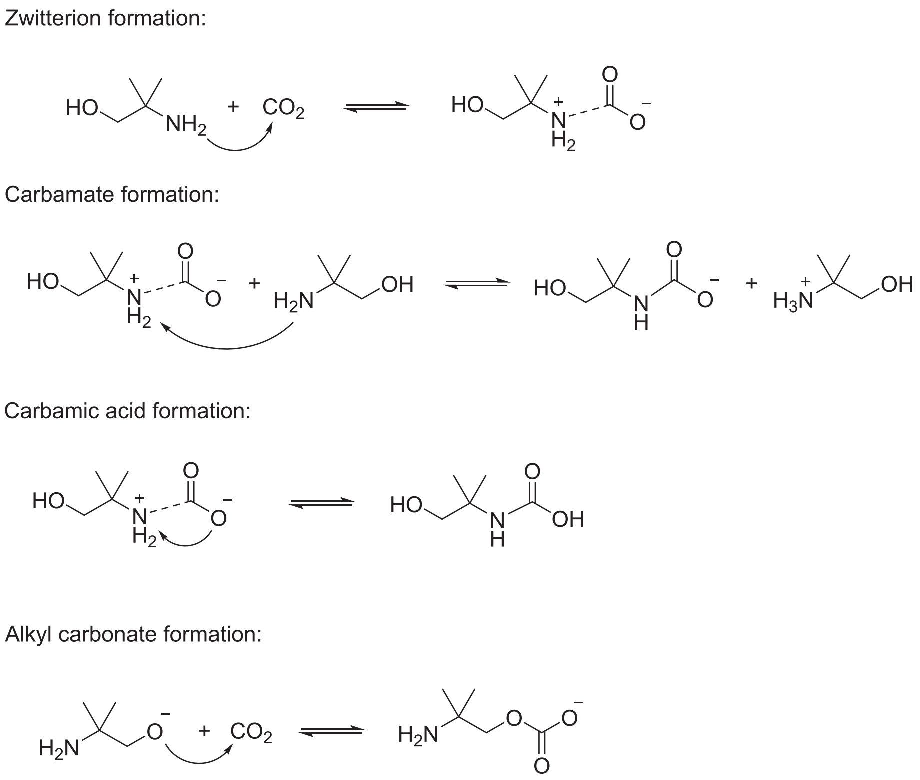
3. Mechanisms of reactions in water-lean solvents

In principle, there are little reasons to suspect that the mechanism of reaction in water-lean solvents containing the usual primary and secondary alkanolamines will be any different than that in aqueous solutions. The formation of a carbamate species between the amine and the CO_2 molecule is often the most thermodynamically favorable among the possible reactions that can happen given the set of chemicals available in either aqueous or water-lean systems. This is so self-evident that early studies on water-lean solvents did not consider an alternative mechanism of absorption before proceeding to calculate kinetic data [37–41]. And they were most certainly right in doing so, as recent spectrography publications [42] have shown that carbamate is the predominant reaction product at moderate CO_2 loadings ($\alpha < 0.5$ mol $CO_2 \cdot$mol MEA^{-1}) and when using strong bases ($pK_a > 8$), conditions typically encountered in those early studies. Under different conditions, Kortunov et al. [42] show that carbamic acid or even undissociated zwitterion might be present upon CO_2 absorption. Similarly, Masuda et al. [43] carried an extensive NMR research on carbamic acid formation when working with mixtures of arylamines and organic solvents. The experimental findings from these authors confirm, and greatly expand, what had been proposed by Takeshita and Kitamoto [44] regarding the effects of solvent polarity and amine basicity on the products of reaction between CO_2 and amines. However, under typical commercial conditions and employing typical amines, it is safe to assume that carbamate formation is the main mechanism of reaction.

At the same time, other authors have found NMR evidence of alkylcarbonate formations when employing water-lean solvents with hindered and tertiary amines [45–49]. Incidentally, alkylcarbonate formation has long been proposed to explain the reactive absorption of CO_2 in nonaqueous tertiary amines [50], though not experimentally verified until very recently. Behrens et al. [51] observed substantial alkylcarbonate formation between CO_2 and MDEA in aqueous solutions via NMR analyses, making it likely that a similar occurrence should happen in nonaqueous media. It is important to differentiate these two observations though. While Barzagli et al. [45] and S. Chen et al. [46] report carbonate formation between the diluent (e.g. ethylene glycol, ethanol) and CO_2, what is shown by Behrens et al. [51] is the formation of a carbonate with MDEA itself. Conversely, both carbonate formation between alcohol and CO_2 and between amine and CO_2 have been shown to take place in the experiments carried out by Skylogianni et al. [47] and by Wanderley et al. [49].

These reaction mechanisms were schematically represented on Fig. 2. In the last reaction, one should notice that the nucleophile is the deprotonated hydroxyl group of the amine. For this reason, Jørgensen and Faurholt [52] had assumed that this reaction cannot take place unless the environment is strongly basic. There are alternative interpretations of this mechanism, some of them involving intramolecular proton transfer [53] or direct reaction with bicarbonate [54]. We will discuss the alkylcarbonate formation pathway a bit more in Section 10. For now, suffice it to say that most interpretations on water-lean solvents rely solely on the carbamate route, which is after all the predominant one for most low-pressure applications.

Beyond these general observations, there are also exceptions in the behavior of some particular solvents, which possibly taking part in the reactions themselves. For example, N-methyl-2-pyrrolidone is suspected of reacting in a similar way as a tertiary amine does [55], slightly increasing the absorption rates of CO_2. Shannon and Bara [56] observed a similar phenomenon with N-alkylimidazoles. Meanwhile, ethylene glycol and other polyalcohols possibly undergo some sort of reaction as well, perhaps even the alkylcarbonate one mentioned above [26,57]. All of these are examples of reactions that would increase CO_2 absorption. On the other end of the spectrum, propylene carbonate has been observed to react with amines a number of times [22,32,34], and a reaction between ethylenediamine and ethylene glycol renders the solvent prepared with both these chemicals virtually unreactive [58]. Another series of self-destructive side-reactions has been reported previously in


Zwitterion formation:

Carbamate formation:

Carbamic acid formation:

Alkyl carbonate formation:

Fig. 2. Possible mechanisms of reaction for CO_2 absorption by an alkanolamine, exemplified with the case of AMP.

Wanderley et al. [59] involving esters and ketones.

Finally, there is one particular issue that must be addressed when mentioning the experimental research on reaction mechanisms in water-lean solvents. Most properties analyzed in this review obey, loosely speaking, a very predictable behavior when one transitions from aqueous solvents to semiaqueous solvents and finally to nonaqueous solvents. This will be further explored in the following sections, where Fig. 4, for example, shows that the equilibrium reaction between CO_2 and amine follows a smooth trend with the increase of water mass fraction in water-lean solvents containing N-methyl-2-pyrrolidone. That is to say, the effect of trace amounts of water present in the solvent during equilibrium experiments and mass transfer rate experiments is not expected to deliver unpredictable results. And yet, this is not necessarily the case with speciation experiments, where very little amounts of water are sufficient to enable the formation of bicarbonate. For example, let us consider the case of 50 %wt. N-methyldiethanolamine (MDEA) in ethylene glycol. Those are equivalent to approximately 0.420 mol of MDEA per 100 g of solvent. For the bicarbonate formation mechanism to be enabled in a stoichiometric basis, one requires one mol of water for each mol of MDEA, which means that 7.55 g of water in 100 g of solution are sufficient to enable every molecule of MDEA to be converted to bicarbonate and protonated MDEA upon CO_2 absorption. This is particularly troubling in the case of ethylene glycol, which is a known hygroscopic substance liable to fixate the moisture of the air. Thus, relatively small amounts of water are theoretically enough to shift the speciation behavior of a water-lean solvent, and speciation experiments should be carried out with a particular attention to detail.

To quickly summarize the conclusions of Section 3:

- The carbamate formation pathway is the predominant one in typical conditions for CO_2 absorption in most water-lean solvents;
- Alkylcarbonate formation also occurs in water-lean solvents, to a lesser degree, and is more easily observable in solvents where carbamate formation is depressed.

4. Vapor-liquid equilibria in water-lean solvents

From their inception, water-lean solvents are mixtures of amines with organic solvents that have higher CO_2 physical solubility than water. Therefore, there are two important aspects to keep in mind when analyzing their vapor–liquid equilibrium (VLE) data:

a. At low CO_2 partial pressures, CO_2 is absorbed mostly through chemical reaction.
b. At high CO_2 partial pressures, CO_2 is absorbed mostly through physical solubilization.

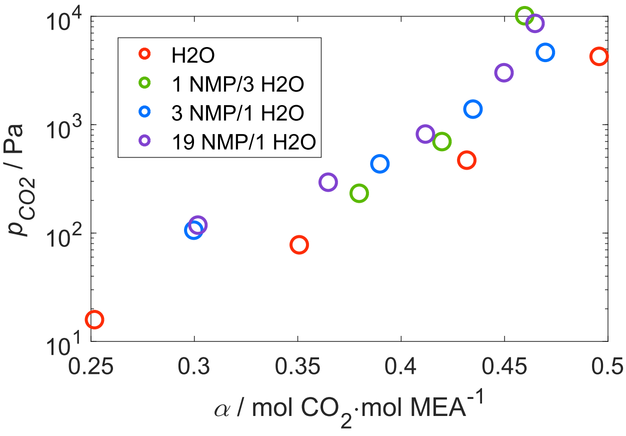


Fig. 3. VLE data obtained by Dugas and Rochelle [61] (aqueous MEA) and Yuan and Rochelle [18] (MEA-NMP blends) for solvents containing different NMP-water proportions and 7 molal MEA at 40 °C. The proportions of NMP and water are given in mass basis.

If one plots the VLE data of a water-lean solvent against that of its aqueous counterpart (i.e. an aqueous solvent with same amine concentration), it is often possible to identify a point in which both datasets cross. We have nicknamed this the cross-over point following the example of Macgregor and Mather [60]. This point loosely divides the VLE curves of water-lean solvents into two distinct areas, which we shall discuss separately.

4.1. Vapor-liquid equilibria below crossing-over

In terms of pure chemical activity and reaction, shifting from an aqueous to a water-lean solvent seems to consistently depress the solubility of CO_2, leading to a shift in equilibrium. This can be seen in practically all the experimental vapor–liquid equilibrium data compiled in Table 2, Table 3, Table 4, except when explicitly stated that the authors suspect the presence of a side-reaction involving the diluent itself.

This shift in equilibrium is often attributed to the destabilization of ionic species in reaction when operating with an organic diluent of low polarity. Yuan and Rochelle [18] have proved how this is mathematically correlated to an increase in the activity of amines in water-lean solvents. If one looks at their data for NMP-MEA-water blends of 7 molal MEA at 40 °C, the effects of changing solvents on CO_2 solubility become evident.

In Fig. 3, it is possible to see how the gradual addition of an organic diluent to the solvent steadily decreases the solubility of CO_2 at moderate pressures. This can also be seen in the vapor–liquid equilibrium data of various researchers [26,57,59,62]. We have employed data from Yuan and Rochelle [18] in Fig. 3 for illustration purposes, but that could have been done with different sets of data.

As elegantly pointed out by Macgregor and Mather [60], the impact of adding new diluents to an already existing solvent is commonly called secondary medium effect [63]. This effect can be roughly assessed by the following expression.

$$K_{wl} = Q_{\gamma} \cdot K$$

In the expression above, K_{wl} is the equilibrium constant of the amine–CO_2 in a water-lean solvent while K is the equilibrium constant in the regular aqueous solvent. The multiplier Q_{γ} will affect directly the activities of all reactive species, and as such it is itself dependent on CO_2 loading. However, we can apply a simple calculation on the data obtained by Yuan and Rochelle [18] shown in Fig. 3 to illustrate this point and derive an 'averaged' Q_{γ}. For a simple CO_2 conversion to carbamate, the equilibrium constant K (and K_{wl}) can be estimated by the expression below.

$$K = \frac{[AmCOO^-]\cdot[AmH^+]}{[Am]^2\cdot[CO_2]} \approx \frac{\left(\alpha\cdot[Am]_0 - \frac{p_{CO2}}{H_{CO2}}\right)^2}{\left([Am]_0\cdot(1-2\cdot\alpha) + 2\cdot\frac{p_{CO2}}{H_{CO2}}\right)^2\cdot\frac{p_{CO2}}{H_{CO2}}}$$

We have applied the expression above to compare the equilibrium constants obtained by Dugas and Rochelle [61] and Yuan and Rochelle [18]. In our calculations, the Henry's coefficient of the solvents was estimated by using data from Hansen [64] plus the Krichevsky mixing rule as given by Shulgin and Ruckenstein [65]. The medians of the equilibrium constants obtained for each one of the four systems is shown on Table 1.

With this example, it becomes evident how a relatively simple substitution from water to NMP can affect the equilibrium conditions of the system. Equilibrium decreases by one order of magnitude when deploying a water-lean solvent, and it must be kept in mind that NMP is a particularly mild chemical in terms of its nonpolarity.

It has often been attempted to explain the equilibrium shift in terms

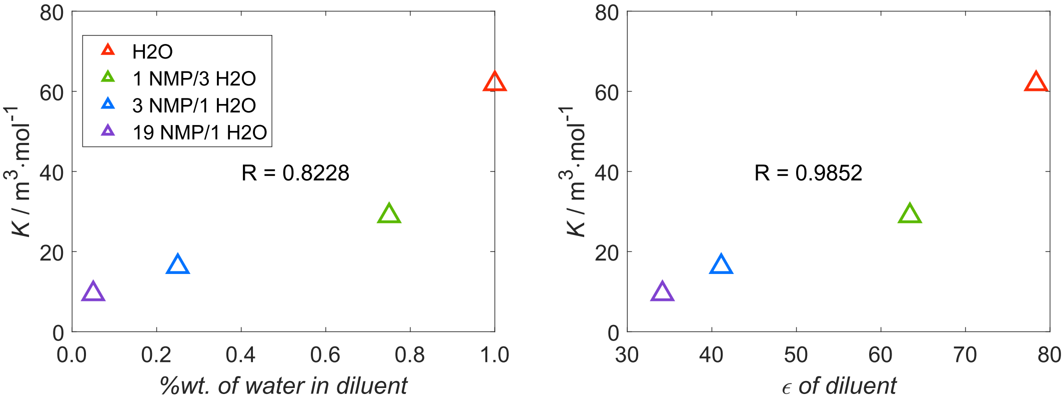


Fig. 4 Equilibrium constants adapted from data by Dugas and Rochelle [61] and Yuan and Rochelle [18] for 7 mol MEA·kg solvent^{-1} at 40 °C shown against water/diluent mass fractions and the dielectric permittivities of the diluent.

Table 1
Equilibrium constants and activity multiplier obtained from data regarding aqueous 7 molal MEA [61] and NMP-MEA-water blends [18] at 40 °C. The proportions of NMP and water are given in mass basis.

Diluent	$K/m^3 \cdot mol^{-1}$	Q_γ
H2O	61.9	1.000
1 NMP/3 H2O	28.9	0.467
3 NMP/1 H2O	16.2	0.262
19 NMP/1 H2O	9.4	0.153

of the dielectric permittivity ε of the diluent. Sen et al. [63] proposed several correlations connecting Q_γ and ε, and we ourselves have attempted some similar approaches [66]. As suggested by Macgregor and Mather [60], electrostatic phenomena associated with electrolyte stabilization are closely tied to the dielectric permittivity of the system, and that is a good reason to always verify the ε of a new diluent. However, we must point out that the amount of data which one can find regarding VLE shifts in water-lean solvents is far too little to justify any conclusive understanding. Furthermore, there are many solvent parameters which follow the same trends of ε with their own peculiarities (such as the Hildebrand solubility parameter δ and the autoprotolysis constant pK_S for example).

In Fig. 4 we have plotted the values calculated on Table 1 against both the water concentrations in the diluents and their respective dielectric permittivities. The dielectric permittivities of mixed solvents can be estimated by single-component data from Rumble et al. [67] and the mixing rules given by Reynolds and Hough [68]. A statistical treatment of these sets of data show that the Pearson correlation coefficient between water mass fraction and ln(K) is $R(\%wt,\ln(K)) = 0.8228$, whereas that between ε and ln(K) is $R(\varepsilon,\ln(K)) = 0.9852$. Despite this difference, one could argue that, due to the already observable correlation between mass fractions and Q_γ, most mass-based mixing properties (such as ε itself) are capable of suggesting promising trends. Naturally, this raises the question of whether one should be using mass-based mixing properties at all. Since an N-methyl-2-pyrrolidone molecule has 5.5 times more mass than a water molecule, even the water-lean solvent with 3 NMP/1 H2O shown in Fig. 4 has more water than NMP on a molecular level. If one would evaluate the Pearson correlation coefficient between the mol percentage of water in the diluent with ln(K), one would find out that $R(\%mol,\ln(K)) = 0.9816$, higher than the $R(\%wt,\ln(K)) = 0.8228$ obtained when correlating the mass percentage of water with the shift in equilibrium. Therefore, one should notice that small shifts in water content have a clear impact on chemical equilibria.

A more interesting analysis than this would be to compare entirely different diluents and consequent equilibrium shifts based solely on their dielectric permittivities. We have carried this analysis in a previous work [66]. Though a trend can indeed be observed for MEA-based solvents, it becomes erratic for other amines (N-methyldiethanolamine, 2-methylpiperazine). Therefore, though a convenient placeholder when discussing electrostatic phenomena, we do not believe that ε offers anything close to a full description of the secondary medium effect in water-lean solvents. A good series of analyses on the effects of the dielectric constants on equilibrium properties of these solvents has been carried by Hamborg et al. [69,70] and by Ramachandran et al. [71].

Among the exceptions to what has been discussed in this section is the peculiar phenomenon of reverse crossing-over, i.e. some water-lean solvents appear to outperform aqueous solvents of same amine concentration at low CO_2 partial pressures, rapidly losing their advantage at higher pressures. This has been reported both by Song et al. [57], who analyzed MEG-MEA-water blends, and by Shamiri et al. [26], who studied glycerol-MEA-water blends. Both these solvents have remarkably high dielectric permittivities (41.4 and 46.53 for MEG and glycerol respectively. The two studies have in common the fact that relatively small amounts of organic diluent were added to aqueous MEA when such events were observed (15.3 %wt. MEG and 10 %wt. glycerol). It might be the case that some chemical or physical enhancement happens at small concentrations of glycols in aqueous amines, but very little information has been found on the topic.

Archane et al. [72] employed FT-IR spectroscopy of systems methanol-DEA-water to show that, at a fixed loading, the concentration of molecular CO_2 increased with the addition of methanol. This shows that, although carbamate formation is still the main mechanism for CO_2 absorption, physical solubilization of gas starts being more relevant in water-lean solvents. Eventually, this aspect becomes so predominant that the cross-over point is observed.

4.2. *Vapor-liquid equilibria at and above crossing-over*

There are three main factors that help defining the locus of the cross-over point. The first one is amine concentration. Some works have shown that, the less amine in a solvent, the lesser is its capacity for chemical absorption, and the lower the CO_2 partial pressure required for crossing-over. An example can be found in the data of Huang et al. [73]. In their water-free DEGDME-MEA solvent, cross-over happens at around 500 kPa for 15 %wt. MEA but only at 1000 kPa for 30 %wt. MEA (T = 40 °C). This phenomenon can be seen in Fig. 5. Something similar has been observed with regards to water-free THFA-MEA formulations by Wanderley et al. [59].

The second factor is the diluent itself, both in terms of its CO_2 physical solubility and its solvating properties. Looking again at the report of Huang et al. [73], the cross-over for water-free NMP-MEA solvents happens before that of DEGDME. However, at even higher CO_2 partial pressures, the DEGDME-MEA curve crosses over that of NMP-MEA itself. This is an interesting case in which both electrostatic phenomena and physical solubility play opposing roles. NMP has better

Table 2
Publications that show VLE data for water-lean solvents with MEA.

Reference	Diluents	Conditions and remarks
[34]	NMP, PC, TMS	C = 15% wt. MEA and T = 25, 100 °C for water-free NMP shown in graph form. For other solvents, authors report equilibrium constants instead of raw data.
[22]	NMP, PC	Water-free C = 5.1, 14.3 %wt. MEA T = 25, 50 °C
[83]	NMP	Water-free C = 15 %wt. MEA T = 25, 50, 100 °C
[24,84]	TMS	Water-free C = 15, 30 %wt. MEA T = 30, 50, 100 °C
[57,85]	MEG, PEG400	D = 15.3, 42.3 %wt. diluent C = 15.3 %wt. MEA T = 40, 60 °C
[31]	Various	C = 2.5 mol$\cdot$l^{-1} MEA and T = 20 °C for a huge array of water-free diluents shown in graph form. C = 2.5 mol$\cdot$l^{-1} MEA and T = −50, −30, −10, 0, 10, 20 °C for water-free methanol shown in graph form.
[86]	TEG	Water-free C = 0.1, 0.2, 0.3, 0.5 mol$\cdot$l^{-1} MEA T = 30, 40, 50, 60,70, 80 °C
[87]	Benzoic acid*	D = 1, 2, 5 %wt. diluent C = 14, 13, 10 %wt. MEA T = 40 °C
[73]	DEGDME	Water-free C = 15, 30, 45 %wt. MEA T = 20, 30, 40, 50, 60 °C
[26]	GLY	D = 5, 10, 15, 20 %wt. diluent C = 30 %wt. MEA T = 40, 50, 60 °C
[88]	MEG	D = 1/1 MEG/water mass basis and water-free C = 30 %wt. MEA T = 40, 80 °C
[89]	GLY	The authors have designed their experiments so as to parametrize a model by using a central composite experimental design matrix. However, the most consistent set of data is at the conditions below: D = 2, 4, 6 mol$\cdot$l^{-1} diluent C = 2.5 mol$\cdot$l^{-1} MEA T = 40 °C
[90]	MEG, MeOH, NMP	Water-free C = 10, 20, 30 %wt. MEA T = 30 °C
[18]	CARB, NMP	D = 1/3 in carbitol/water mass basis and 19/1, 3/1, 1/3 in NMP/water mass basis C = 7 mol MEA$\cdot$kg solvent^{-1} T = 40 °C
[80]	2ME	Water-free C = 5 mol$\cdot$l^{-1} MEA T = 40, 60, 80, 100, 120 °C
[91]	2EE, 2ME	Water-free C = 5 mol$\cdot$l^{-1} MEA T = 40, 100 °C
[92]	L92	D = 60 %wt. diluent C = 10 %wt. MEA T = 30 °C
[66]	1MIMI, DMSO, MEG, NMP, TMS	D = 3/1 in diluent/water mass basis C = 5 mol MEA$\cdot$kg solvent^{-1} T = 40 °C
[59]	ACE, CC5, FA, GBL, MEG, MeOH, NMP, THFA, TMS	A specific analysis of aqueous THFA solutions was performed at 40 °C with different THFA-MEA-water compositions. However, the most consistent set of data is at the conditions below: Water free C = 30 %wt. MEA T = 40, 80, 120 °C

*Benzoic acid is clearly not a proposed diluent for water-lean solvent formulation. Instead, the authors [87] proposed the addition of an acid to the rich amine for releasing CO_2 at lower reboiler duty costs. The MEA-benzoate precipitates upon reaction and can then be mechanically separated, though at which cost the amine itself is recovered is not addressed. In a later publication they proposed oxalic acid instead of benzoic acid [93].

electrostatic properties than DEGDME, and its curve crosses over that of aqueous MEA first. However, DEGDME has higher CO_2 physical solubility than both water and NMP, surpassing NMP in capacity afterwards.

It might be instructive to mention other instances of observable crossing-over. Ai et al. [78] observed the cross-over in acetoacetamide-MDEA-water (5/48/47 %wt.) above 100 kPa at 25 °C. Macgregor and Mather [60] identified a cross-over for TMS-MDEA-water (30.5/20.9/48.6 %wt.) above 2000 kPa at 40 °C. Roberts and Mather [79] reported a cross-over for TMS-AMP-water (32.2/16.5/51.3 %wt.) above 60 kPa at 40 °C. Finally, Isaacs et al. [25] mark the cross-over for the proprietary Sulfinol-D® solution (TMS-DIPA-water 40/40/20 %wt.) over about 4000 kPa at 40 °C. With the exception of the example from Roberts and Mather [79], all of the crossing-overs mentioned above happen at pretty high CO_2 partial pressures.

The third and final factor is temperature. Rivas and Prausnitz [34] show that water-lean solvents experience a stronger VLE dependence on temperature than in their aqueous counterparts. They convincingly demonstrate that with example of 15 %wt. MEA + water-free NMP, suggesting that this could lead to easier solvent recovery. Observations of this kind have been made repeatedly by several authors [59,60,80,81]. What this means in practical terms is that the cyclic capacity, as defined by the CO_2 loading at absorber temperatures minus the CO_2 loading at desorber temperatures and fixed CO_2 partial pressure, is higher in water-lean solvents. And that is true even despite the fact that, due to the equilibrium shift mentioned previously, rich loadings in water-lean solvents are almost inevitably lower than in aqueous solvents.

We must mention that these larger cyclic capacities verified experimentally seem to contradict the argument given by Moore [82] that, due to the low entropy of absorption in water-lean solvents, solvent regeneration should become less thermodynamically favorable. Their observation stems from the fact that water molecules form more structured lattices than most organic diluents, making it so that CO_2 experiences a larger drop in entropy while being absorbed by aqueous solvents than when it is absorbed by non-aqueous ones. We are in no position to give a thermodynamic explanation regarding why desorption in water-lean solvents seems to be facilitated. From a molecular point of view, one could suggest that the hydrogen bonds connecting water molecules are less susceptible to breaking/shifting due to increases in temperature than the looser, weaker dipole–dipole ones connecting organic diluents. Perhaps this translates into a more temperature-dependent entropy of absorption than Moore [82] initially assumes.

4.3. Literature data for VLE in water-lean solvents

What follows in Table 2, Table 3 and Table 4 is a comprehensive list of all the published data regarding vapor–liquid equilibrium in water-lean solvents that we were able to find in the open literature. We have appended the list with some remarks regarding the conditions in which the datasets were obtained.

Unfortunately, a certain amount of data published in Russian in the Soviet Union regarding water-lean solvents (including supposedly even pilot plant data) is now hardly accessible to most Western investigators. One can see references to it in the work of Roberts and Mather [79] and, more recently, a quick summary of findings and conclusions elaborated by Leites [31]. We have been unable to assess most of these referred studies, with the sole exception of the book published by Semenova and Leites [17], of which we have translated and discussed one chapter.

Curiously, we have found only one instance in literature where the

Table 3
Publications that show VLE data for water-lean solvents with DEA, MDEA, AMP.

Reference	Diluents	Conditions and remarks
Data for water-lean solvents with DEA		
[22]	NMP	Water-free C = 5.1, 14.3 %wt. DEA T = 25, 50 °C
[62,94]	MEG	D = water-free, then approximately 20, 40, 60 and 80 %wt. diluent C = approximately 1, 2 mol·l^{-1} DEA T = 25 °C
[24]	TMS	Water-free C = 15 %wt. DEA T = 30 °C
[83]	NMP	Water-free C = 15, 30 %wt. DEA T = 25, 50, 100 °C
[72]	MeOH	D = 10, 20, 30 %wt. diluent C = 30 %wt. DEA T = 25 °C
[95]	MeOH	D = 20, 40 %wt. diluent C = 20, 40 %wt. DEA T = 50, 60, 80, 100, 120 °C
[96]	PEG200	Water-free C = 30 %wt. DEA T = 40, 80, 120 °C
Data for water-lean solvents with MDEA		
Reference	Diluents	Conditions and remarks
[60]	TMS	The authors identify the formation of a second liquid phase at high CO$_2$ loadings. D = 30.5 %wt. diluent C = 20.9 %wt. MDEA T = 40, 100 °C
[97]	MeOH	D = water-free and 40 %wt. diluent C = 40, 50 %wt. MDEA T = 40, 100 °C
[98]	TEGMME	The authors identify the formation of a second liquid phase at high CO$_2$ loadings. D = water-free and 40 %wt. diluent C = 40, 50 %wt. MDEA T = 40, 100 °C
[99]	EtOH	The authors believe that nonaqueous MDEA can only act as a physical solvent. Therefore, they report Henry's coefficients. Water-free C = 10, 20, 30, 50, 60, 70, 85, 100 %wt. MDEA T = 20 °C
[100]	MEG	D = 60, 65, 70 %wt. diluent C = 30 %wt. MDEA T = 25, 40, 60, 90 °C
[78]	ACEA, DACE, EC	D = 5 %wt. diluent C = 48 %wt. MDEA T = 25, 30 °C
[101]	PC	The solvent developed by the authors has 0.05 %wt. of undisclosed activators. D = 91.95 %wt. diluent C = 6 %wt. MDEA T = 25 °C
[102]	TMS	D = 0.36, 0.86, 1.36 mol·l^{-1} diluent C = 3.0, 2.5, 2.0 mol·l^{-1} MDEA T = 40, 55, 70 °C
[103]	NMP	The authors identify the formation of a second liquid phase at high CO$_2$ loadings. D = 50 %wt. diluent C = 40 %wt. MDEA T = 0, 25, 50, 75, 100, 125, 150 °C
[96]	PEG200	Water-free C = 30 %wt. MDEA T = 40, 80, 120 °C
[46]	EtOH	Water-free C = 15 %wt. MDEA T = 40 °C
[66]	1MIMI, DMSO, MEG, NMP, TMS	D = 1/1 in diluent/water mass basis C = 3.5 mol MDEA·kg solvent^{-1} T = 40 °C
Data for water-lean solvents with AMP		
Reference	Diluents	Conditions and remarks
[79,104]	TMS	D = 32.2 %wt. diluent C = 16.5 %wt. AMP T = 40, 100 °C
[105]	TMS	D = 19.4, 27.7, 32.2, 41.2 %wt. diluent C = 30.6, 22.3, 16.5, 8.2 %wt. AMP T = 40, 60, 80, 100 °C
[106]	DEG, TEG	Water-free C = 0.2, 0.4, 0.6 mol·l^{-1} AMP T = 30, 45, 60, 80 °C
[81]	MEG	Water-free C = 0.4, 0.6, 1.0 mol·l^{-1} AMP T = 30, 45, 60, 80 °C
[107,108]	NMP, TEGDME	The precipitation of AMP-carbamate is observed for both diluents. Water-free C = 15, 25 %wt. AMP T = 25, 50 °C
[109]	NMP	Precipitation was observed at pressures above 3 bars in some of the solvents. D = 41.2, 32.2, 27.7, 19.4 %wt. diluent C = 8.2, 16.5, 22.3, 30.6 %wt. AMP T = 40, 60, 80 °C
[32]	1MIMI, 3DMAPN, 4H, CH, DMSO, PC, 1PeOH	Precipitation was observed at 25 °C in all diluents minus 1MIMI and CH (which is solid at that temperature). Data at 25 °C is not given for CH. Data at 40 °C is not given for systems with 1MIMI, 4H and PC. Water-free C = 25 %wt. AMP T = 25, 40 °C
[110]	MeOH	D = 41.2, 32.2, 27.7, 19.4 %wt. diluent C = 8.2, 16.5, 22.3, 30.6 %wt. AMP T = 40, 60, 80 °C

solubility of methane has been measured in water-lean solvents [22]. As these solvents are formulated with organic diluents, one would think that methane solubility (and thus the possibility of methane slip) should be properly assessed. Fortunately, Murrieta-Guevara and Trejo Rodriguez [22] report very low methane solubility in mixtures of N-methyl-2-pyrrolidone and DEA, so that this might indeed not be a cause for concern even for those working with biogas upgrading or natural gas treating.

To quickly summarize the conclusions of Section 4:

- Water-lean solvents tend to have less capacity for CO$_2$ absorption (i.e. less CO$_2$ solubility) than their corresponding aqueous solvents at low-to-moderate CO$_2$ partial pressures typical of post-combustion carbon capture;
- At higher CO$_2$ partial pressures, water-lean solvents have more capacity for CO$_2$ absorption than the corresponding aqueous solvents due to physical solubility of CO$_2$;
- The crossing-over pressure that delimits these two loci of CO$_2$ solubility is dependent on temperature and amine concentration;
- This loss of CO$_2$ solubility can often be said to be a product of electrostatic phenomena (i.e. secondary medium effect), which affects the carbamate reaction equilibrium;
- Larger cyclic capacities have been experimentally observed in some water-lean solvents, though this is not guaranteed for every solvent formulation.

5. Kinetics in water-lean solvents

In Section 3, we have pointed out that carbamate formation is quite probably not the only reaction that takes place upon CO$_2$ absorption in water-lean solvents. However, it is surely frequently the most important one. Therefore, the treatment of kinetics will rely mostly on the

Table 4

Publications that show VLE data for water-lean solvents with other amines or blends.

Reference	Amines	Diluents	Remarks
[25]	DIPA	TMS	D = 40 %wt. diluent C = 40 %wt. DIPA T = 40, 100 °C
[34]	DGA	TMS, NMP, PC	Authors report equilibrium constants instead of raw data.
[111]	2PDE	TMS	D = 10 %wt. diluent C = 55 %wt. amine T = 40, 100 °C
[112]	TEA	PC	D = 2, 5, 10 %wt. diluent C = 98, 95, 90 %wt. TEA T = 10, 40 °C
[102]	MDEA/PZ	TMS	D = 0.84, 0.68, 0.43 $mol \cdot l^{-1}$ diluent C = 1.68/0.84, 2.0/0.68, 2.5/0.43 MDEA/PZ in $mol \cdot l^{-1}$ T = 40, 55, 70 °C
[113]	AEEA	BP, DEG, TEG	The data for diluents DEG and TEG is provided only at 40 °C. Water-free C = 30 %wt. AEEA T = 30, 40, 50 °C
[96]	DGA	PEG200	Water-free C = 30 %wt. DGA T = 40, 80, 120 °C
[114]	EMEA	1BuOH, BP, DEEA, DEG, PEG200, TEG	Water-free C = 40 %wt. EMEA T = 40 °C
[46]	EMEA/MDEA	EtOH	D = 60, 65, 70, 75 %wt. diluent C = 25/15, 20/15, 15/15, 10/15 EMEA/MDEA in %wt. T = 40 °C
[115]	MDEA/PZ	TMS	D = 10 %wt. diluent C = 42/8, 45/5, 48/2 MDEA/PZ in %wt. T = 40, 50, 60 °C
[116]	2FPEA	OFP	Water-free C = undisclosed T = 30, 40, 60, 80, 120 °C
[117]	AMP/PZ	2EE	D = 2.5 $mol \cdot l^{-1}$ diluent C = 2.5/0.6 AMP/PZ in $mol \cdot l^{-1}$ T = 30 °C
[118,119]	AMP/DMHDA	TEG	D = 2.0 $mol \cdot l^{-1}$ diluent C = 2.5/0.5 AMP/DMHDA in $mol \cdot l^{-1}$ T = 30 °C
[66]	2MPZ	1MIMI, DMSO, MEG, NMP, TMS	D = 1/1 in diluent/water mass basis C = 2.5 mol $2MPZ \cdot kg$ $solvent^{-1}$ T = 40 °C
[120]	TETA, DEEA	NMP	The solvent exhibits separation of two liquid phases. D = 46, 30, 25, 20 %wt. water content C = 1/3 TETA/DEEA in $mol \cdot l^{-1}$ T = 40, 50, 60 °C

assumption that carbamate is the only product between the reaction of CO_2 and amine in these solvents.

Historically, this means that a fair amount of reaction data involving carbamic acid production and/or monoalkyl carbonate formation has probably been lumped together with that referring to the zwitterion mechanism for CO_2 conversion. However, this should not be a great cause of concern. As discussed before, these reactions are practically negligible in most commercial conditions for the majority of benchmark amines.

5.1. Theoretical framework for kinetics

There are at least two competing ways of interpreting kinetics data. Some authors employ the framework of the zwitterion mechanism, as proposed by Caplow [121] and then championed by Danckwerts and Versteeg et al. [122] among others. This framework is wildly popular, and most of the data discussed in this section has been treated following its prerogatives. Conversely, one could employ the termolecular mechanism proposed by Crooks and Donnellan [123], which also has its fair share of support [124]. Though we shall not delve into a debate regarding both frameworks, as their implications when applied to water-lean solvents are practically the same, both of them warrant a short introduction.

According to the zwitterion mechanism, the reaction between CO_2 and amines follows in two steps. The first is the direct reaction between one molecule of amine and one molecule of CO_2 forming a zwitterion. The second is the deprotonation of this zwitterion by a base (which can be the amine itself or any other basic species in solution) forming the amine carbamate species.

$$AmH + CO_2 \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} AmH^+COO^-$$

$$AmH^+COO^- + B \xrightarrow{k_b} AmCOO^- + BH^+$$

The rate of conversion of CO_2 following the zwitterion mechanism is thus given by the equation below.

$$-R_{CO_2} = \frac{[CO_2]\cdot[Am]}{\frac{1}{k_2} + \frac{k_{-1}}{k_2\cdot\sum k_b\cdot[B]}}$$

Since this mechanism assumes two consecutive reactions, the final rate will depend on which step is the rate-determining one (i.e. the slowest). Therefore, the final rate will follow two asymptotic behaviors. If $1/k_2 \gg k_{-1}/(k_2 \cdot \Sigma k_b \cdot [B])$, then the equation below holds. This is equivalent to a reaction where the zwitterion formation is the slowest step, typically due to the instability of the zwitterionic species.

$$-R_{CO_2} \approx k_2\cdot[CO_2]\cdot[Am]$$

Conversely, if $1/k_2 \ll k_{-1}/k_2 \cdot \Sigma kb \cdot [B]$, then it follows that the equation below holds.

$$-R_{CO_2} \approx \frac{k_2}{k_{-1}}\cdot[CO_2]\cdot[Am]\cdot\sum k_b\cdot[B]$$

This means that the conversion rate of CO_2 will be between 1st and 2nd order with respect to the amine. And particularly in the case of water-lean solvents, where the possibility of the diluent itself acting as a base is usually quite remote, Versteeg et al. [122] suggest the approximation given by the equation below.

$$-R_{CO_2} \approx \frac{k_b}{k_{-1}}\cdot k_2\cdot[CO_2]\cdot[Am]^2$$

The termolecular mechanism, on the other hand, proposes that the reaction between amine and CO_2 happens in one singular step, and involves three molecules at once. These three are the amine, molecular CO_2, and a third that can either be the amine itself or the diluent. A loosely bonded species is formed and quickly dissociated, so that the rate determining step of this mechanism is the three-molecular complexation. In other words, the equation below holds. The products of this reaction are the amine carbamate and a protonated species, which could either be the amine or the diluent.

$$-R_{CO_2} = k_{Am}\cdot[CO_2]\cdot[Am]^2 + k_D\cdot[CO_2]\cdot[Am]\cdot[D]$$

Crooks and Donnellan [123] have argued that the zwitterion mechanism rate equation is overparametrized, and Da Silva and Svendsen

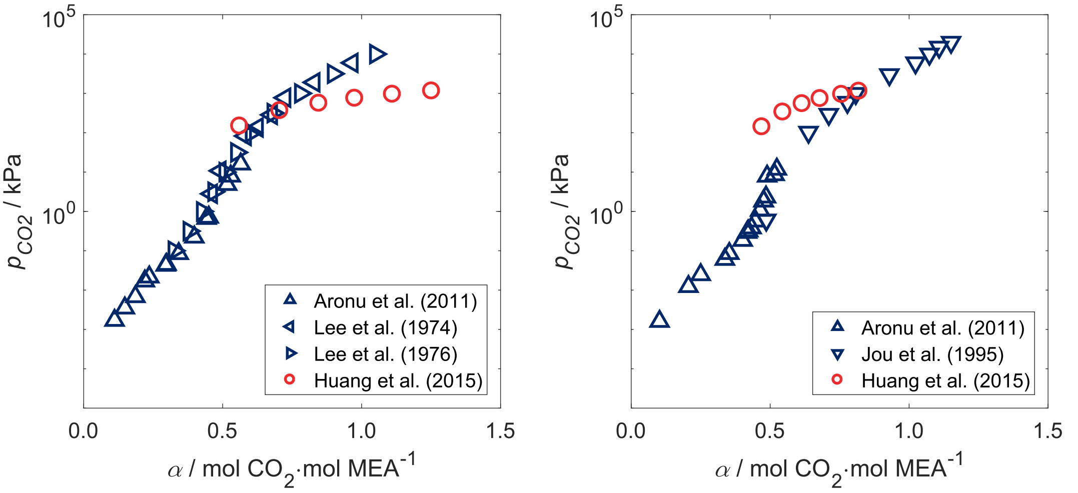


Fig. 5. Crossing-over in VLE data for solvents containing MEA at 40 °C. The data in blue refers to aqueous MEA whereas the data in red refers to water-free DEGDME + MEA. On the right-hand side, one can see the VLE for solutions 15 %wt. MEA. On the left-hand side, the VLE for solutions 30 %wt. MEA. Data adapted from Aronu et al. [74], Lee et al. [75,76], Jou et al. [77] and Huang et al. [73].

[124] have shown that both expressions satisfactorily cover the same range of experimental data. Therefore, results expressed in the language of the zwitterion framework can be readily converted to that of the termolecular mechanism and vice-versa.

The discussion above applies for primary and secondary amines. Ternary amines cannot form carbamates, and it has been often assumed that they absorb CO_2 simply be enabling the formation of bicarbonate in aqueous solutions [125].

$$Am + H_2O \rightarrow AmH^+ + OH^-$$

$$CO_2 + OH^- \rightarrow HCO_3^-$$

A corollary of this mechanism is that tertiary amines should not be able to chemically absorb CO_2 in nonaqueous solutions. This has been supported not only by Versteeg and van Swaaij [40] but by numerous other researchers. It is a fact that reactions in nonaqueous tertiary amine solvents are severely depressed. Li et al. [96] have identified that PEG200 mixed with 30 %wt. MDEA has properties similar to those of a physical solvent. Presumably the absence of water renders the amine almost, if not wholly, unreactive. S. Chen et al. [46] saw the same for ethanol–MDEA, while Pohorecki and Mozeński [112] saw the same for PC–TEA. All three authors, however, report an increase in the solubility of CO_2 with the addition of the tertiary amine. Conversely, many others were able not only to identify these reactions, but also to measure them [37,126,127].

The dismissal of tertiary amine reactions in nonaqueous solvents comes together with the assumption that alkylcarbonates cannot be formed at relevant rates during CO_2 absorption, a thesis also sustained by Versteeg and van Swaaij [40]. And yet, in recent years, several studies based on NMR spectroscopy have come out supporting the existence of alkylcarbonates in water-lean solvents [42,128–130], with one study by Behrens et al. [54] even proving that alkylcarbonates are present in CO_2-loaded aqueous MEA. A good summary on recent findings is present in Cieslarova et al. [131]. Alkylcarbonate formation seems to be a promising thesis to explain the reactivity of tertiary amines in water-lean solvents.

5.2. *Kinetic depression in water-lean solvents*

In general, most kinetic data available for alkanolamine reaction with CO_2 shows that this reaction becomes slower with the addition of organic diluents. This holds equally for primary, secondary and ternary amines.

Adopting the zwitterion mechanism as a framework, this result can be broken down into two correlated phenomena: a decrease in k_2 and a simultaneous decrease in k_b/k_{-1}. The interpretation of these effects inside this framework is that the zwitterion species is particularly unstable in water-lean solvents, which would have the effect of slowing down the direct reaction to form zwitterion (k_2 decreases) and speeding up the reverse reaction (k_{-1} increases, k_b/k_{-1} decreases). Some authors have argued that, due to the low polarities of organic diluents, electrolytic species become inherently less stable in water-lean solvents than they are in aqueous ones [38,39].

Another way that this phenomenon is felt, still in the zwitterion framework, is that the apparent reaction order with respect to the amine itself is reduced when shifting to water-lean solvents. For example, Usubharatana and Tontiwachwuthikul [132] report a reaction order approaching 1.09 for MEA in water, 1.61 in methanol/water 1/1 in mass basis, and 1.73 in pure methanol. These fractionary reaction orders are perfectly consistent with the mathematical formulation of the CO_2 rate of conversion following the zwitterion mechanism.

If one adopts the termolecular framework, the corresponding conclusion would be that the formation of the three-molecular complex leading to carbamate formation is destabilized by the removal of water from the solvent, causing an overall slowing down of reaction rates. The shifting of reaction order means that the solvent itself is less apt to act as base in the termolecular reaction. Thus, in aqueous MEA, water is able to take part in the deprotonation of the termolecule and the apparent overall reaction order with respect to MEA approaches unity. On the other hand, when considering MEA + methanol, the reactivity of the solvent relies heavily on MEA itself acting as a base, meaning its reaction order increases to 1.73. The determining factor on whether a diluent takes part in the reaction or not is better explained by its autoprotolysis constant, which expresses its potential to donate/receive electrons.

Sada et al. [39] were the first to connect this depression of reaction rates and increase of reaction order with the Hildebrand solubility parameter (δ), a parameter which, as they helpfully pointed out afterwards [58], seems to correlate pretty well to the reciprocal of the dielectric permittivity (ε). A number of publications followed swift, in which more amines and diluents were screened, each time ending with a $\log(k_2)$ vs. $1/\varepsilon$ plot to reinforce the initial observations of Sada et al. [39]. Among these publications, we must note the meticulous work carried by the researchers of Pusan National University, who have screened the kinetics of a large array of amines in diverse organic diluents [126,127,133–135]. Dinda et al. [136,137] have validated this relationship even for aniline, an organic amine, in solvents such as chloroform, toluene, methyl ethyl ketone and acetonitrile.

While these results are interesting, it must be noticed that neither Sada et al. [58] nor any of their followers have ever explained in depth the effects of the solvent dielectric permittivity on reaction rates, being content with acknowledging the influence that electrostatic forces have on carbamate destabilization. This explanation ties in nicely with the framework of the zwitterion mechanism, and also has its due implications in the framework of the termolecular mechanism. However, as pointed out by Da Silva and Svendsen [124], the autoprotolysis constant of the diluent (pK_S) might also be able to indicate whether they are able to partake in the termolecular reaction or not, thus elucidating the apparent increasing reaction orders in water-lean solvents. To illustrate this, we have taken the liberty of plotting the rate data obtained by Son et al. [135] for AMP 1 – 3 $mol \cdot l^{-1}$ at 25 °C against the ε of their diluents and against their pK_S. By doing this, we have obtained Figs. 6 and 7.

In Figs. 6 and 7, we see that the apparent trend between ε and pK_S means that both the zwitterion and termolecular explanation for fractionary orders of reaction are consistent with the data available for reaction rates in water-lean solvents. Sadly, the biggest outlier in Fig. 6 is also an outlier in Fig. 7 (propylene carbonate, $\varepsilon = 65$, $pK_S = 29.2$). We might mention that there are suspicions that propylene carbonate is reactive with AMP itself [32]. Minus this exception, it seems as if there are observable trends between reaction rates, orders, dielectric permittivities and autoprotolysis constants.

We have carried out a statistic analysis on the data presented in Fig. 6. The Pearson correlation coefficients between ε and $\ln(k_2)$, $\ln(k_b/k_{-1})$ and $\ln(N)$ are respectively $R(\varepsilon,\ln(k_2)) = 0.8005$, $R(\varepsilon,\ln(k_b/k_{-1})) = 0.7935$ and $R(\varepsilon, \ln(N)) = -0.7869$. However, when the data points corresponding to propylene carbonate are removed, these increase to $R(\varepsilon,\ln(k_2)) = 0.9874$, $R(\varepsilon,\ln(k_b/k_{-1})) = 0.9609$ and $R(\varepsilon, \ln(N)) = -0.9408$. Those are fairly good indications of pattern behavior, notwithstanding the relatively small size of the available dataset. A similar analysis can be performed on the data shown in Fig. 7, resulting in that the correlation coefficients are respectively $R(pK_S,\ln(k_2)) = -0.4908$, $R(pK_S,\ln(k_b/k_{-1})) = -0.4902$ and $R(pK_S,\ln(N)) = 0.4972$, while removal of the data points corresponding to propylene carbonate increases those values to $R(pK_S,\ln(k_2)) = -0.7979$, $R(pK_S,\ln(k_b/k_{-1})) = -0.8434$ and $R(pK_S,\ln(N)) = 0.8911$. Therefore, it looks as if the dielectric permittivity correlation has a statistical edge over the autoprotolysis constant correlation.

Though a similar behavior is observed in nonaqueous solvents containing tertiary amines, we have not encountered any publication that reports reaction orders different than unity regarding the amine itself [37,126,127].

To compare both mechanisms, we have attempted to interpret a set of kinetic data employing the termolecular approach instead of the zwitterion approach. We have treated the data obtained by Park et al. [134] for mixtures between DEA and a row of different diluents (water, methanol, ethanol, 1-propanol, 1-butanol, ethylene glycol, propylene glycol and propylene carbonate). Their observations are presented in the form of the overall kinetic coefficient k_{ov}, which in the case of the zwitterion mechanism is defined as below. The choice of disregarding the reaction between CO_2 and free hydroxide anions came from the authors themselves.

$$k_{ov} = \frac{[Am]}{\frac{1}{k_2} + \frac{k_{-1}}{k_2 \cdot k_b} \cdot \frac{1}{[Am]}}$$

Having presented their data in terms of k_{ov}, the kinetic rates k_2 and k_b/k_{-1} can be calculated by the authors by following a simple linear regression.

$$\frac{[Am]}{k_{ov}} = \frac{1}{k_2} + \frac{k_{-1}}{k_2 \cdot k_b} \cdot \frac{1}{[Am]}$$

Conversely, if one employed the termolecular mechanism equation for reaction rates, the linear regression required for obtaining the kinetic coefficients would be the one shown below.

$$\frac{k_{ov}}{[Am]^2} = k_{Am} + k_D \cdot \frac{[D]}{[Am]}$$

We have estimated the molar concentration of diluent in the solutions prepared by Park et al. [134] by assuming ideal mixing rules for calculating their liquid densities. The kinetic coefficients regressed from their data is presented in Fig. 8 in terms of the dielectric permittivity ε. The data points referring to propylene glycol have been omitted due to our suspicions that this compound takes part in side-reactions with the amine.

As one can see in Fig. 8, though the behavior of the kinetic coefficient k_{Am} seems to be correlated to the dielectric permittivity of the diluent, the behavior of k_D appears to be more erratic. Since, as we have seen before, ε and kP_S follow a similar trend, Fig. 8 does not look much different once it is plotted in terms of the autoprotolysis constant. For effect of comparison, the same data was regressed in terms of the zwitterion mechanism kinetic coefficients, and the results are presented in Fig. 9. Naturally, these results are the same as the ones calculated by Park et al. [134] themselves. Though there are variations from the trend, the appearance of a regular behavior in Fig. 9 is certainly stronger than in Fig. 8. A more thorough statistical approach to these visual observations is shown on Table 5. One can see that the regression of the kinetic coefficients k_{Am} and k_D, for the termolecular mechanism, and k_2 and k_b/k_{-1}, for the zwitterion mechanism, is carried out with fairly good values for the Pearson correlation coefficients. In general, both approaches seem to produce a reliable parametrization of the kinetic data (with the caveat that we are considering that k_b and k_{-1} are always

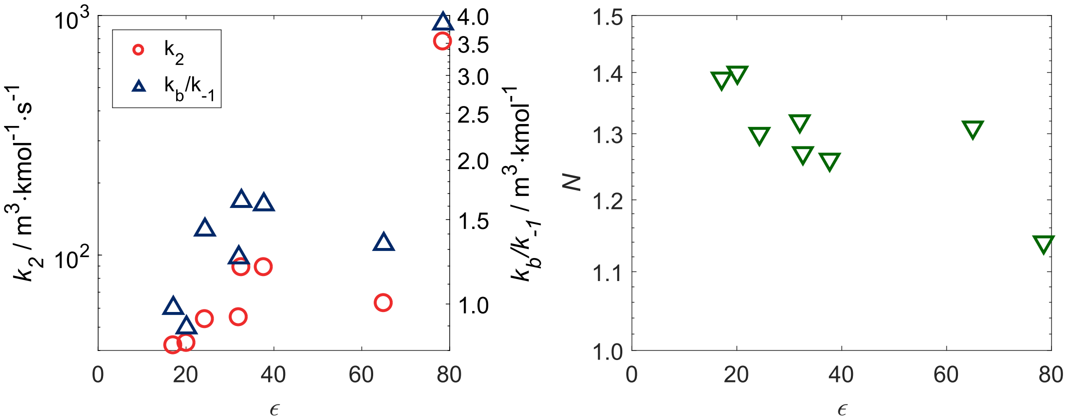


Fig. 6. Kinetic rates and reaction order of AMP at 25 °C and concentrations between 1 and 3 $mol \cdot l^{-1}$ in water-free solvents containing methanol, ethanol, 1-propanol, 1-butanol, ethylene glycol, propylene glycol and propylene carbonate. Viewed from the dielectric permittivity perspective. Adapted from Son et al. [135].

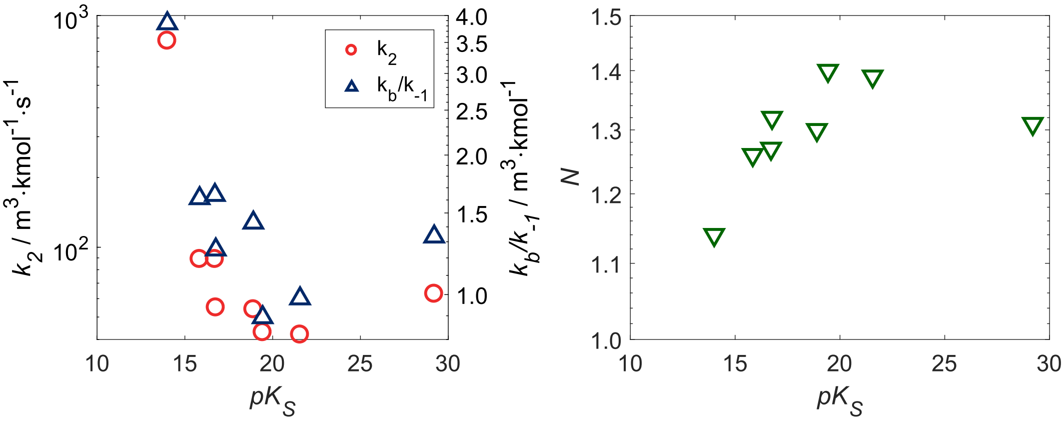


Fig. 7. Kinetic rates and reaction order of AMP at 25 °C and concentrations between 1 and 3 mol·l^{-1} in water-free solvents containing methanol, ethanol, 1-propanol, 1-butanol, ethylene glycol, propylene glycol and propylene carbonate. Viewed from the autoprotolysis constant perspective. Adapted from Son et al. [135]. Autoprotolysis constants obtained in Izutsu [138] and Kundu and Das [139].

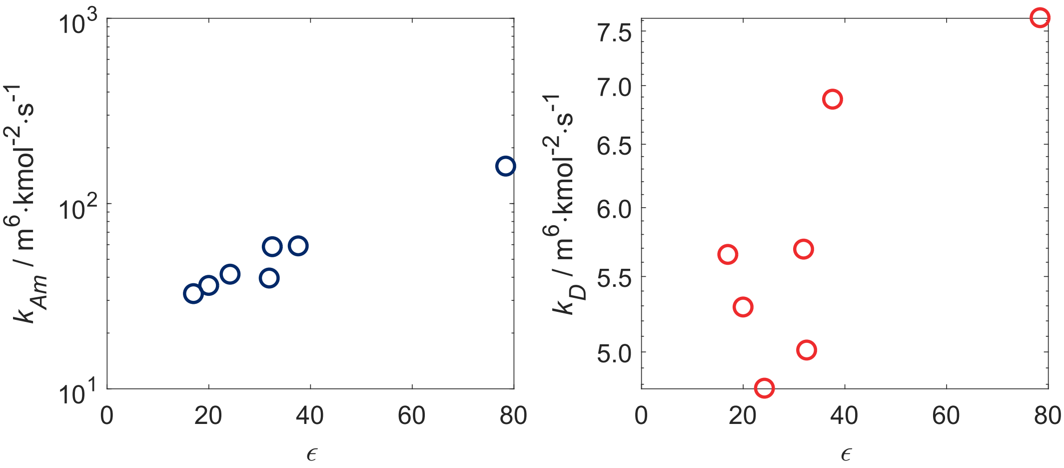


Fig. 8. Termolecular mechanism kinetic coefficients for DEA at 25 °C and concentrations between 1 and 3 mol·l^{-1} in water-free solvents containing methanol, ethanol, 1-propanol, 1-butanol, ethylene glycol and propylene glycol. Regressed from data obtained by Park et al. [134]. Demonstration of their behavior with shifting dielectric permittivities.

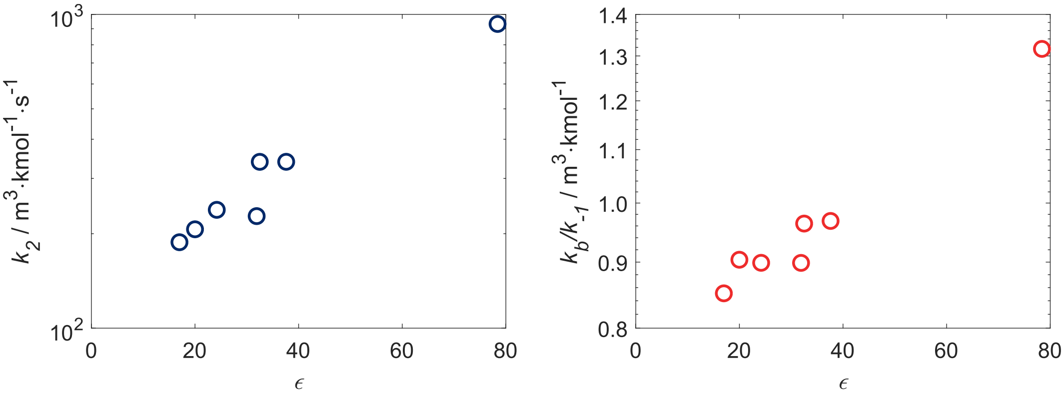


Fig. 9. Zwitterion mechanism kinetic coefficients for DEA at 25 °C and concentrations between 1 and 3 mol·l^{-1} in water-free solvents containing methanol, ethanol, 1-propanol, 1-butanol, ethylene glycol and propylene glycol. Regressed from data obtained by Park et al. [134]. Demonstration of their behavior with shifting dielectric permittivities.

lumped together in k_b/k_{-1}, meaning that both mechanisms result in the same number of parameters). However, when one tries to correlate the kinetic coefficients with properties of the pure diluents such as their dielectric permittivity ε or autoprotolysis constant pK_S, the best Pearson coefficients are observed for the zwitterion kinetic constants and the dielectric permittivities. Interestingly thus, it seems that the approach initially adopted by Sada et al. [39] and then by the researchers of the Pusan National University [126,127,133–135] turns out to be the most adequate one for this particular case of water-lean solvents containing DEA (see Table 5).

Table 5

Kinetic coefficients and statistical parameters R (Pearson correlation coefficients) for treatment of the data from solvents containing DEA by Park et al. [134]. Both k_{Am} amd k_D are given in $m^6 \cdot kmol^{-2} \cdot s^{-1}$, k_2 is given in $m^3 \cdot kmol^{-1} \cdot s^{-1}$, and k_b/k_{-1} is given in $m^3 \cdot kmol^{-1}$.

	k_{Am}	k_D	R (Term.)	k_2	k_b/k_{-1}	R (Zwit.)
Water	157.8	7.621	0.9899	928.6	1221.2	0.9677
MeOH	57.98	5.008	0.9914	337.6	0.9632	0.9640
EtOH	41.20	4.773	0.9696	237.4	0.8981	0.9391
1PrOH	35.84	5.289	0.9840	205.8	0.9030	0.9931
1BuOH	32.35	5.651	0.9726	187.2	0.8505	0.9749
MEG	58.59	6.856	0.9821	337.7	0.9677	0.9923
PG	39.27	5.711	0.9935	226.7	0.8979	0.9994
Correlation coefficients between kinetic coefficients and properties of the diluent						
	$R(k_{Am},\ln(\varepsilon))$ =		0.9143	$R(k_2,\ln(\varepsilon))$ =		0.9130
	$R(k_D,\ln(\varepsilon))$ =		0.7798	$R(k_b/k_{-1},\ln(\varepsilon))$ =		0.9212
	$R(k_{Am},\ln(pK_S))$ =		−0.7986	$R(k_2,\ln(pK_S))$ =		−0.7965
	$R(k_D,\ln(pK_S))$ =		−0.7118	$R(k_b/k_{-1},\ln(pK_S))$ =		−0.8170

This performance is not always observed, as for example Kadiwala et al. [140] have obtained a better parametrization of their data through the termolecular rate equation. Finally, we do not intend in this review to proselytize over any of these approaches, and neither do we imply that either ε or pK_S are able to individually explain each phenomenon reported in literature. All of these frameworks and parameters together help understanding the depression of reaction rates in water-lean solvents. Hopefully, this discussion can give a perspective on the difficulties of narrowing the explanation down to one single factor.

5.3. *Literature data for kinetics in water-lean solvents*

A comprehensive list of published articles dealing with kinetics in water-lean solvents can be seen on Table 6. Most of the empirical data found in literature either reinforces or at least does not contradict entirely what has been found out by Sada et al. [37–39,58] and discussed in the previous section. However, some exceptions should be noted carefully.

Alvarez-Fuster et al. [141] have reported reduced absorption and kinetic rates in mixtures of ethylene glycol and MEA when compared to aqueous MEA. Indeed, most of the literature on amine-MEG mixtures reports a reduction in kinetic rates when operating with MEG [133–135,142]. Another reduction in mass transfer rates is exemplified in the data of Jiru and Eimer [143] when shifting from a water-MEA to a MEG-MEA solvent. On the other hand, Kang et al. [88] report an enormous increase both in kinetic and mass transfer rates by shifting from aqueous 30 %wt. MEA to water-free MEG-MEA. Garcia et al. [144] also describe moderate enhancements in both rates when adding MEG to MEA and DEEA/MAPA (3/2 in $mol \cdot l^{-1}$) blends, and Zheng et al. [145] report an increment in kinetic rates (but not in mass-transfer rates) in AMP-MEG mixtures. We shall discuss more about the distinction between kinetic rates and mass transfer rates in the next section, but it is remarkable that so many discrepancies transpire from data regarding amine-glycol mixing.

More notably, the data from Garcia et al. [144] shows that the kinetics of water-lean solvents containing MEA surpass those of aqueous MEA at higher temperatures (>50 °C). Since most of the kinetic data obtained by other researchers consists only in measurements taken at a single temperature, usually 25 °C, it is quite difficult to properly discuss these results.

Through analysis of these exceptions, one can begin to understand the troubles of dealing with separate sets of kinetic data. This mostly stems from the fact that this data is not directly measurable. Reaction rates have to be extracted from mass transfer rates under a predetermined set of assumptions, such as pseudo-first order conditions, and mass transfer rates themselves have to be calculated under the assumption of an estimated gas phase resistance. Jiru and Eimer [143] have demonstrated how small deviations from these conditions might propagate into enormous errors in the measured kinetic rates.

Table 6

Publications that show kinetic data for water-lean solvents.

Solvents with MEA, DEA, MDEA and AMP		
Reference	Amines	Diluents
[141]	MEA, DEA, CHA	EtOH, MEG
[39]	MEA, DEA	MeOH, EtOH, 2PrOH
[55]	MEA	NMP/DEG
[132]	MEA	MeOH
[146]	MEA	MEG
[144]	MEA, DEEA/MAPA	CARB, MEG, DEG, TEG
[147]	DEA	EtOH
[148]	DEA	EtOH
[41]	DEA	EtOH, 1BuOH
[142]	DEA	MEG
[149]	DEA, DIPA	PEG400
[134]	DEA	MeOH, EtOH, 1PrOH, 1BuOH, MEG, PG, PC
[40]	MDEA	EtOH
[126]	MDEA	MeOH, EtOH, 1PrOH, 1BuOH, MEG, PG, PC
[150]	AMP	1PrOH
[135]	AMP	MeOH, EtOH, 1PrOH, 1BuOH, MEG, PG, PC
[145]	AMP	MEG
Solvents with other alkanolamines and piperazines		
Reference	Amines	Diluents
[37]	TEA	MeOH, EtOH, 2PrOH
[127]	TEA	MeOH, EtOH, 1PrOH, 1BuOH, MEG, MPG, PC
[38]	MIPA, CHA	MeOH, EtOH, 2PrOH, TOL
[133]	DIPA	MeOH, EtOH, 1PrOH, 1BuOH, MEG, PG, PC
[140]	EDA, MPA	MeOH, EtOH
[151]	AEEA	MeOH, EtOH
[152]	DETA, MIPA	MeOH, EtOH
[153]	EMEA	DEEA
[154]	AEPD, AMPD, PZ	EtOH
Solvents with organic amines and aminoacids		
Reference	Amines	Diluents
[155]	CHA	TOL/2PrOH
[58]	EDA	MeOH, EtOH, MEG
[156]	Aniline, CHA, HA	EtOH
[136]	Aniline	Acetonitrile, MEK, TOL, m-xylene
[137]	Aniline	CCL4, CHCL3
[157]	ProK	MEG
[158]	ProK	EtOH

Additionally, trouble also comes from the fact that we are trying to treat an enormous array of chemicals, both amines and organic diluents, through the perspective of a single reaction mechanism. Surely one is bound to find exceptions. And finally, though both the zwitterion mechanism and the termolecular mechanism offer practical frameworks for treating and analyzing data, none of them is entirely satisfying. It might be that another framework would lead to a better understanding of the discrepancies observed regarding amine-glycol mixtures. Though we attempt to offer an overview on what is known about kinetics in water-lean solvents, there is no consensus among the investigators in this field.

To quickly summarize the conclusions of Section 5:

- A kinetic depression can be observed in water-lean solvents when compared to their corresponding aqueous solvents;
- It is not entirely clear if this depression comes as a product of electrostatic phenomena (represented by the dielectric permittivity ε) or as a product of less active reactants (represented by the autoprotolysis constant pK_S), though the former explanation is more often found in the literature;
- Both the termolecular mechanism and the zwitterion mechanism are consistent with the slower rates of reaction in water-lean solvents, though explanations for the observable phenomena may differ.

6. Rate of absorption in water-lean solvents

Kinetic rates show a partial image of how fast absorption proceeds in water-lean solvents. Another part of the image is given by parameters such as CO_2 physical solubility (i.e. its Henry's coefficient in the solvent) and diffusivities of CO_2 and amine species.

Part of the interest in developing water-lean formulations can be attributed to the possibility that, due to their enhanced physical solubility of CO_2, absorption rates could be faster in these solvents [18,66]. This is indeed true, as rates of absorption, especially those measured in unloaded solutions, appear to be higher in solvents containing good physical absorbers for CO_2 [144]. In loaded solutions, however, this advantage is minimized due to the steep increase of viscosity upon CO_2 absorption in water-lean solvents.

In Section 6.1, we shall discuss the dependency of absorption rates on solvent viscosity and physical CO_2 solubility. Then, the increase of viscosity with loadings in water-lean solvents is addressed in Section 6.2.

6.1. *Theoretical framework for rate of absorption*

In loose terminology terms, from the bulk of the vapor phase to the bulk of the liquid phase, each CO_2 molecule has to overcome resistances coming from the gas and liquid sides. This means that the three equations below describe this system.

$$N_{CO_2} = k_g \cdot \left(p_{CO_2} - p_{CO_2,i}\right)$$

$$N_{CO_2} = k_l \cdot \left([CO_2]_i - [CO_2]\right)$$

$$p_{CO_2,i} = H_{CO_2} \cdot [CO_2]_i$$

Applying the three equations shown before, the molar flux of CO_2 can be calculated by the following equation.

$$N_{CO_2} = \frac{p_{CO_2} - H_{CO_2} \cdot [CO_2]}{\frac{1}{k_g} + \frac{H_{CO_2}}{k_l}}$$

Considering the equation above, we must notice that the numerator is given by the difference between the CO_2 partial pressure in the vapor phase (p_{CO2}) and the CO_2 partial pressure in equilibrium with the solvent at a given loading. This driving force is the Δp_{CO2} of a process and is not a function of the solvent itself, but merely of how reversibly one chooses to operate the absorption of gas. Similarly, the vapor phase mass transfer coefficient k_g is not generally dependent on the solvent, though solvent volatility does have an effect on k_g in very particular experimental applications [143]. Conversely, the Henry's coefficient of CO_2 and the liquid phase mass transfer coefficient are strong functions of the solvent inherent properties.

Supposing one wants to develop a water-lean solvent that provides faster absorption rates than an aqueous amine, the following equation should hold.

$$\frac{\Delta p_{CO_2}}{\frac{1}{k_g} + \frac{H_{CO_2,wl}}{k_{l,wl}}} > \frac{\Delta p_{CO_2}}{\frac{1}{k_g} + \frac{H_{CO_2}}{k_l}}$$

Song et al. [159] have empirically demonstrated in a packed column that k_l is a function of liquid velocity, CO_2 diffusivity and solvent viscosity. By normalizing the effects of velocity and applying the consideration that diffusivities themselves vary with viscosity, they show that k_l and viscosity are correlated following a slope of approximately -0.7. In other words, the equation given previously could be rewritten as the one shown below. The equation below completely ignores the effects that organic diluents have on kinetic rates, since the expression for k_l obtained by Song et al. [159] is valid only for liquid phase mass transfer coefficients in the absence of chemical reaction.

$$\frac{\Delta p_{CO_2}}{\frac{1}{k_g} + \frac{H_{CO_2,wl}}{\eta_{wl}^{-0.7}}} > \frac{\Delta p_{CO_2}}{\frac{1}{k_g} + \frac{H_{CO_2}}{\eta^{-0.7}}}$$

As we have seen, kinetic rates are typically depressed in water-lean solvents. Therefore, the expression above delimits a best-case scenario for these mixtures, i.e. one cannot reasonably assert that water-lean solvents that obey this relationship will absorb CO_2 faster, but that water-lean solvents that do not obey it will probably absorb CO_2 slower.

Reorganizing this expression, one finally ends up with the relationship below between the Henry's coefficient and the viscosity for a fast water-lean solvent for CO_2 capture.

$$\left(\frac{H_{CO_2,wl}}{H_{CO_2}}\right) < \left(\frac{\eta_{wl}}{\eta}\right)^{-0.7}$$

This relationship, though far from perfect, has some interesting implications. Fig. 10 has been obtained by plotting this equation. The locus for finding fast absorbing organic solvents seems smaller than one would initially think, being entirely delimited by the area below the red line. It is imaginable that a similar locus should also be observed in the context of mixing these diluents with amines.

In Fig. 10 one can also see the relative properties of some pure diluents at 25 °C. These diluents are shown to illustrate the fact that, though there are several organic solvents that deliver CO_2 solubilities higher than water, their viscosities might often be problematic if one is looking for high mass transfer rates.

Another consequence of that relationship is that variations in temperature will affect the relative advantage of shifting from aqueous to water-lean solvents. This is because the temperature dependency of Henry's coefficients and viscosities are not alike for water and organic diluents, though they might be similar. Fig. 11 illustrates this fact. One can observe that increases of temperature move sulfolane towards the 'right direction' in terms of enabling a faster CO_2 absorption than water.

Fig. 11 might perhaps help explaining the observations of Garcia et al. [144], who have experimentally identified a steeper increase in mass transfer rates with temperatures while absorbing CO_2 in water-lean solvents than in aqueous ones.

However, one should be careful to note that both Fig. 10 and Fig. 11 show the relative Henry's coefficients and viscosities only for pure diluents, with no addition of amines nor loadings of CO_2. As we shall see in Section 6.2, the viscosity dependency on CO_2 loading is quite an important aspect in water-lean solvents.

6.2. *Viscosity and loading effects on viscosity*

Viscosity in water-lean solvents is usually higher than that of aqueous ones. This is particularly true for water-lean solvents with low volatility. Mixtures of amine and methanol, for example, have

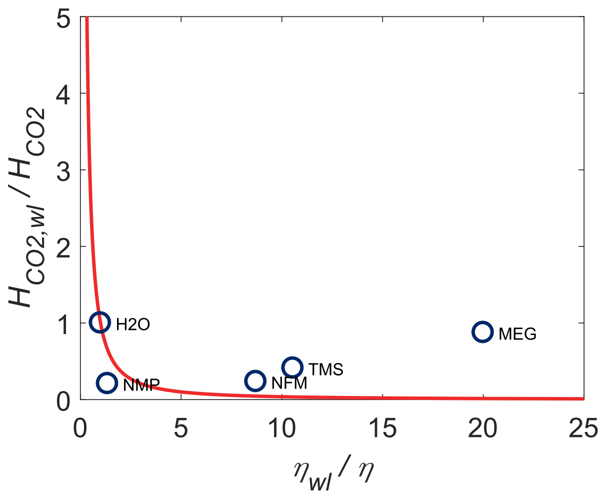


Fig. 10. Relationship between Henry's coefficient and viscosity for a fast absorbing organic solvent. The relative Henry's coefficients and viscosities of some typical diluents, pure and at 25 °C, are plotted for comparison. Their CO_2 solubilities were obtained in Hansen [64] while their viscosities were obtained in Yaws [160].

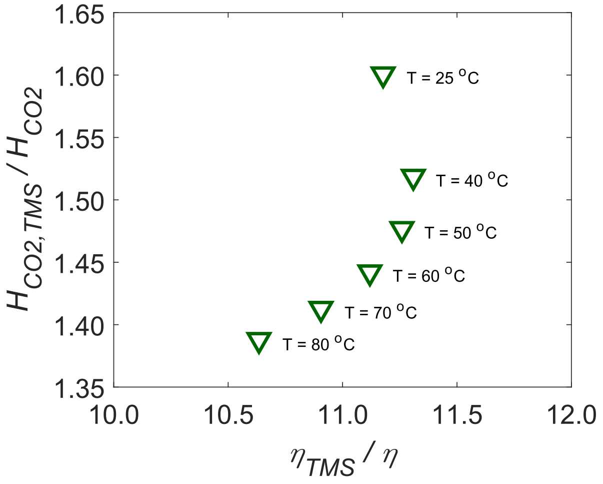


Fig. 11. Dependency on temperature of relative Henry's coefficients and viscosities for sulfolane. Henry's coefficients at different temperatures for CO_2 in sulfolane were obtained in Murrieta-Guevara et al. [23], whereas those for CO_2 in water were obtained in NIST. Viscosities and their variations with temperature were obtained in Yaws [160].

comparatively low viscosity when unloaded, but their viscosity increases steeply upon CO_2 absorption [59]. Amine and ethanol mixtures also have low viscosities when unloaded [161], which is only natural as both methanol and ethanol have lower viscosity than water. For formulations with diluents such as N-methyl-2-pyrrolidone and ethylene glycol, the unloaded mixtures have higher viscosities than those of aqueous solvents, and loading with CO_2 increases them even more. This has been observed also by Yuan and Rochelle [18], Bougie et al. [162] and by Guo et al. [80]. The liquid crystal MEA-based solvent developed by Rodríguez-Fabià et al. [92] shows an unbelievable increase of viscosity with loading that ultimately ends with a phase transition towards solid crystal. Unfortunately, though there is a huge amount of published data for the viscosities of unloaded water-lean solvents, little is reported on their viscosities when loaded. As such, we are unable to find any exception to this trend in literature.

In an interesting theoretical work, Esteves et al. [163] have demonstrated how the viscosity of liquid mixtures of electrolytes have a behavior, according to the Debye-Hückel approach, that follows the following expression.

$$\ln(\eta)\propto\frac{I^{3/2}}{\varepsilon^{3/2}}$$

In the expression above, I is the ionic strength of the electrolytes and ε is the dielectric constant of the medium. Notice that the ionic strength of an amine solvent generally varies between zero and the molarity of the amine itself (when every amine molecule has been protonated), with half the molarity of the amine being a typical value in the case of carbamate formation. A solvent containing 30 %wt. monoethanolamine (MEA) will contain typically around 4.9 mols per liter of MEA, and its ionic strenght will vary from 0 mol/l (unloaded) to 2.45 mol/l (maximum carbamate formation) to 4.9 mol/l (maximum bicarbonate/carbonate formation). The ionic strengths of loaded amine solvents are undoubtedly higher than those for which the Debye-Hückel approach is valid, which account solely for long-range interactions between elecrolytes, typically below $I = 1$ mol/l. To this effect, Esteves et al. [163] also propose the Guggenheim correction (dependent on I^2 and independent on ε) to extend the range of applicability of their equation. Nonetheless, in general terms, the more loaded with CO_2, the more ions in solution a solvent will have, and therefore the higher its ionic strength. Similarly, for solvents at a fixed ionic strength (which can be loosely correlated to having the same CO_2 loading), lower dielectric permittivities imply higher viscosities. As discussed previously in Section 4.1, water has the highest of all dielectric permittivities among diluents for amine solvents. It can be suggested that every possible water-lean solvent will, due to electrostatic phenomena, inevitably experience steeper viscosity increase with loading.

Fig. 12 illustrates the issue being discussed here with data for aqueous MEA and for nonaqueous 2-methoxyethanol plus MEA, both at 30 %wt. concentration of the amine and 40 °C. The data was obtained by Amundsen et al. [164] and by Guo et al. [80]. One can easily observe how drastic is the increase in viscosity through CO_2 loading with water-lean solvents when compared to aqueous ones.

We have also exemplified the relationship between viscosity, ionic strength and dielectric permittivity outlined by Esteves et al. [163] in Fig. 12 by treating the data obtained by Amundsen et al. [164] and Guo et al. [80]. The dielectric permittivities of water and 2-methoxyethanol at 40 °C (respectively 73.15 and 16) were found in Wohlfarth [165], though it must be pointed out that in deriving Fig. 12 we have employed only the ε of the pure diluents, with no considerations on the effects of the ε of MEA itself. The parallel lines were forced to be parallel by performing a simultaneous linear regression on the data for both solvents (i.e. only one angular coefficient was calculated with the double set of data). Regardless of this mathematical trickery, it does look like this approach has some depth to it. Therefore, it might be fair to suggest that evaluation of viscosity of loaded and unloaded solutions should be prioritized when developing a water-lean solvent formulation. Moreover, the Pearson correlation coefficient between $(I/\varepsilon)^{3/2}$ and $\ln(\eta)$ for aqueous MEA is $R((I/\varepsilon)^{3/2},\ln(\eta)) = 0.9823$, whereas that between I^2 and $\ln(\eta)$ is $R(I^2,\ln(\eta)) = 0.9738$. These are inconclusive results for evaluating whether the Guggenheim extension is necessary to aid the Debye-Hückel approach or not, though this is not the main focus of this discussion.

Besides its obvious effect in lowering mass transfer rates, as discussed by Garcia et al. [144] and by Yuan and Rochelle [18], high solvent viscosities have an enormous impact on other parts of the CO_2 capture plant [166]. This will be discussed further in Section 8.3. Now that the theory on mass transfer rates has been addressed, one can proceed to analyze the literature data on mass transfer rates in water-lean solvents.

6.3. Literature data for absorption rates in water-lean solvents

This Section 6.3 will concern itself on literature data for mass transfer parameters that are somehow applicable to industrial operations. This means either liquid phase mass transfer coefficients, overall mass transfer coefficients or CO_2 molar fluxes in water-lean solvents. These parameters are often measured in equipment such as string of discs, wetted wall columns, stirred cell reactors or even bench scale absorber columns. Another sort of rate information, obtained in more loosely controlled environments and typically just comparative in nature, will be dealt with in a different part of this review (Section 7).

Mass transfer rates of water-lean solvents have been measured by multiple authors. Of all chemical combinations, by far the most investigated one was that of MEA + methanol + water. Studies carried by Sema et al. [9], Fu et al. [10], Gao et al. [11–13] and Rashidi et al. [14] have all exhaustively observed the increase in absorption rates when shifting from aqueous MEA to mixtures containing methanol. Tamajón et al. [167] also obtain enhanced absorption rates in MDEA + methanol solutions. Conversely, Chen et al. [46] saw the absorption rates dropping in MDEA + ethanol solutions, probably because the kinetics of this tertiary amine in ethanol are so depressed that chemical absorption is almost precluded.

As implied before, methanol is a special organic diluent since its viscosity is fairly lower than that of water. Therefore, even if its dielectric permittivity is also lower, ε ≈ 29 according to Wohlfarth [165], viscosity shall not be a big issue when operating with methanol mixtures. When adding this up to the high CO_2 solubility in pure methanol, mass transfer rates are understandably higher in hybrid formulations with this alcohol.

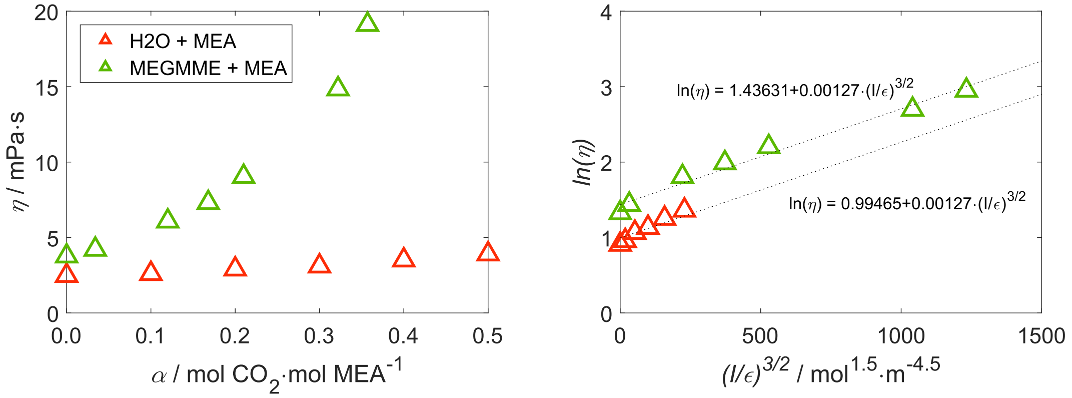


Fig. 12. Viscosity increase with loading for aqueous 30 %wt. MEA and 2-methoxyethanol + 30 %wt. MEA at 40 °C, plus demonstration of its dependency on ionic strength. Data obtained from Amundsen et al. [164], Guo et al. [80] and Wohlfarth [165].

Of course, methanol has the issue of its high volatility, and both solvent losses and high latent heat expenses are consequences of its employment. Gao et al. [168] have attempted to address this problem by adding glycerol into a methanol–MEA solvent. The problem was addressed, but absorption rates were evidently reduced (though remaining higher than those of aqueous MEA).

For the cases involving chemicals with low volatility, several researchers have found similar behavior among distinct solvents. Initially, absorption rates are clearly higher in water-lean solvents containing diluents with good physical CO_2 absorption capacities. The investigation of Garcia et al. [144] on unloaded water-lean solvents containing blends of MEA or DEEA/MAPA with glycols and carbitol is quite illustrative of this phenomenon. However, as solvents are loaded and their viscosities increase, this advantage starts disappearing. This has been observed by Yuan and Rochelle [18,169] and by Wanderley et al. [66] in clear terms, and can be also interpreted from the data of Zou et al. [170] regarding CO_2 absorption in a blend of MEA, sulfolane and water. An example of this behavior can be seen on Fig. 13, which was plotted based on data from Dugas and Rochelle [61] and from Yuan and Rochelle [169].

In terms of performance, N-methyl-2-pyrrolidone is perhaps the best diluent found so far for enhancing absorption rates [18,66,169,170]. Its low Henry's coefficient and viscosity, which can be seen on display in Fig. 10, plus its dielectric permittivity at 25 °C of $\varepsilon \approx 32.6$ [165] (lower than that of water, but higher than that of any alcohol) would make this a great candidate for water-lean solvent formulation, were it not reproductively toxic [32]. As the industry is slowly backing away from using N-methyl-2-pyrrolidone, it is hard to make a case for solvents relying on this chemical. Sulfolane has also been seen to deliver enhancements in mass transfer rates [66,169,170], which is somewhat unexpected due to the high viscosity of this diluent (see Figs. 10 and 11). However, since sulfolane has also been identified at eventually promoting phase separation upon loading in all most water-lean solvents, one should wonder what exactly is being measured when mass transfer rates are identified in sulfolane–MEA or sulfolane–piperazine mixtures.

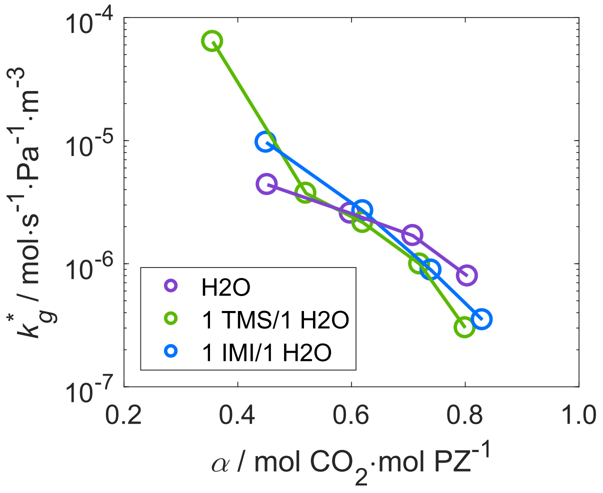


Fig. 13. Decrease in liquid phase mass transfer coefficient with loading observed for mixtures of 5 molal piperazine with water, water + sulfolane and water + imidazole at 40 °C. The organic diluent/water ratio is given in mass basis. Data obtained from Dugas and Rochelle [61] and Yuan and Rochelle [169].

Liu et al. [171] have tried developing water-lean solvents targeted at having low viscosity when absorbing CO_2. Their case is quite special, as the proposed water-lean solvent is a pure amine with no diluent. Functionalized variations of ethylenediamine were proposed by the authors, with the functional groups being added with the goal of reducing viscosity and sustaining high absorption capacity. In the end, the authors were able to obtain an amine which did not become excessively viscous when loaded, though still quite so when compared to traditional aqueous amines.

In regards to phase separating solvents, identifying the effect of adding organic diluents is particularly difficult, since one cannot be sure if the absorption rates change due to phase separation or due to the new organic diluent itself. It is also not clear whether these rates change for the better or for the worse. Karlsson et al. [172] verified higher mass transfer rates in precipitating NMP–AMP systems, while Ye et al. [120] saw that substituting water by NMP in TETA/DEEA demixing systems steadily decreased the absorption rates. Investigating precipitating potassium prolinate + ethanol mixtures, Shen et al. [173], Bian and Shen [174] and Bian et al. [158] have identified that, though mass transfer rates initially increase by opting for alcohol instead of water in their mixtures, those quickly decrease as precipitation starts. Demixing drastically decreases absorption rates in MEA + 2,4,7,10-tetraoxaundecane solvents [175] (a diluent whose structure is strikingly similar to that of TEGDME). Clearly, a better understanding on phase separation effects on CO_2 absorption rates is required for those studying biphasic systems.

To quickly summarize the conclusions of Section 6:

- Due to the high CO_2 physical solubility in many organic solvents, rates of absorption in unloaded water-lean solvents are often faster than in their aqueous counterparts;
- However, as the solvent becomes loaded, its viscosity increases steeply – likely due to electrostatic phenomena;
- Coupled with the depressed kinetics mentioned in Section 5, the high viscosities of water-lean solvents tend to bring a reduction of absorption rates at higher CO_2 loadings;
- This effect is more pronounced at lower temperatures.

7. Quick evaluations: capacity and rate in new solvents

Obtaining and treating vapor–liquid equilibrium data, kinetic rate data and mass transfer rate data can be incredibly time-consuming. For a quick evaluation of a large number of new solvents, fast methods such as checking their CO_2 absorption capacities and absorption rates in a bubbling cell can be very practical.

Surely, this type of data is hierarchically less meaningful than VLE or kinetics. We are not making an unfair distinction in stating so. The CO_2 capacity of a solvent is nothing more than one single vapor–liquid equilibrium point, taken at one single CO_2 partial pressure and one single temperature. Similarly, its rate of absorption is confined by the very specific, hardly scalable experiment of bubbling CO_2 into one flask of solvent. In other words, one can obtain capacity and rate information from VLE and kinetic data, but not the opposite.

And yet, some reports on rate and capacity are the most interesting one can find regarding water-lean solvents. Woertz [33] screened more than 20 different solvents at about 540 kPa of CO_2 partial pressure and 25 °C, and many of the combinations that outperformed their aqueous counterparts (e.g.: aqueous MEA mixed DEGDME or NMP) are still being studied and re-invented to this day. Woertz [33] was also the first to note down the shifting in absorption rates in water-lean solvents, simply by writing down 'fast' or 'slow' on a list with diverse formulations, thus registering that absorption in TEG-MEA-water mixtures is particularly morose.

Going into details over each one of the publications presented on Table 7 would be too much for this review. Instead, we will quickly mention some of the topics that stand out as particularly interesting. Woertz et al. [33] identify remarkable performances in water-lean solvents with N-methyl-2-pyrrolidone and N,N-dimethylformamide. Another remarkable performance for N-methylformamide is observed by Bougie et al. [162]. Bougie et al. [162] additionally demonstrate how the temperatures of water-lean solvents with low volatility increase the most upon absorbing CO_2, following the order N-methylformamide > DEGMEE > ethylene glycol/1-propanol > water in nonaqueous solvents with MEA.

Unremarkable or rather bad performances are observed for all oils [27] and polyethylene glycols [96,176–178], which have been seen to decrease both capacities and absorption rates when mixed with amines. Sridharan and Sharma [179] were the first authors to register the reduction of mass transfer coefficients with the addition of glycols.

Table 7
Publications that compare capacity and rate in water-lean solvents.

Reference	Amines	Diluents
Solvents with typical alkanolamines and piperazines		
[33]	MEA, DEA, DIPA	Various
[179]	MEA, DEA, CHA	BP, CH, DEG, MeOH, PEG400
[31]	MEA	Various
[177]	MEA	PEG20000
[176]	MDEA	PEG20000
[56]	MEA	1BuIMI
[178]	MEA, DEA, DGA	PEG200, PEG300, PEG400
[175]	MEA, DEA/PZ, MDEA/PZ, AMP/PZ	TOU
[180]	PZ/DETA	DEG, MeOH
[27]	MEA, DEA, TEA, AMP, MMEA	Various vegetable oils
[181]	DETA/PZ	DEG
[162]	MEA	1PrOH, CARB, MEG, NMF
[182]	MEA, LysK, ProK	CARB, 2EE
[48]	MEA, AMP, EAE, IPAE	Various alcohols
Solvents with organic amines and aminoacids		
Reference	Amines	Diluents
[183]	DMA	MeOH, NMP, TMS
[184]	DBA	EtOH
[173]	ProK	EtOH
[174]	ProK	EtOH
[185]	TBA	EtOH
[171]	Various ethylenediamines	
Solvents relying on phase separation		
Reference	Amines	Diluents
[186]	MEA, DEA	1HeOH, 1OcOH, 2EHeOH
[187]	AMP	NMP, TEGDME
[188]	TETA	EtOH
[189]	MAPA	DMF
[190]	MEA	1PrOH
[191]	DETA	DEGDME, DMC, EtOH, NMP
[192]	PZ	DMF
[193]	TETA, AMP	EtOH
[194]	TETA	PEG200
[195]	DETA	TMS

8. Energy efficiency of water-lean solvents

Most investigators who claim that water-lean solvents might be able to deliver lower regeneration heat duties employ the following equation to sustain their argument.

$$Q \approx C_p \cdot \frac{\Delta T}{\Delta q} + \frac{L_D}{M_{CO_2}} \cdot \frac{p_D}{p_{CO_2}} + \frac{\Delta H^{abs}_{CO_2}}{M_{CO_2}}$$

On the right-hand side of the equation above, the first term refers to sensible heat, the second term refers to latent heat and the last term refers to absorption (or desorption) heat. In literature, one will find investigators claiming that each one of these terms can be reduced by shifting from aqueous to water-lean solvents. Therefore, we shall look at each one separately, starting from the right and coming back to the left.

8.1. Heat of absorption

Authors such as Leites [31] have reported water-lean solvents absorbing CO_2 above their theoretical stoichiometric limit (i.e. after the depletion of amines for chemical reaction) and releasing less heat than regular aqueous solvents. The reason is that, for example, aqueous MEA absorbs CO_2 above loadings of 0.5 mol CO_2·mol MEA^{-1} by means of reactions forming bicarbonate, whereas nonaqueous MEA absorbs CO_2 above the same loadings by pure physical solvation, a process less exothermical than any chemical reaction. This can be visualized on Fig. 14 in data adapted from our previous work [59]. Authors such as Shamiri et al. [26] seem to think that this behavior in itself might bring a reduction in regeneration costs.

However, Leites [31] also registers the heat of absorption before the stoichiometric limit of 0.5 mol CO_2·mol MEA^{-1}. According to that report, the heat of absorption in aqueous MEA is of about 81 kJ·mol CO_2^{-1}, whereas nonaqueous solvents with ethylene glycol, NMP and

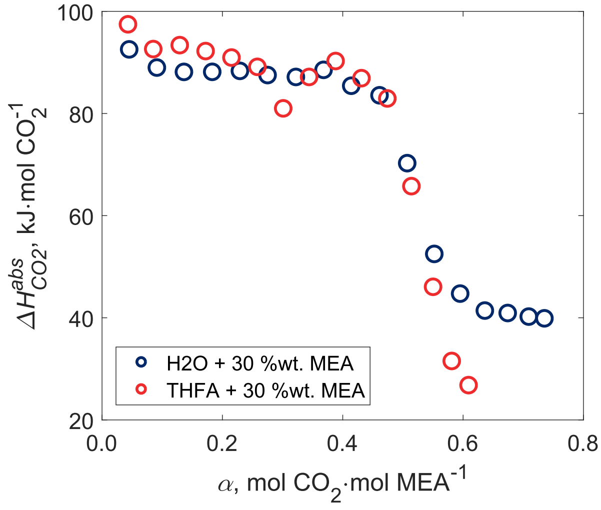


Fig. 14. Heat of absorption of aqueous 30 %wt. MEA compared to nonaqueous MEA measured at 40 °C. Adapted from Wanderley et al. [59].

THFA all present the same heat of absorption of 92 kJ·mol CO_2^{-1} (values remarkably similar to those obtained experimentally by Wanderley et al. [59]). In other words, though reductions in heat of absorption after maximum loading are indeed attainable, this is hardly advantageous for water-lean solvents unless one is planning to operate the capture plant at high pressures. This is the case for pre-combustion CO_2 capture, with the treatment of CO_2 partial pressures above 700 kPa as seen on the Fundamentals of Natural Gas Processing [19].

A number of researchers have applied the Gibbs-Helmholtz correlation on their vapor–liquid equilibrium data to calculate the heat of absorption in water-lean solvents. For example, Murrieta-Guevara et al. [83] estimate heats of 89.1 kJ·mol CO_2^{-1} for MEA in water-free NMP, while Tan et al. [86] estimate 87.6 kJ·mol CO_2^{-1} for MEA in water-free TEG solutions. Heat of absorption calculations with the Gibbs-Helmholtz equation might be ridden with huge uncertainties, evaluated at ± 20% by Murrieta-Guevara et al. [83], but it is still remarkable that these authors do not deduce heats of absorptions below those of aqueous amines.

$$\left[\frac{\mathrm{dln}p_{CO2}}{\mathrm{d}\left(\frac{1}{T}\right)}\right]_{\alpha} = -\frac{\Delta H^{abs}_{CO_2}}{R}$$

One exception we should point out is that of Zheng et al. [106], who estimate a reduction of heat of absorption in DEG-AMP blends when comparing to aqueous AMP. All of these calculations assume a heat of absorption that is independent of temperature, since integration of the Gibbs-Helmholtz expression below removes temperature from the equation. At least for aqueous amines, however, heat of absorption has been seen to increase slightly with increasing temperatures (Kim et al., 2014; Kim and Svendsen, 2007).

If the VLE in water-lean solvents is indeed more sensitive to changes in temperature, as proposed by Rivas and Prausnitz [34] and verified by a number of researchers, then it makes sense that the heat of absorption calculated with the expression above will be consistently higher for water-lean solvents as well.

We should refer to other examples of studies that have measured the heat of absorption in water-lean solvents experimentally. Most of them did so in biphasic systems [32,108,174], wherein the exothermicity of CO_2 absorption is greatly enhanced by the spontaneous phase separation phenomenon. Mobley et al. [116] have measured the heat of absorption of a very interesting hydrophobic mixture of 2-fluorophenethylamine and octafluoropentanol that, though having many properties in common with other hybrid solvents, show an abrupt reduction of heat of absorption with temperature, from around 85 down to 50 kJ·mol CO_2^{-1} between 40 and 120 °C. This is unlike most amine solvents. However, this is one exceptional blend formulated with complex molecules specifically to attain this target behavior.

8.2. *Latent heat*

Many researchers such as Huang et al. [73], Babamohammadi et al. [89] and Wanderley et al. [59] have proposed that the low volatility of water-lean blends is proof that these solvents can be regenerated while incurring in less parasitic heat losses to diluent vaporization than aqueous amines do. In fact, the same has been proposed by Rivas and Prausnitz [34], who nevertheless advise that CO_2 desorption should be carried with stripping gases in hybrid solvents. Tan et al. [86] suggest that their TEG–MEA solvent can be recovered at 10 kPa of CO_2 with neither MEA nor TEG evaporation. However, it is worth considering how this would be feasible, as some pressure is certainly required if one does not want to operate the desorber at vacuum or with the aid of stripping gases.

Data obtained by Guo et al. [80] at 120 °C for water-free mixtures of 2-methoxyethanol and 5 mol·l^{-1} MEA (≈ 31 %wt. MEA) is compared to data for aqueous 30 %wt. MEA and MEG + 30 %wt. MEA [59] in Fig. 15. Two distinct options are presented. The first one is for regeneration of the solvent in a reboiler operating at 100 kPa. In this scenario, the nonaqueous solutions could be regenerated with loadings of 0.26 mol CO_2·mol MEA^{-1} (for MEG) and 0.05 mol CO_2·mol MEA^{-1} (for 2ME). Aqueous MEA cannot be regenerated at 100 kPa and 120 °C because the partial pressure of the unloaded solvent is already above 100 kPa. The second one is for regeneration at 200 kPa, in which the nonaqueous solutions would be possibly regenerated with loadings of 0.33 mol CO_2·mol MEA^{-1} (for MEG) and 0.19 mol CO_2·mol MEA^{-1} (for 2ME), while the aqueous one would achieve the loading of 0.22 mol CO_2·mol MEA^{-1}.

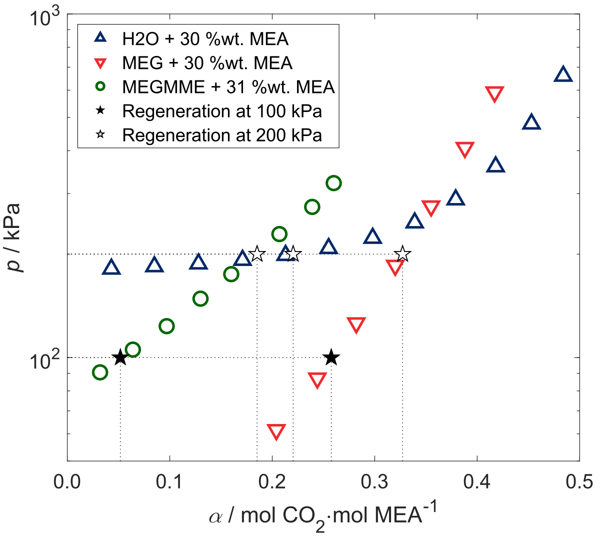


Fig. 15. Loading of aqueous MEA and MEG + MEA [59] compared to that of 2ME + MEA [80] against total pressure at 120 °C.

Fig. 15 shows that water-lean solvents are not alike. Both MEG and 2ME have very low partial pressures when compared to water. Both allow for regeneration at 100 kPa, whereas water does not. However, a crucial point often made is that it is advantageous for CCS separation processes to operate the regeneration step at higher pressures [198]. The reason is that, after its separation, CO_2 must necessarily be compressed for storage or injection. Compression work is energetically more costly when done with electric power than when done with heat, since there are inherent losses in the heat-to-electricity gas turbine cycle. Therefore, though it is possible to recover CO_2 at 100 kPa with both these water-lean solvents, it would be more interesting for industrial applications to recover CO_2 at 200 kPa.

At 200 kPa and 120 °C, the lean loading obtained with 2ME is marginally smaller than that obtained for aqueous 30 %wt. MEA, and both are smaller than that obtained with MEG. The determinant factor in this case is clearly the slope of the VLE curves. This is a point that is often overlooked when searching for diluents with low volatility. Although the boiling point of 2-methoxyethanol (124 °C) is lower than that of ethylene glycol (198 °C), 2-methoxyethanol will enable a lean loading smaller than that of aqueous MEA when operating in a conventional reboiler at 200 kPa and 120 °C, while MEG will not. Unless, of course, that CO_2 desorption is performed with a stripping gas or under vacuum. A similar discussion has been carried out in Wanderley et al. [199].

Evidently, higher lean loadings such as the one found for MEG + MEA will directly impact every aspect of the CO_2 capture plant, as more solvent becomes necessary to perform the same absorption task. Counter-intuitively, picking the diluent with lowest volatility might backfire in terms of avoiding high reboiler duties.

At pressures of 300 kPa and above, both nonaqueous solvents are indeed more competitive than aqueous MEA in the sense that they should deliver leaner loadings at 120 °C. Under this perspective, shifting from aqueous to water-lean solvents might be a solution for operating the desorption at higher pressures without necessarily having to increase temperatures, while still achieving reasonable lean loadings. This possibility has been pointed out by Barzagli et al. [5].

8.3. Sensible heat

In a superficial analysis, the sensible heat duties with water-lean solvents should be lower than those with aqueous formulations simply because the heat capacity (C_P) of organic diluents is usually smaller than that of water. For a given cyclic capacity Δq and a given difference in temperatures ΔT, this advantage is clear. What is obscure is if Δq and ΔT are the same in both types of solvents.

The cyclic capacity Δq is determined by the rich loading obtained in the absorber and the lean loading recovered in the desorber. As discussed in Section 4.1, because of the equilibrium shift, the rich loading in water-lean solvents will conventionally be lower than that of aqueous solvents. As for the lean loading, the previous Section 8.2 has shown that whether the lean loading is smaller or higher is somewhat dependent on the volatility of the diluent that is chosen, particularly for CCS applications. Therefore, it is unclear how different Δq can be in a water-lean solvent, making it a safe choice to suppose it is the same.

Meanwhile, ΔT shall be discussed with care. This temperature difference is calculated between the desorber feed and the reboiler, and between the absorber product and the desorber feed there is typically a cross-heat exchanger designed for warming up the rich solvent. Yuan and Rochelle [166] and Liu et al. [200] have pointed out that the amount of heat which can be recovered by an equipment will be directly correlated to the viscosity η, the heat capacity C_P and the thermal conductivity λ of the solvent, and that this fact can be possibly detrimental to water-lean solvents.

Suppose we consider the solvents mentioned in the previous section. The physical properties of water, ethylene glycol and 2-methoxyethanol were obtained at 40 °C in Yaws [160,201], Svoboda et al. [202] and Islam et al. [203]. These, together with the Reynolds, Prandtl and Nusselt numbers of each diluent calculated in a theoretical cross-heat exchanger, are shown on Table 8. For the calculation of the Reynolds number, the liquid velocity $u = 0.40\ \mathrm{m \cdot s^{-1}}$ and characteristic length $D = 0.004$ m were adopted following the suggestion of Lin and Rochelle [204] for liquid flow in a plate-and-frame type equipment. For the calculation of the Nusselt number, the correlation suggested by Okada et al. [205] was employed as shown below.

$$Nu = 0.157 \cdot Re^{0.66} \cdot Pr^{0.4}$$

With the three dimensionless numbers Re, Pr and Nu, the convective heat transfer coefficient for each diluent can be calculated. These are also shown on Table 8.

Table 8 does not take into account the effect of CO_2 loading in shifting solvent properties such as viscosity. As we have discussed in Section 6.2, the viscosities of water-lean mixtures are not only typically higher than those of aqueous ones, they also increase more steeply with CO_2 loading. Guo et al. [80] have reported the viscosity of loaded 2ME with 30 %wt. MEA as being 10.97 mPa·s (40 °C, $\alpha = 0.357$ mol CO_2·mol MEA^{-1}). For comparison, a water-lean solvent containing MEG has $\eta \approx 31$ mPa·s, while aqueous 30 %wt. MEA has $\eta \approx 2$ mPa·s at similar loading and temperature [59,164]. This implies convective heat transfer coefficients far lower for water-lean solvents than for aqueous amines. And still, even if one ignores the effects of loading on viscosities, Table 8 already shows how this discrepancy arises.

Table 8
Physical properties of water, ethylene glycol and 2-methoxyethanol at 40 °C. Values obtained from Yaws [160,201], Svoboda et al. [202] and Islam et al. [203]. Dimensionless numbers calculated under assumptions of $u = 0.40\ \mathrm{m \cdot s^{-1}}$ and $D = 0.004$ m.

Parameter	Water	MEG	2ME
$\rho / \mathrm{g \cdot cm^{-3}}$	1.000	1.100	0.943
$\eta / \mathrm{mPa \cdot s}$	0.646	9.906	0.942
$C_P / \mathrm{kJ \cdot K^{-1} \cdot kg^{-1}}$	4.241	2.486	2.363
$\lambda / \mathrm{W \cdot m^{-1} \cdot K^{-1}}$	0.624	0.132	0.260
Re ($\rho \cdot D \cdot u \cdot \eta^{-1}$)	2480	180	1600
Pr ($C_P \cdot \eta \cdot \lambda^{-1}$)	4.4	186	8.6
Nu ($h \cdot D \cdot \lambda^{-1}$)	49.3	38.8	48.4
$h / \mathrm{W \cdot m^{-2} \cdot K^{-1}}$	7700	1280	3145

The global heat transfer coefficient of a cross-heat exchanger is directly proportional to the average convective heat transfer coefficient of the solvent inside it [204]. Therefore, as seen on Table 8, thermal recovery with aqueous solvents will be about two times as effective as in nonaqueous ones, sevenfold so if one considers the particular case of ethylene glycol, and higher than that once CO_2 loadings are taken into account. The reasons can be pinpointed by analyzing each row of Table 8. The high viscosity of organic diluents, their low thermal conductivity and even the low heat capacity will have an impact on the performance of the equipment, meaning that one of two options will apply:

a. The cross-heat exchanger in plants operating with water-lean solvents will be typically bigger, and therefore more expensive than the ones operating with aqueous solvents.
b. The amount of heat that can be recovered from the lean solvent leaving the reboiler will be less for water-lean solvents than for aqueous ones, meaning that the ΔT associated with sensible heat duties in the reboiler will be typically higher.

How much bigger the ΔT is will depend on other parameters of the cross-heat exchanger. What becomes clear, however, is that there are more factors at play than the diluent C_P to determine if sensible heat duties are higher or lower in water-lean solvents. Still, this is typically not really that relevant since sensible heat duties have the least impact on overall reboiler heat duties [206].

8.4. Literature data for energy efficiency of water-lean solvents

There is surprisingly a fair amount of data concerning the mixture of methanol plus MEA, also known as the original Amisol® formulation. From bench-scale absorber columns [9–12,207,208], to bench-scale absorber strippers [209], to complete bench scale-absorber-desorber loops [13,14], one could easily claim that this process is quite well understood. However, it is difficult to make a case for reviving the Amisol® solvent after it has been picked up industrially and steadily lost favor over the years.

A single instance of a bench-scale absorber operating with a novel solvent, NMP–MEA–water, has been found in Tan et al. [16]. However, the authors did not record data such as temperature profiles or mass transfer rates for their solvents, simply reporting CO_2 capture efficiencies as function of inlet gas pressures. Conversely, there are interesting studies showing the operation of water-lean solvents in purely theoretical basis through the use of computer simulations [210–213], and thus lacking the hard credibility of a true report on a pilot plant campaign.

With that being said, we find it particularly instructive to fully reproduce in Table 9 the only comprehensive pilot plant data that we could find regarding CO_2 absorption with water-lean solvents. These values were reported by Semenova and Leites [17] in Russian. We shall analyze some aspects of their data and how they relate to what has been discussed so far.

Before proceeding to a proper analysis of the results, one should notice that the water-lean solvent based on ethylene glycol was not able to deliver a CO_2 removal comparable to that of the other solvents.

All water-lean solvents analyzed by Semenova and Leites [17] achieved rich loadings below that of aqueous MEA, which is consistent with what has been discussed in Section 4.1. Solvent temperatures were overall higher in water-lean solvents, a fact that perhaps stems from the

Table 9
Data regarding pilot plant operation with water-lean solvents as reported in Semenova and Leites [17]. The water-lean solvents are based on MEA plus N-methyl-2-pyrrolidone, tetrahydrofurfuryl alcohol and ethylene glycol.

Parameter	H2O	NMP	THFA	MEG
Solvent concentrations/%wt.				
MEA	20	19	20	21
H_2O	80	3	9	6
Diluent	0	78	71	73
CO_2 concentrations in gas/%v.				
Flue gas	20.4	19.2	19.1	20.8
Treated gas	2.6	1.3	1.7	9.1
CO_2 concentrations in solvent/mol $CO_2 \cdot$mol MEA^{-1}				
Lean solvent	0.210	0.070	0.080	0.143
Rich solvent	0.423	0.348	0.286	0.331
Solvent temperature in absorber/°C				
Inlet	23	39	40	38
Outlet	39	74	70	57
Temperature difference in heat exchanger/°C				
Hot end	12	25	23	24
Cold end	9	4	10	15
Solvent temperature in desorber/°C				
Inlet	103	110	112	113
Bottom	115	135	135	140
Top	99	103	85	105
Heat consumption/$MJ \cdot m^3\ CO_2^{-1}$*				
Sensible heat	2.24	0.544	1.34	3.10
Latent heat	2.39	0.335	3.25	0.109
Absorption heat	3.35	4.48	3.25	3.77
Overall heat	7.98	5.34	5.38	6.97

*1 $MJ \cdot m^3\ CO_2^{-1} \approx 0.509\ GJ \cdot ton\ CO_2^{-1}$ (assuming 1 mol CO_2 = 22.4 l CO_2).

authors aiming to compensate for the low volatility of these absorbents in the reboiler as discussed in Section 8.2. As such, the temperatures of the rich solvent leaving the absorber were higher in water-lean solvents, and thus the temperatures of the desorber feeds were all comparable, even though the cross-heat exchanger efficiencies (as evaluated by the temperature differences in the hot and cold ends) seem to have been indeed lower for water-lean solvents.

The overall heat duties in aqueous MEA and in solvents with NMP, THFA and MEG as reported by Semenova and Leites [17] are respectively 4.1, 2.7, 2.7 and 3.5 $GJ \cdot ton\ CO_2^{-1}$. Moreover, although NMP and THFA have reduced the overall reboiler heat duties, they did so for different reasons. Shifting from water to NMP provoked a reduction in latent heat, whereas the shift to THFA brought a reduction in sensible heat, both leading to overall lower parasitic costs of solvent regeneration. Meanwhile, the heat of desorption of CO_2 is quite comparable among all solvents, with those of water-lean formulations with NMP and MEG being higher than that of aqueous MEA, as discussed in Section 8.1.

There is a final aspect to be mentioned. Recent CO_2 capture plants have been slowly approaching the 2 $GJ \cdot ton\ CO_2^{-1}$ mark for reboiler duties [214]. Rochelle et al. [215] report a similar performance during pilot plant operations. They achieve these reboiler duties not solely because of their amine solvent (aqueous 5 m piperazine), but because of intelligent process modifications. Plant design seems to be capable of providing an effective reduction in energy costs. This poses a complicated problem. Not all researchers have access to these improved equipments for CO_2 capture, but one still has to compare very distinct solvents somehow. And though it is tempting to perform these comparisons in a purely percentual basis, the fact is simply that one cannot analyze solvents in conditions that do not enable their peak performance. As one might argue that shifting from aqueous MEA to a hybrid solvent with NMP reduces reboiler duties in 33% based on the data from Semenova and Leites [17], another might correctly reply that there is margin to reduce these duties in aqueous MEA with clever process modifications (for example, their sensible heat duties are unreasonably high). Whether these process modifications would work equally as well in water-lean solvents remains to be seen. We do not believe that pointing this out is being particularly harsh on new solvents. Quoting Leites [31] himself, thermodynamical analyses of CO_2 capture processes show that sensible and latent heat expenses can be reduced almost to zero with sophisticated plant designs. Rochelle et al. [215] prove this point by almost eliminating latent heat duties with the advanced flash stripper.

To quickly summarize the conclusions of Section 8:

- Water-lean solvents will generally incur in similar heats of CO_2 absorption as their aqueous counterparts;
- Water-lean solvents can reduce latent heat expenditures if they are less volatile than water, though they will probably result in more inefficient heat transfer phenomena;
- There is indeed a potential for reduction of overall energy duties in CO_2 capture plants with water-lean solvents, yet it is discussable if these same reductions could not be obtained with proper reconfiguration of the process operating with aqueous amines.

9. Degradation and corrosion in water-lean solvents

There is so few information regarding degradation and corrosion in water-lean solvents that one could think that this comes as an afterthought, when quite possibly this should be one of the most pressing issues to be addressed when dealing with a whole new class of solvents. Unfortunately, there is indeed very limited amount of data, which will make this discussion very short.

Shoukat et al. [216,217] have analyzed the thermal degradation of mixtures between amines, water and glycols, and drawn comparisons with the thermal degradation of aqueous amines. The results do not look very promising for water-lean solvents in this aspect. In Shoukat et al. [216], it has been shown that aqueous 30%wt . MEA mixtures loaded up to 0.5 mol CO_2.mol MEA^{-1} experience about 40% of amine loss after 50 days at 135 °C. In comparison, mixtures with triethylene glycol suffer more than 60% of amine loss, while mixtures with ethylene glycol lose 80% of their amine content. Though the results for a similar experiment carried with MDEA are a lot better, once MDEA is inherently more resistant to degradation than MEA, the substitution of water for glycol increase all degradation rates. This behavior can be observed in Fig. 16, adapted from data available in Shoukat [218]. In Shoukat et al. [217], an array of various tertiary amines mixed with glycols plus water was tested. This time, the result was more mixed, quite often being advantageous for water-lean solvents. More recently, Høisæter and Knuutila [219] observed high thermal degradation rates in MEA-based water-lean solvents when compared to aqueous amines. However, information is still very limited to form an overall picture of how degradation occurs in these mixtures.

There is valuable published data regarding the degradation of the DEEA–EMEA solvent developed by Chen et al. [220], which is wasted by reacting with SO_2 present in flue gases, and of the Sulfinol-X® solvent (aqueous TMS + MDEA + PZ), whose oxidative degradation produces sulfate, sulfite and thiosulfate [221].

Many other studies do try to carry some sort of stability analysis. These, however, are mostly constrained to a few hours of absorption–desorption loops, far from the thousands of hours to be expected of a realistic solvent application. And even then they sometimes return quite unpromising results. As an example, Tao et al. [194] observed terrible losses of solvent in mixtures 30 %wt. MEA + water-free PEG200 at high temperatures. Their solvent lost 20% of mass after 5 h of N_2 purging at 40 °C, and 30% after 50 min at 80 °C. This seems to indicate some severe degradation reaction between the strong base and the ether groups of PEG200. With DEA, MDEA and DGA, the mass losses at 80 °C after 5 h of N_2 purging were kept at 19%, 8% and 26% respectively.

Results for corrosion studies are similarly incongruent. While in Shoukat et al. [216] one can clear that shifting from water to glycol reduces the corrosion caused by MEA solutions, a phenomenon understood since the 1950 s [222], this effect is not necessarily observed for tertiary amines. In a following paper, the results for corrosion in tertiary

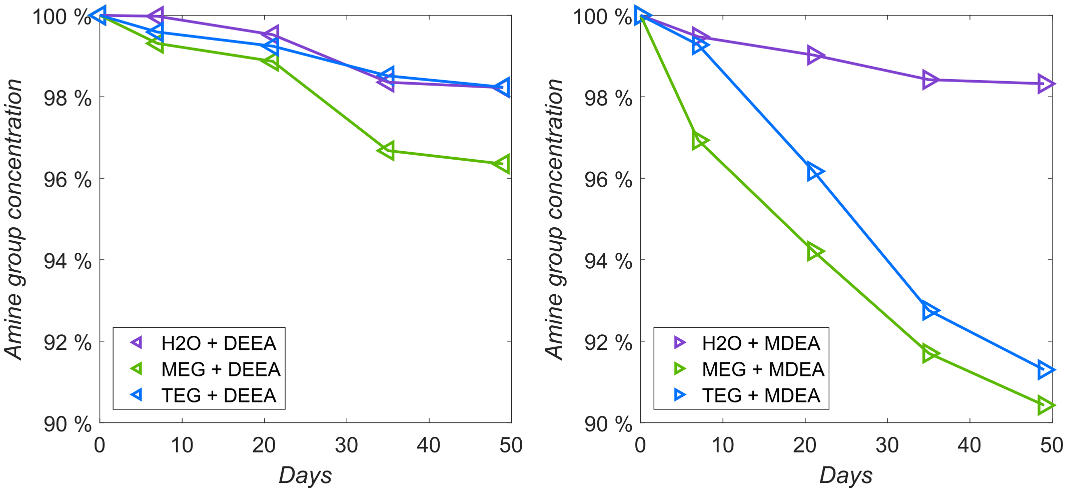


Fig. 16. Thermal stability of mixtures between tertiary amines and glycols, obtained from Shoukat [218]. All solutions were prepared with 30 %wt. amine and loaded up to 0.1 mol $CO_2 \cdot$mol amine^{-1}, then thermally degraded at 135 °C.

amine–glycol mixtures is even more difficult to interpret [217]. This is not to the detriment of the authors, but it might just be a very hard task to form general opinions about a wide range of different chemical compounds. It is also difficult to assess the effect of trace amounts of water in corrosion experiments with glycols, since these are hygroscopic compounds, and water concentrations after loading are usually untested for. Other results for water-lean solvents found in the literature indicate that the addition of MDEA reduces corrosion in systems operating with propylene carbonate [101], shifting from water to dimethyl formamide decreases the corrosivity of piperazine solutions [192] (and also causes the precipitation of piperazine carbamate, being a biphasic solvent). Finally, the addition of a series of organosulfur compounds in small concentrations to aqueous MEA, among them sulfolane, has been verified as successful in inhibiting corrosion mechanisms [223].

10. Some perspectives for the future

In our historical review (Section 2), we have pointed out how the perceived benefits from employing water-lean solvents have changed with time. Hybrid solvents were created with the intention of increasing the absorption capacity of CO_2 under high pressures. Later, as the enthusiasm for this aspect of water-lean mixtures started to subside, there came a revived interest in the promised energetic savings that these solvents might deliver. Now, it has become more and more clear that amine systems are approaching an apparent minimum of energy necessary for CO_2 absorption–desorption cycles [166,214].

Some interesting perspectives for water-lean solvents in the future are related to their use to bypass the carbamate route and absorb CO_2 in a different manner. As discussed in Section 5.1, the alkylcarbonate route of CO_2 conversion has been experiencing a renewal in interest lately. Recent NMR spectrography analyses have identified alkylcarbonate pathways even in aqueous primary alkanolamines and well understood amines such as MDEA [42,51,54,128,131]. These pathways attract the attention of researchers especially due to their potential for generating reaction products that can be reversed more easily, i.e. with less energetical input, or at least using a cheaper source of energy by desorbing CO_2 at lower temperatures.

Water-lean solvents might have a role to play in developing alkylcarbonate-forming solvents. Eimer [50] has proposed that the alkylcarbonate pathway is more likely to happen when using organic diluents with high autoprotolysis constants and weak amines. His example was that of MDEA mixed with ethylene glycol, which has a $pK_S = 15.84$ at 25 °C [138]. In an interesting study, Takeshita and Kitamoto [44] demonstrated how solvent polarity can determine whether the products of the reaction between CO_2 and amines are mostly carbamic acid, undissociated zwitterion or carbamate and protonated amine.

Naturally, Takeshita and Kitamoto [44] were able to carry this study by using nonpolar organic amines instead of alkanolamines. Alkanolamines would very probably demix either instantly or upon CO_2 absorption in a solvent as nonpolar as octane, which is what they have employed. However, this serves as a motivation for understanding that water-lean solvents might be practical precisely for enabling the use of these very same amines, with their own particular CO_2 reaction routes. Other researchers who have taken the opportunity to work with nonpolar amines in water-lean solvents were Yogish [183], Dinda et al. [136,137] and Gómez-Díaz et al. [185]. Gómez-Díaz et al. [185] were interested in using tributylamine for its high stability with regards to thermal degradation. Conversely, Dinda et al. [136,137] were simply developing a process for the production of isocyanates and urethanes.

Alkylcarbonate formation was observed by Jing et al. [184] in mixtures of dibutylamine, water and ethanol. In their case, ethanol was essential for avoiding biphasic phenomena, since pure dibutylamine is immiscible in water. Their solvent absorbed CO_2 up to a loading of 0.82 mol $CO_2 \cdot$mol amine^{-1} while its viscosity barely increased from 1.56 mPa·s to 1.72 mPa·s. This is even more interesting than their reported higher regeneration efficiency. It is puzzling that this viscosity increase is so small. The authors themselves have suggested that the presence of water in the solvent might have something to do with this. Indeed, their formulations seem to suffer more with mounting viscosities upon loading the higher the ethanol-to-water ratio in the diluent.

Furthermore, there are some groups that should be addressed individually. The first is that of the University of Florence. This team has been working with water-lean solvents for almost a decade, and an important part of their research is focused on mixing hindered or tertiary amines (e.g. AMP and MDEA) with organic solvents such as ethylene glycol/ethanol, ethylene glycol/1-propanol, and DEGMME, purposefully promoting alkylcarbonate formation [6,45,129,130,224]. Conversely, alkylcarbonates were not observed in nonaqueous solvents with amines such as DGA and DEA [5]. They also have employed organic diluents to force demixing and precipitation of products upon CO_2 absorption [225–227], and studied CO_2 absorption in solvent-free amines [228] (one could call this an extreme example of water-lean solvent). In our opinion, it is the pioneering work of this group in NMR spectrography and alkylcarbonate identification in amino-organic mixtures that stands out as essential literature on water-lean solvents.

The group from RITE [229,230] and the group from RTI International [116,231,232] have both carried researches on proprietary water-lean solvents in the past decade. Yamamoto et al. [229] developed a mixture between a tertiary amine and an organic diluent that has high absorption capacity and can be regenerated at high pressures. Because of this, their formulations are called HPRT (High Pressure Regenerative Type) solvents. Meanwhile, Lail et al. [232] designed a mixture of a hindered amine with a solvent with low volatility which they have nicknamed NAS (Non Aqueous Solvents). Lail et al. [232] report that their solvent absorbs CO_2 through the carbamate route and that its heat of absorption at desorber temperatures is lower than at absorber temperatures. In both cases the authors refuse to disclose precise information on which chemicals they have employed. Conversely, Mobley et al. [116] and Tanthana et al. [231] developed their solvent-based on a very complex fluorinated amine (2-fluorophenethylamine) mixed into a fluorinated alcohol (2,2′,3,3′,4,4′,5,5′-octafluoropentanol). Their solvent consciously avoids the carbamate formation route, and its curious heat of absorption behavior, perhaps similar to that of the NAS of Lail et al. [232], has already been mentioned in Section 8.1. These are called HPS (Hydrophobic Solvents). The HPRT solvents, the NAS and the HPS show that, decades after the Amisol® and the Sulfinol® processes, development of water-lean solvents seem to have increased in complexity and sophistication.

Finally, the CO_2BOLs (CO_2-Binding Organic Liquids) developed by the group from the Pacific Northwest National Laboratory are certainly worth mentioning due to their very interesting properties. They were initially designed as nonpolar mixtures of alcohols and amines that, upon CO_2 absorption, become highly polarized ionic liquids [4,233]. These amines are guanidines and amidines. Later, both diluent and reactant were synthesized into single molecules, alkanolamidines and alkanolguanidines, for the 2nd generation CO_2BOLs[1] [3,234–237]. The reaction products in both generations are always alkylcarbonates.

On the bright side, CO_2BOLs have a high capacity for CO_2 absorption (since the whole solution is the reactant itself) and can be regenerated at fairly low temperatures, 75–85 °C [3,236]. Though this does not imply lower reboiler duties, it does dispense the requirement of high-pressure steam for solvent recovery. On the other hand, the high viscosity of these solvents, especially after CO_2 loading, renders their absorption rates lower than those of aqueous MEA even though their reactants have stronger basicity than most primary amines [237]. Zheng et al. [236] have tried to develop a CO_2BOL that achieved maximum viscosity of 20 $mPa \cdot s$ after absorbing CO_2, but the minimum that they have reached experimentally was 356 $mPa \cdot s$. They then employed computational methods to try designing a molecule with lower viscosity when loaded, this time settling for a maximum of 100 $mPa \cdot s$ in the rich solvent [238]. The CO_2 mass transfer rates in loaded CO_2BOLs appear to be one order of magnitude below that of aqueous MEA and aqueous piperazine [61,239,240], which is not bad considering the high viscosities of those nonaqueous systems.

If the idea of a solvent that becomes an ionic liquid when absorbing CO_2 sounds too far-fetched, one might consider that this process is similar to what happens when CO_2 reacts with pure amines in the absence of diluents. In this sense, the CO_2BOLs are similar to the functionalized ethylenediamines of A. Liu et al. [171] or the absorption into solvent-free alkanolamines of Barzagli et al. [228]. This has led the Pacific Northwest National Laboratory group to also work on water-free amine solvents [235,241,242]. They have also investigated precipitating nonaqueous amine solvents [243] and single-phase nonaqueous aminosilicones [244], making this one of the most productive research teams working on water-lean solvents at the moment of this writing.

We believe this goes to show how far water-lean solvents have come from their original conception as hybrid solvents. As the demand for CO_2 capture becomes more focused, specified and urgent, the degree of sophistication of new solvents keeps on growing. And yet, aqueous amines have an enormous staying power. This is partially because the benchmark amines are simply too cheap. At the time of its writing, Rochelle [214] gave the price of monoethanolamine as being around 2 $US\$ \cdot kg^{-1}$. Piperazine is one step away from MEA in terms of synthesis, so its price is not so high either. Conversely, the new water-lean solvents discussed in this chapter have structures as complex as those shown on Fig. 17, and their cost should be accordingly elevated.

In energetic terms, their performance approaches that of conventional aqueous amines implemented with novel CO_2 capture plant configurations. The CO_2BOLs have an energetic demand of approximately 2.57 $GJ \cdot ton\ CO_2^{-1}$ captured [245]. The ION solvent, another water-lean proprietary mixture, achieves a performance of 2.54 $GJ \cdot ton\ CO_2^{-1}$ [246], and the NAS delivered 2.3 $GJ \cdot ton\ CO_2^{-1}$ in pilot plant testing [247]. For comparison, aqueous amines in novel configurations have been achieving 2.1–2.4 $GJ \cdot ton\ CO_2^{-1}$ as in the cases of the MHI process with the KS-1 [248], the Shell Cansolv process in Boundary Dam [249] and the latest pilot plant data with the advanced flash stripper [215].

Section 10 has given a quick overview on new concepts for water-lean solvents. A better reference to understand all of these new trends is the excellent review prepared by Heldebrant et al. [7] themselves. As we initially set out to study and compare hybrid solvents, it seems that some of the solvent-free mixtures discussed above verge too far away from our initial focus.

Heldebrant et al. [240] pointed out that perhaps the typical aqueous amine configuration for CO_2 capture is far from ideal for water-lean solvents. If that is true, then it is about time a process is developed that harvests the full potential of these mixtures.

11. Conclusions

Water-lean solvents have come a long way, from once simple hybrid solvents to becoming sophisticated mixtures of tailor-made organic compounds and amines. In the meantime, their appeal shifted together with the industrial and academic perception of what makes a solvent valuable. However, certain things have remained quite similar in these past 50 years of solvent development.

- Generally, water-lean solvents still have lower CO_2 solubility than aqueous amines at CO_2 partial pressures below 700 kPa.
- Generally, water-lean solvents still deliver reaction rates a tad slower than aqueous amines.
- Generally, water-lean solvents still experience large increases in viscosity upon CO_2 loading.

Aggregating water-lean solvents in concise groups is quite challenging, and several exceptions are liable to complicate any overarching conclusions. However, a very rough understanding of nonaqueous water-lean solvents can be schematically represented in Fig. 18, with semiaqueous water-lean solvents behaving generally somewhere in between the aqueous solvents and the nonaqueous ones. Fig. 18 is evidently a very rough and imprecise sketch of everything that has been discussed so far in this review, and serves merely as a general reminder of some of the topics that we have approached. Also, Fig. 18 seems to imply that nonvolatile diluents must be viscous while volatile diluents must be nonviscous, both of which are not always the case. However, Fig. 18 works well as a simplification of what new researchers to the field of water-lean solvents might often find.

The past few years have seen a renaissance of water-lean solvents, in part due to their apparent unlimited possibilities. However, it is not surprising that an extra room for maneuver should be found amongst the pool of organic solvents for preparing amine mixtures. The astounding part is that one might even be able to speak in generalities about a seemingly infinite group of solvents. This is only possible because water is such a special molecule. Its high potential for building complex electrostatic structures and thus easily stabilizing electrolytic species, its

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[1] In reality, the solvents developed by Philip Jessop [4,233] were originally called '*switchable solvents*'. In a way, it seems like the 2nd generation CO_2BOLs were really the 1st generation CO_2BOLs.

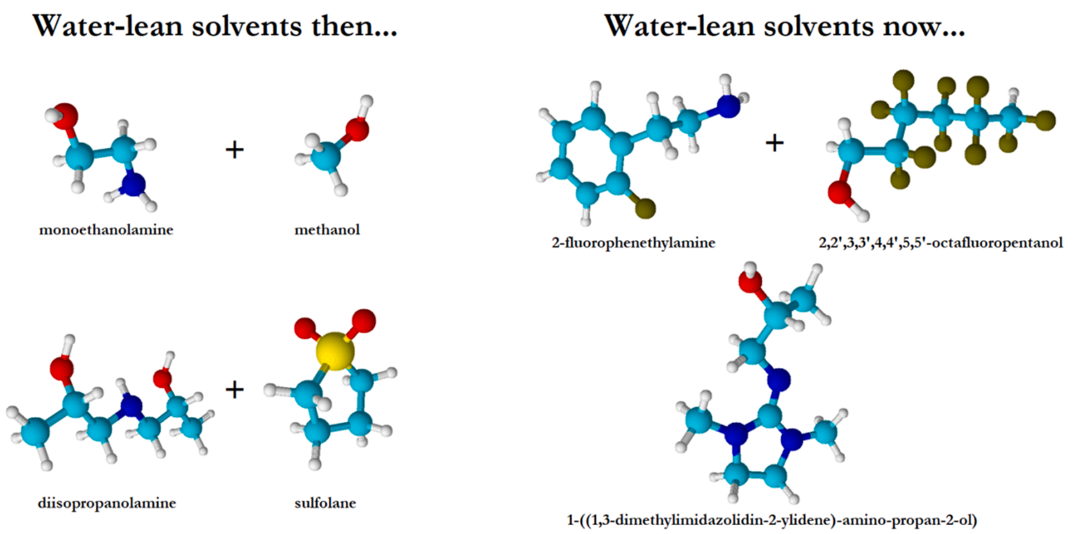
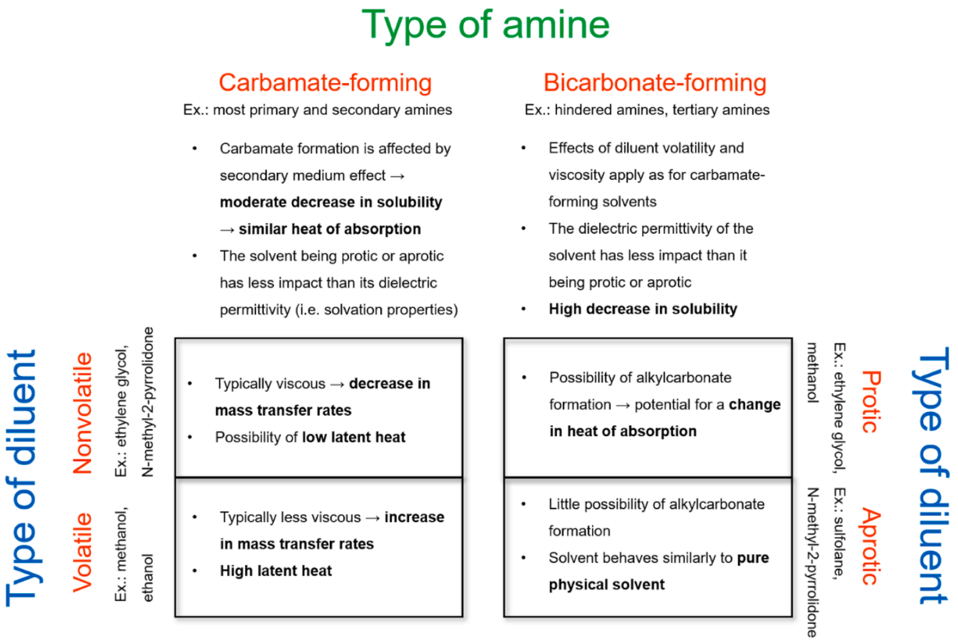


Fig. 17. Chemical composition of water-lean solvents then and now. On the left, the compositions of the Amisol® solvent [20] and of the Sulfinol-D® solvent [25]. On the right, the compositions of the HPS [116] and of one particularly promising CO_2BOL [236].



Type of amine

Carbamate-forming
Ex.: most primary and secondary amines

- Carbamate formation is affected by secondary medium effect → **moderate decrease in solubility → similar heat of absorption**
- The solvent being protic or aprotic has less impact than its dielectric permittivity (i.e. solvation properties)

Bicarbonate-forming
Ex.: hindered amines, tertiary amines

- Effects of diluent volatility and viscosity apply as for carbamate-forming solvents
- The dielectric permittivity of the solvent has less impact than it being protic or aprotic
- **High decrease in solubility**

Type of diluent	Carbamate-forming	Bicarbonate-forming	Type of diluent
Nonvolatile Ex.: ethylene glycol, N-methyl-2-pyrrolidone	Typically viscous → **decrease in mass transfer rates** Possibility of **low latent heat**	Possibility of alkylcarbonate formation → potential for a **change in heat of absorption**	Protic Ex.: ethylene glycol, methanol
Volatile Ex.: methanol, ethanol	Typically less viscous → **increase in mass transfer rates** **High latent heat**	Little possibility of alkylcarbonate formation Solvent behaves similarly to **pure physical solvent**	Aprotic Ex.: sulfolane, N-methyl-2-pyrrolidone

Fig. 18. Schematic understanding of nonaqueous water-lean solvents.

capacity in doing so through hydrogen bonding and thus not experiencing huge increases in viscosity, its high thermal conductivity, relatively high (for its molecular size) boiling point, all of these make it very easy to talk at once about water and then about 'the rest'.

The bar set by aqueous amines is very high. Interpolating Leites [31] once again, a good water-lean solvent should be able to address all the issues posed by this critical review, at the same time, and doing so compared with aqueous amines at their peak performance.

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Declaration of Competing Interest

None.

References

[1] G.T. Rochelle, Amine scrubbing for CO2 capture, Science (80-.). 325 (2009) 1652–4. doi:10.1126/science.1176731.
[2] S. Yeh, R.E. Peterson, Solubility of carbon dioxide, krypton, and xenon in lipids, J. Pharm. Sci. 52 (1963) 453–458, https://doi.org/10.1002/jps.2600520511.
[3] J. Zhang, I. Kutnyakov, P.K. Koech, A. Zwoster, C. Howard, F. Zheng, C. J. Freeman, D.J. Heldebrant, CO2-binding-organic-liquids-enhanced CO2 capture using polarity-swing-assisted regeneration, Energy Proc., Elsevier Ltd (2013) 285–291, https://doi.org/10.1016/j.egypro.2013.05.113.
[4] L. Phan, D. Chiu, D.J. Heldebrant, H. Huttenhower, E. John, X. Li, P. Pollet, R. Wang, C.A. Eckert, C.L. Liotta, P.G. Jessop, Switchable solvents consisting of amidine/alcohol or guanidine/alcohol mixtures, Ind. Eng. Chem. Res. 47 (2008) 539–545, https://doi.org/10.1021/ie070552r.
[5] F. Barzagli, C. Giorgi, F. Mani, M. Peruzzini, Reversible carbon dioxide capture by aqueous and non-aqueous amine-based absorbents: A comparative analysis carried out by 13C NMR spectroscopy, Appl. Energy. 220 (2018) 208–219, https://doi.org/10.1016/j.apenergy.2018.03.076.
[6] F. Barzagli, S. Lai, F. Mani, P. Stoppioni, Novel Non-aqueous Amine Solvents for Biogas Upgrading, Energy Fuels 28 (2014) 5252–5258, https://doi.org/10.1021/ef501170d.

[7] D.J. Heldebrant, P.K. Koech, V.-A. Glezakou, R. Rousseau, D. Malhotra, D. C. Cantu, Water-Lean Solvents for Post-Combustion CO2 Capture, Fundam., Uncertainties, Opportunities, Outlook (2017), https://doi.org/10.1021/acs.chemrev.6b00768.

[8] Q. Zhuang, B. Clements, J. Dai, L. Carrigan, Ten years of research on phase separation absorbents for carbon capture: Achievements and next steps, Int. J. Greenh. Gas Control. 52 (2016) 449–460, https://doi.org/10.1016/j.ijggc.2016.04.022.

[9] T. Sema, A. Naami, P. Usubharatana, X. Wang, R. Gao, Z. Liang, R. Idem, P. Tontiwachwuthikul, Mass transfer of CO2 absorption in hybrid MEA-methanol solvents in packed column, Energy Proc., Elsevier Ltd (2013) 883–889, https://doi.org/10.1016/j.egypro.2013.05.181.

[10] K. Fu, W. Rongwong, Z. Liang, Y. Na, R. Idem, P. Tontiwachwuthikul, Experimental analyses of mass transfer and heat transfer of post-combustion CO2 absorption using hybrid solvent MEA–MeOH in an absorber, Chem. Eng. J. 260 (2015) 11–19, https://doi.org/10.1016/J.CEJ.2014.08.064.

[11] J. Gao, J. Yin, F. Zhu, X. Chen, M. Tong, W. Kang, Y. Zhou, J. Lu, Experimental study of a hybrid solvent MEA-Methanol for post-combustion CO2 absorption in an absorber packed with three different packing: Sulzer BX500, Mellapale Y500, Pall rings 16 × 16, Sep. Purif. Technol. 163 (2016) 23–29, https://doi.org/10.1016/j.seppur.2016.02.043.

[12] J. Gao, J. Yin, F. Zhu, X. Chen, M. Tong, W. Kang, Y. Zhou, J. Lu, Orthogonal test design to optimize the operating parameters of a hybrid solvent MEA–Methanol in an absorber column packed with three different packing: Sulzer BX500, Mellapale Y500 and Pall rings 16 × 16 for post-combustion CO2 capture, J. Taiwan Inst. Chem. Eng. 68 (2016) 218–223, https://doi.org/10.1016/j.jtice.2016.08.040.

[13] J. Gao, J. Yin, F. Zhu, X. Chen, M. Tong, W. Kang, Y. Zhou, J. Lu, Integration study of a hybrid solvent MEA-Methanol for post combustion carbon dioxide capture in packed bed absorption and regeneration columns, Sep. Purif. Technol. 167 (2016) 17–23, https://doi.org/10.1016/j.seppur.2016.04.033.

[14] H. Rashidi, P. Valeh-e-Sheyda, S. Sahraie, A multiobjective experimental based optimization to the CO2 capture process using hybrid solvents of MEA-MeOH and MEA-water, Energy. (2019), 116430, https://doi.org/10.1016/j.energy.2019.116430.

[15] S.-M. Yih, H.-C. Lai, Simultaneous absorption of CO2 and H2S in sulfinol solutions in a set of packed absorber-stripper, Chem. Eng. Commun. 88 (1990) 119–125, https://doi.org/10.1080/00986449008940551.

[16] L.S. Tan, A.M. Shariff, K.K. Lau, M.A. Bustam, Impact of high pressure on high concentration carbon dioxide capture from natural gas by monoethanolamine/N-methyl-2-pyrrolidone solvent in absorption packed column, Int. J. Greenh. Gas Control. 34 (2015) 25–30, https://doi.org/10.1016/j.ijggc.2014.12.020.

[17] T.A. Semenova, I.L. Leites (Eds.), The Purification of Technological Gases, 2nd ed., Chimia, Moscow, 1977.

[18] Y. Yuan, G.T. Rochelle, CO2 absorption rate in semi-aqueous monoethanolamine, Chem. Eng. Sci. 182 (2018) 56–66, https://doi.org/10.1016/J.CES.2018.02.026.

[19] A.J. Kidnay, W.R. Parrish, Fundamentals of Natural Gas Processing, 1st ed., CRC Press, 2006.

[20] M. Kriebel, Improved Amisol Process for gas purification, Energy Prog.; (United States). 4:3 (1984). https://www.osti.gov/biblio/6121828-improved-amisol-process-gas-purification (accessed March 5, 2019).

[21] A.L. Kohl, R.B. Nielsen, A.L. Kohl, R.B. Nielsen, Physical Solvents for Acid Gas Removal, Gas Purif. (1997) 1187–1237, https://doi.org/10.1016/B978-088415220-0/50014-8.

[22] F. Murrieta-Guevara, A. Trejo Rodriguez, Solubility of carbon dioxide, hydrogen sulfide, and methane in pure and mixed solvents, J. Chem. Eng. Data. 29 (1984) 456–460, https://doi.org/10.1021/je00038a027.

[23] F. Murrieta-Guevara, A. Romero-Martinez, A. Trejo, Solubilities of carbon dioxide and hydrogen sulfide in propylene carbonate, N-methylpyrrolidone and sulfolane, Fluid Phase Equilib. 44 (1988) 105–115, https://doi.org/10.1016/0378-3812(88)80106-7.

[24] F. Murrieta-Guevara, E. Rebolledo-Libreros, A. Trejo, Gas solubilities of carbon dioxide and hydrogen sulfide in sulfolane and its mixtures with alkanolamines, Fluid Phase Equilib. 53 (1989) 1–6, https://doi.org/10.1016/0378-3812(89)80066-4.

[25] E.E. Isaacs, F.D. Otto, A.E. Mather, Solubility of hydrogen sulfide and carbon dioxide in a Sulfinol solution, J. Chem. Eng. Data. 22 (1977) 317–319, https://doi.org/10.1021/je60074a024.

[26] A. Shamiri, M.S. Shafeeyan, H.C. Tee, C.Y. Leo, M.K. Aroua, N. Aghamohammadi, Absorption of CO2 into aqueous mixtures of glycerol and monoethanolamine, J. Nat. Gas Sci. Eng. 35 (2016) 605–613, https://doi.org/10.1016/j.jngse.2016.08.072.

[27] A.U. Maheswari, K. Palanivelu, Absorption of carbon dioxide in alkanolamine and vegetable oil mixture and isolation of 2-amino-2-methyl-1-propanol carbamate, J. CO2 Util. 6 (2014) 45–52, https://doi.org/10.1016/j.jcou.2014.03.003.

[28] M. Aghaie, N. Rezaei, S. Zendehboudi, A systematic review on CO2 capture with ionic liquids: Current status and future prospects, Renew. Sustain. Energy Rev. 96 (2018) 502–525, https://doi.org/10.1016/j.rser.2018.07.004.

[29] I.I.I. Alkhatib, L.M.C. Pereira, A. AlHajaj, L.F. Vega, Performance of non-aqueous amine hybrid solvents mixtures for CO2 capture: A study using a molecular-based model, J. CO2 Util. 35 (2019) 126–144, https://doi.org/10.1016/j.jcou.2019.09.010.

[30] M.T. Mota-Martinez, J. Hallett, N. MacDowell, Screening Solvents Properties for CO2 Capture Based on the Process Performance, in, Energy Proc., Elsevier Ltd (2017) 1551–1557, https://doi.org/10.1016/j.egypro.2017.03.1285.

[31] I.L.L. Leites, Thermodynamics of CO2 solubility in mixtures monoethanolamine with organic solvents and water and commercial experience of energy saving gas purification technology, Energy Convers. Manag. 39 (1998) 1665–1674 (accessed November 27, 2018), http://linkinghub.elsevier.com/retrieve/pii/S0196890498000764.

[32] H.K. Karlsson, P. Drabo, H. Svensson, Precipitating non-aqueous amine systems for absorption of carbon dioxide using 2-amino-2-methyl-1-propanol, Int. J. Greenh. Gas Control. 88 (2019) 460–468, https://doi.org/10.1016/j.ijggc.2019.07.001.

[33] B.B. Woertz, Experiments with solvent-amine-water for removing CO2 from gas, Can. J. Chem. Eng. 50 (1972) 425–427, https://doi.org/10.1002/cjce.5450500321.

[34] O.R. Rivas, J.M. Prausnitz, Sweetening of sour natural gases by mixed-solvent absorption: Solubilities of ethane, carbon dioxide, and hydrogen sulfide in mixtures of physical and chemical solvents, AIChE J. 25 (1979) 975–984, https://doi.org/10.1002/aic.690250608.

[35] L. de O. Arinelli, T.A.F. Trotta, A.M. Teixeira, J.L. de Medeiros, O. de Q.F. Araújo, Offshore processing of CO2 rich natural gas with supersonic separator versus conventional routes, J. Nat. Gas Sci. Eng. 46 (2017) 199–221. doi:10.1016/j.jngse.2017.07.010.

[36] O. de Q.F. Araújo, A. de C. Reis, J.L. de Medeiros, J.F. do Nascimento, W.M. Grava, A.P.S. Musse, Comparative analysis of separation technologies for processing carbon dioxide rich natural gas in ultra-deepwater oil fields, J. Clean. Prod. 155 (2017) 12–22. doi:10.1016/j.jclepro.2016.06.073.

[37] E. Sada, H. Kumazawa, Y. Ikehara, Z.Q. Han, Chemical kinetics of the reaction of carbon dioxide with triethanolamine in non-aqueous solvents, Chem. Eng. J. 40 (1989) 7–12, https://doi.org/10.1016/0300-9467(89)80038-3.

[38] E. Sada, H. Kumazawa, Y. Osawa, M. Matsuura, Z.Q. Han, Reaction kinetics of carbon dioxide with amines in non-aqueous solvents, Chem. Eng. J. 33 (1986) 87–95, https://doi.org/10.1016/0300-9467(86)80038-7.

[39] E. Sada, H. Kumazawa, Z.Q. Han, H. Matsuyama, Chemical kinetics of the reaction of carbon dioxide with ethanolamines in nonaqueous solvents, AIChE J. 31 (1985) 1297–1303, https://doi.org/10.1002/aic.690310808.

[40] G.F. Versteeg, W.P.M. van Swaaij, On the kinetics between CO2 and alkanolamines both in aqueous and non-aqueous solutions-II. Tertiary amines, Chem. Eng. Sci. 43 (1988) 587–591, https://doi.org/10.1016/0009-2509(88)87018-0.

[41] G.F. Versteeg, W.P.M. van Swaaij, On the kinetics between CO2 and alkanolamines both in aqueous and non-aqueous solutions—I. Primary and secondary amines, Chem. Eng. Sci. 43 (1988) 573–585, https://doi.org/10.1016/0009-2509(88)87017-9.

[42] P.V. Kortunov, M. Siskin, L.S. Baugh, D.C. Calabro, In Situ Nuclear Magnetic Resonance Mechanistic Studies of Carbon Dioxide Reactions with Liquid Amines in Non-aqueous Systems: Evidence for the Formation of Carbamic Acids and Zwitterionic Species, Energy Fuels 29 (2015) 5940–5966, https://doi.org/10.1021/acs.energyfuels.5b00985.

[43] K. Masuda, Y. Ito, M. Horiguchi, H. Fujita, Studies on the solvent dependence of the carbamic acid formation from ω-(1-naphthyl)alkylamines and carbon dioxide, Tetrahedron 61 (2005) 213–229, https://doi.org/10.1016/j.tet.2004.10.033.

[44] K. Takeshita, A. Kitamoto, Chemical equilibria of absorption of CO2 into nonaqueous solution of amine, J. Chem. Eng. Japan. 21 (1988) 411–417, https://doi.org/10.1252/jcej.21.411.

[45] F. Barzagli, C. Giorgi, F. Mani, M. Peruzzini, Comparative Study of CO2 Capture by Aqueous and Nonaqueous 2-Amino-2-methyl-1-propanol Based Absorbents Carried Out by 13C NMR and Enthalpy Analysis, Ind. Eng. Chem. Res. 58 (2019) 4364–4373, https://doi.org/10.1021/acs.iecr.9b00552.

[46] S. Chen, S. Chen, Y. Zhang, H. Chai, L. Qin, Y. Gong, An investigation of the role of N-methyl-diethanolamine in non-aqueous solution for CO2 capture process using 13C NMR spectroscopy, Int. J. Greenh. Gas Control. 39 (2015) 166–173, https://doi.org/10.1016/j.ijggc.2015.05.011.

[47] E. Skylogianni, C. Perinu, B.Y. Cervantes Gamerosa, H.K. Knuutila, Carbon Dioxide solubility in mixtures of methyldiethanolamine with monoethylene glycol, monoethylene glycol – water, water and triethylene glycol, J. Chem. Thermodyn. (2020), 106176, https://doi.org/10.1016/j.jct.2020.106176.

[48] F.A. Chowdhury, K. Goto, H. Yamada, Y. Matsuzaki, A screening study of alcohol solvents for alkanolamine-based CO2 capture, Int. J. Greenh. Gas Control. 99 (2020), 103081, https://doi.org/10.1016/j.ijggc.2020.103081.

[49] R.R. Wanderley, G.J.C. Ponce, H.K. Knuutila, Solubility and Heat of Absorption of CO2 into Diisopropylamine and N, N-Diethylethanolamine Mixed with Organic Solvents, Energy Fuels (2020), https://doi.org/10.1021/acs.energyfuels.0c00880.

[50] D. Eimer, Simultaneous removal of water and hydrogen sulphide from natural gas, The Norwegian Institute of Technology (1994).

[51] R. Behrens, E. von Harbou, W.R. Thiel, W. Böttinger, T. Ingram, G. Sieder, H. Hasse, Monoalkylcarbonate Formation in Methyldiethanolamine–H2O–CO2, Ind. Eng. Chem. Res. 56 (2017) 9006–9015, https://doi.org/10.1021/acs.iecr.7b01937.

[52] E. Jørgensen, C. Faurholt, C. Faurholt, N.A. Sörensen, Reactions between Carbon Dioxide and Amino Alcohols. II. Triethanolamine, Acta Chem. Scand. 8 (1954) 1141–1144, https://doi.org/10.3891/acta.chem.scand.08-1141.

[53] J.E. Rainbolt, P.K. Koech, C.R. Yonker, F. Zheng, D. Main, M.L. Weaver, J. C. Linehan, D.J. Heldebrant, Anhydrous tertiary alkanolamines as hybrid chemical and physical CO 2 capture reagents with pressure-swing regeneration, Energy Environ. Sci. 4 (2011) 480–484, https://doi.org/10.1039/c0ee00506a.

[54] R. Behrens, E. Kessler, K. Münnemann, H. Hasse, E. von Harbou, Monoalkylcarbonate formation in the system monoethanolamine–water–carbon

dioxide, Fluid Phase Equilib. 486 (2019) 98–105, https://doi.org/10.1016/j.fluid.2018.12.031.

[55] P.D. Vaidya, V.V. Mahajani, Kinetics of the Reaction of CO2 with Aqueous Formulated Solution Containing Monoethanolamine, N-Methyl-2-pyrrolidone, and Diethylene Glycol, Ind. Eng. Chem. Res. 44 (2005) 1868–1873, https://doi.org/10.1021/ie049226r.

[56] M.S. Shannon, J.E. Bara, Properties of Alkylimidazoles as Solvents for CO2 Capture and Comparisons to Imidazolium-Based Ionic Liquids, Ind. Eng. Chem. Res. 50 (2011) 8665–8677, https://doi.org/10.1021/ie200259h.

[57] J.-H. Song, J.-H. Yoon, H. Lee, K.-H. Lee, Solubility of Carbon Dioxide in Monoethanolamine + Ethylene Glycol + Water and Monoethanolamine + Poly (ethylene glycol) + Water, J. Chem. Eng. Data. 41 (1996) 497–499, https://doi.org/10.1021/je9502758.

[58] E. Sada, H. Kumazawa, Z.Q. Han, Kinetics of reaction between carbon dioxide and ethylenediamine in nonaqueous solvents, Chem. Eng. J. 31 (1985) 109–115, https://doi.org/10.1016/0300-9467(85)80049-6.

[59] R.R. Wanderley, D.D.D. Pinto, H.K. Knuutila, Investigating opportunities for water-lean solvents in CO2 capture: VLE and heat of absorption in water-lean solvents containing MEA, Sep. Purif. Technol. 231 (2020), 115883, https://doi.org/10.1016/j.seppur.2019.115883.

[60] R.J. Macgregor, A.E. Mather, Equilibrium solubility of H2S and CO2 and their mixtures in a mixed solvent, Can. J. Chem. Eng. 69 (1991) 1357–1366, https://doi.org/10.1002/cjce.5450690618.

[61] R.E. Dugas, G.T. Rochelle, CO2 Absorption Rate into Concentrated Aqueous Monoethanolamine and Piperazine, J. Chem. Eng. Data. 56 (2011) 2187–2195, https://doi.org/10.1021/je101234t.

[62] M.H. Oyevaar, H.J. Fontein, K.R. Westerterp, Equilibria of carbon dioxide in solutions of diethanolamine in aqueous ethylene glycol at 298 K, J. Chem. Eng. Data. 34 (1989) 405–408, https://doi.org/10.1021/je00058a010.

[63] B. Sen, R.N. Roy, J.J. Gibbons, D.A. Johnson, L.H. Adcock, Computational Techniques of Ionic Processes in Water—Organic Mixed Solvents, in: 1979: pp. 215–248. doi:10.1021/ba-1979-0177.ch015.

[64] C.M. Hansen, Hansen Solubility Parameters: A User's Handbook, CRC Press, 2007 https://www.crcpress.com/Hansen-Solubility-Parameters-A-Users-Handbook-Second-Edition/Hansen/p/book/9780849372483 (accessed November 28, 2018).

[65] I. Shulgin, E. Ruckenstein, Henry's Constant in Mixed Solvents from Binary Data, (2002). doi:10.1021/ie010911x.

[66] R.R. Wanderley, Y. Yuan, G.T. Rochelle, H.K. Knuutila, CO2 solubility and mass transfer in water-lean solvents, Chem. Eng. Sci. 202 (2019) 403–416, https://doi.org/10.1016/J.CES.2019.03.052.

[67] J.R. Rumble, D.R. Lide, T.J. Bruno, CRC handbook of chemistry and physics: a ready-reference book of chemical and physical data, 2008.

[68] J.A. Reynolds, J.M. Hough, Formulae for Dielectric Constant of Mixtures, Proc. Phys. Soc. Sect. B. 70 (1957) 769–775, https://doi.org/10.1088/0370-1301/70/8/306.

[69] E.S. Hamborg, C. van Aken, G.F. Versteeg, The effect of aqueous organic solvents on the dissociation constants and thermodynamic properties of alkanolamines, Fluid Phase Equilib. 291 (2010) 32–39, https://doi.org/10.1016/J.FLUID.2009.12.007.

[70] E.S. Hamborg, P.W.J. Derks, E.P. van Elk, G.F. Versteeg, Carbon dioxide removal by alkanolamines in aqueous organic solvents. A method for enhancing the desorption process, Energy Proc. 4 (2011) 187–194, https://doi.org/10.1016/j.egypro.2011.01.040.

[71] N. Ramachandran, E.S. Hamborg, G.F. Versteeg, The effect of aqueous alcohols (methanol, t-butanol) and sulfolane on the dissociation constants and thermodynamic properties of alkanolamines, Fluid Phase Equilib. 360 (2013) 36–43, https://doi.org/10.1016/j.fluid.2013.08.040.

[72] A. Archane, L. Gicquel, E. Provost, W. Fürst, Effect of methanol addition on water-CO2-diethanolamine system: Influence on CO2 solubility and on liquid phase speciation, Chem. Eng. Res. Des. 86 (2008) 592–599, https://doi.org/10.1016/j.cherd.2008.03.005.

[73] W. Huang, Y. Mi, Y. Li, D. Zheng, An Aprotic Polar Solvent, Diglyme, Combined with Monoethanolamine to Form CO2 Capture Material: Solubility Measurement, Model Correlation, and Effect Evaluation, Ind. Eng. Chem. Res. 54 (2015) 3430–3437, https://doi.org/10.1021/ie504739t.

[74] U.E. Aronu, S. Gondal, E.T. Hessen, T. Haug-Warberg, A. Hartono, K.A. Hoff, H. F. Svendsen, Solubility of CO2 in 15, 30, 45 and 60 mass% MEA from 40 to 120 °C and model representation using the extended UNIQUAC framework, Chem. Eng. Sci. 66 (2011) 6393–6406 (accessed May 7, 2019), https://www.sciencedirect.com/science/article/pii/S0009250911006117.

[75] J.I. Lee, F.D. Otto, A.E. Mather, The solubility of H2S and CO2 in aqueous monoethanolamine solutions, Can. J. Chem. Eng. 52 (1974) 803–805, https://doi.org/10.1002/cjce.5450520617.

[76] J.I. Lee, F.D. Otto, A.E. Mather, Equilibrium between carbon dioxide and aqueous monoethanolamine solutions, J. Appl. Chem. Biotechnol. 26 (1976) 541–549, https://doi.org/10.1002/jctb.5020260177.

[77] F.-Y. Jou, A.E. Mather, F.D. Otto, The solubility of CO2 in a 30 mass percent monoethanolamine solution, Can. J. Chem. Eng. 73 (1995) 140–147, https://doi.org/10.1002/cjce.5450730116.

[78] N. Ai, J. Chen, W. Fei, Solubility of Carbon Dioxide in Four Mixed Solvents, J. Chem. Eng. Data. 50 (2005) 492–496, https://doi.org/10.1021/je049696s.

[79] B.E. Roberts, A.E. Mather, Solubility of CO2 and H2S in a Mixed Solvent, Chem. Eng. Commun. 72 (1988) 201–211, https://doi.org/10.1080/00986448808940017.

[80] H. Guo, L. Hui, S. Shen, Monoethanolamine+2-methoxyethanol mixtures for CO2 capture: Density, viscosity and CO2 solubility, J. Chem. Thermodyn. 132 (2019) 155–163, https://doi.org/10.1016/j.jct.2018.12.028.

[81] C. Zheng, J. Tan, Y.J. Wang, G.S. Luo, CO2 Solubility in a Mixture Absorption System of 2-Amino-2-methyl-1-propanol with Ethylene Glycol, Ind. Eng. Chem. Res. 52 (2013) 12247–12252, https://doi.org/10.1021/ie401805n.

[82] T. Moore, Immobilised solvent systems for carbon capture, 2018.

[83] F. Murrieta-Guevara, E. Rebolledo-Libreros, A. Trejo, Solubility of carbon dioxide in binary mixtures of N-methylpyrrolidone with alkanolamines, J. Chem. Eng. Data. 37 (1992) 4–7, https://doi.org/10.1021/je00005a002.

[84] F. Murrieta-Guevara, E. Rebolledo-Libreros, A. Trejo, Gas solubility of carbon dioxide and hydrogen sulfide in mixtures of sulfolane with monoethanolamine, Fluid Phase Equilib. 86 (1993) 225–231, https://doi.org/10.1016/0378-3812(93)87178-4.

[85] J.-H. Song, S.-B. Park, J.-H. Yoon, H. Lee, K.-H. Lee, Solubility of Carbon Dioxide in Monoethanolamine + Ethylene Glycol + Water and Monoethanolamine + Poly(ethylene glycol) + Water at 333.2 K, J. Chem. Eng. Data. 42 (1997) 143–144, https://doi.org/10.1021/je960203w.

[86] J. Tan, H. Shao, J. Xu, L. Du, G. Luo, Mixture Absorption System of Monoethanolamine−Triethylene Glycol for CO2 Capture, Ind. Eng. Chem. Res. 50 (2011) 3966–3976, https://doi.org/10.1021/ie101810a.

[87] H.S. Lee, M. Do Seo, J.W. Kang, D.R. Yang, Measurement and Correlation of the Solubility of Carbon Dioxide in the Mixtures of Aqueous Monoethanolamine Solution and Benzoic Acid, J. Chem. Eng. Data. 57 (2012) 3744–3750, https://doi.org/10.1021/je301009d.

[88] M.-K. Kang, S.-B. Jeon, J.-H. Cho, J.-S. Kim, K.-J. Oh, Characterization and comparison of the CO2 absorption performance into aqueous, quasi-aqueous and non-aqueous MEA solutions, Int. J. Greenh. Gas Control. 63 (2017) 281–288, https://doi.org/10.1016/j.ijggc.2017.05.020.

[89] S. Babamohammadi, A. Shamiri, T. Nejad Ghaffar Borhani, M.S. Shafeeyan, M.K. Aroua, R. Yusoff, Solubility of CO2 in aqueous solutions of glycerol and monoethanolamine, J. Mol. Liq. 249 (2018) 40–52. doi:10.1016/j.molliq.2017.10.151.

[90] R.R. Wanderley, S. Evjen, D.D.D. Pinto, H.K. Knuutila, The Salting-out Effect in Some Physical Absorbents for CO2 Capture, in, Chem. Eng. Trans. (2018) 97–102, https://doi.org/10.3303/CET1869017.

[91] H. Guo, C. Li, X. Shi, H. Li, S. Shen, Nonaqueous amine-based absorbents for energy efficient CO2 capture, Appl. Energy. 239 (2019) 725–734, https://doi.org/10.1016/j.apenergy.2019.02.019.

[92] S. Rodríguez-Fabià, J. Norrman, H.K. Knuutila, J. Sjöblom, K. Paso, CO2 in Lyotropic Liquid Crystals: Phase Equilibria Behavior and Rheology, Polymers (Basel). 11 (2019) 309, https://doi.org/10.3390/polym11020309.

[93] H.S. Lee, N.R. Lee, D.R. Yang, A new method of amine solvent recovery with acid addition for energy reduction in the CO2 absorption process, Chem. Eng. Res. Des. 91 (2013) 2630–2638, https://doi.org/10.1016/j.cherd.2013.05.030.

[94] M.H. Oyevaar, R.W.J. Morssinkhof, K.R. Westerterp, Density, viscosity, solubility, and diffusivity of carbon dioxide and nitrous oxide in solutions of diethanolamine in aqueous ethylene glycol at 298 K, J. Chem. Eng. Data. 34 (1989) 77–82, https://doi.org/10.1021/je00055a022.

[95] K.N.H. Tounsi, A. Barreau, E. Le Corre, P. Mougin, E. Neau, Measurement of Carbon Dioxide Solubility in a Solution of Diethanolamine Mixed with Methanol, Ind. Eng. Chem. Res. 44 (2005) 9239–9243, https://doi.org/10.1021/ie0580250.

[96] J. Li, L. Chen, Y. Ye, Z. Qi, Solubility of CO2 in the Mixed Solvent System of Alkanolamines and Poly(ethylene glycol) 200, J. Chem. Eng. Data. 59 (2014) 1781–1787, https://doi.org/10.1021/je400947t.

[97] A. Henni, A.E. Mather, Solubility of Carbon Dioxide in Methyldiethanolamine + Methanol + Water, J. Chem. Eng. Data. 40 (1995) 493–495, https://doi.org/10.1021/je00018a030.

[98] A. Henni, A.E. Mather, Solubility of carbon dioxide in aqueous and anhydrous mixtures of methyldiethanolamine and triethylene glycol monomethyl ether, Chem. Eng. Commun. 138 (1995) 183–192, https://doi.org/10.1080/00986449508936389.

[99] H. Kierzkowska-Pawlak, R. Zarzycki, Solubility of Carbon Dioxide and Nitrous Oxide in Water + Methyldiethanolamine and Ethanol + Methyldiethanolamine Solutions, J. Chem. Eng. Data. 47 (2002) 1506–1509, https://doi.org/10.1021/je020093v.

[100] H.-J. Xu, C.-F. Zhang, Z.-S. Zheng, Solubility of Hydrogen Sulfide and Carbon Dioxide in a Solution of Methyldiethanolamine Mixed with Ethylene Glycol, (2002). doi:10.1021/ie020375o.

[101] L.Q. Hua, Y. Shuo, T.J. Lin, A new complex absorbent used for improving propylene carbonate absorbent for carbon dioxide removal, Sep. Purif. Technol. 16 (1999) 133–138, https://doi.org/10.1016/S1383-5866(98)00119-1.

[102] M. Hosseini Jenab, M. Abedinzadegan Abdi, S.H. Najibi, M. Vahidi, N.S. Matin, Solubility of Carbon Dioxide in Aqueous Mixtures of N-Methyldiethanolamine + Piperazine + Sulfolane, J. Chem. Eng. Data. 50 (2005) 583–586, https://doi.org/10.1021/je049666p.

[103] F.Y. Jou, A.E. Mather, Solubility of carbon dioxide in an aqueous mixture of methyldiethanolamine and N-methylpyrrolidone at elevated pressures, in, Fluid Phase Equilib. (2005) 465–469, https://doi.org/10.1016/j.fluid.2004.10.004.

[104] T.T. Teng, A.E. Mather, Solubility of acid gases in chemical and mixed solvents, Gas Sep. Purif. 5 (1991) 29–34.

[105] C.W. Wang, A.N. Soriano, Z.Y. Yang, M.H. Li, Solubility of carbon dioxide in the solvent system (2-amino-2-methyl-1-propanol + sulfolane + water), Fluid Phase Equilib. 291 (2010) 195–200, https://doi.org/10.1016/j.fluid.2010.01.011.

[106] C. Zheng, J. Tan, Y.J. Wang, G.S. Luo, CO2 Solubility in a Mixture Absorption System of 2-Amino-2-methyl-1-propanol with Glycol, Ind. Eng. Chem. Res. 51 (2012) 11236–11244, https://doi.org/10.1021/ie3007165.

[107] H. Svensson, J. Edfeldt, V. Zejnullahu Velasco, C. Hulteberg, H.T. Karlsson, Solubility of carbon dioxide in mixtures of 2-amino-2-methyl-1-propanol and organic solvents, Int. J. Greenh. Gas Control. 27 (2014) 247–254, https://doi.org/10.1016/j.ijggc.2014.06.004.

[108] H. Svensson, V. Zejnullahu Velasco, C. Hulteberg, H.T. Karlsson, Heat of absorption of carbon dioxide in mixtures of 2-amino-2-methyl-1-propanol and organic solvents, Int. J. Greenh. Gas Control. 30 (2014) 1–8, https://doi.org/10.1016/J.IJGGC.2014.08.022.

[109] P. Pakzad, M. Mofarahi, A.A. Izadpanah, M. Afkhamipour, C.H. Lee, An experimental and modeling study of CO2 solubility in a 2-amino-2-methyl-1-propanol (AMP) + N-methyl-2-pyrrolidone (NMP) solution, Chem. Eng. Sci. 175 (2018) 365–376, https://doi.org/10.1016/j.ces.2017.10.015.

[110] P. Pakzad, M. Mofarahi, A.A. Izadpanah, M. Afkhamipour, Experimental data, thermodynamic and neural network modeling of CO2 absorption capacity for 2-amino-2-methyl-1-propanol (AMP) + Methanol (MeOH) + H2O system, J. Nat. Gas Sci. Eng. 73 (2020), https://doi.org/10.1016/j.jngse.2019.103060.

[111] D. Lal, F.D. Otto, A.E. Mather, Solubility of acid gases in a mixed solvent, Can. J. Chem. Eng. 76 (1998) 964–966, https://doi.org/10.1002/cjce.5450760515.

[112] R. Pohorecki, C. Mozeński, A new absorbent for carbon dioxide and hydrogen sulphide absorption process, Chem. Eng. Process. Process Intensif. 37 (1998) 69–78, https://doi.org/10.1016/S0255-2701(97)00038-X.

[113] C. Guo, S. Chen, Y. Zhang, G. Wang, Solubility of CO2 in Nonaqueous Absorption System of 2-(2-Aminoethylamine)ethanol + Benzyl Alcohol, J. Chem. Eng. Data. 59 (2014) 1796–1801, https://doi.org/10.1021/je401028g.

[114] S. Chen, S. Chen, X. Fei, Y. Zhang, L. Qin, Solubility and Characterization of CO2 in 40 mass % N-Ethylmonoethanolamine Solutions: Explorations for an Efficient Nonaqueous Solution, Ind. Eng. Chem. Res. 54 (2015) 7212–7218, https://doi.org/10.1021/acs.iecr.5b01654.

[115] S.K. Dash, S.S. Bandyopadhyay, Studies on the effect of addition of piperazine and sulfolane into aqueous solution of N-methyldiethanolamine for CO2 capture and VLE modelling using eNRTL equation, Int. J. Greenh. Gas Control. 44 (2016) 227–237, https://doi.org/10.1016/j.ijggc.2015.11.007.

[116] P.D. Mobley, A.V. Rayer, J. Tanthana, T.R. Gohndrone, M. Soukri, L.J.I. Coleman, M. Lail, CO2 Capture Using Fluorinated Hydrophobic Solvents, Ind. Eng. Chem. Res. 56 (2017) 11958–11966, https://doi.org/10.1021/acs.iecr.7b03088.

[117] M.P. Patil, P.D. Vaidya, Characterization of the superior CO2-capturing absorbent blend AMP/PZ/EGMEE/Water, Int. J. Greenh. Gas Control. 84 (2019) 29–35, https://doi.org/10.1016/j.ijggc.2019.03.005.

[118] M.P. Patil, P.D. Vaidya, Aqueous mixtures of AMP, HMDA-N, N′-dimethyl and TEG for CO2 separation: a study on equilibrium and reaction kinetics, Chem. Eng. Commun. (2019) 1–11, https://doi.org/10.1080/00986445.2019.1657419.

[119] M.P. Patil, P.D. Vaidya, Kinetics of CO2 Absorption into Aqueous AMP/HMDA/TEG Mixtures, ChemistrySelect. 3 (2018) 195–200, https://doi.org/10.1002/slct.201702464.

[120] J. Ye, C. Jiang, H. Chen, Y. Shen, S. Zhang, L. Wang, J. Chen, Novel Biphasic Solvent with Tunable Phase Separation for CO2 Capture: Role of Water Content in Mechanism, Kinetics, and Energy Penalty, Environ. Sci. Technol. 53 (2019) 4470–4479, https://doi.org/10.1021/acs.est.9b00040.

[121] M. Caplow, Kinetics of carbamate formation and breakdown, J. Am. Chem. Soc. 90 (1968) 6795–6803, https://doi.org/10.1021/ja01026a041.

[122] G.F. Versteeg, L.A.J. Van Dijck, W.P.M. Van Swaaij, On the kinetics between CO2 and alkanolamines both in aqueous and non-aqueous solutions. An overview, Chem. Eng. Commun. 144 (1996) 133–158, https://doi.org/10.1080/00986449608936450.

[123] J.E. Crooks, J.P. Donnellan, Kinetics and mechanism of the reaction between carbon dioxide and amines in aqueous solution, J. Chem. Soc. Perkin Trans. 2 (1989) 331–333, https://doi.org/10.1039/p29890000331.

[124] E.F. Da Silva, H.F. Svendsen, Ab initio study of the reaction of carbamate formation from CO2 and alkanolamines, Ind. Eng. Chem. Res. 43 (2004) 3413–3418, https://doi.org/10.1021/ie030619k.

[125] T.L. Donaldson, Y.N. Nguyen, Carbon Dioxide Reaction Kinetics and Transport in Aqueous Amine Membranes, Ind. Eng. Chem. Fundam. 19 (1980) 260–266, https://doi.org/10.1021/i160075a005.

[126] S.W. Park, J.W. Lee, B.S. Choi, J.W. Lee, Absorption of carbon dioxide into non-aqueous solutions of N-methyldiethanolamine, Korean J. Chem. Eng. 23 (2006) 806–811, https://doi.org/10.1007/BF02705932.

[127] S.W. Park, B.S. Choi, J.W. Lee, Chemical absorption of carbon dioxide with triethanolamine in non-aqueous solutions, Korean J. Chem. Eng. 23 (2006) 138–143, https://doi.org/10.1007/BF02705705.

[128] P.V. Kortunov, L.S. Baugh, M. Siskin, D.C. Calabro, In Situ Nuclear Magnetic Resonance Mechanistic Studies of Carbon Dioxide Reactions with Liquid Amines in Mixed Base Systems: The Interplay of Lewis and Brønsted Basicities, Energy Fuels 29 (2015) 5967–5989, https://doi.org/10.1021/acs.energyfuels.5b00988.

[129] V. Barbarossa, F. Barzagli, F. Mani, S. Lai, P. Stoppioni, G. Vanga, Efficient CO2 capture by non-aqueous 2-amino-2-methyl-1-propanol (AMP) and low temperature solvent regeneration, RSC Adv. 3 (2013) 12349–12355, https://doi.org/10.1039/c3ra40933c.

[130] F. Barzagli, S. Lai, F. Mani, Novel non-aqueous amine solvents for reversible CO2 capture, Energy Proc., Elsevier Ltd (2014) 1795–1804, https://doi.org/10.1016/j.egypro.2014.11.186.

[131] Z. Cieslarova, V.B. dos Santos, C.L. do Lago, Both carbamates and monoalkyl carbonates are involved in carbon dioxide capture by alkanolamines, Int. J. Greenh. Gas Control. 76 (2018) 142–149. doi:10.1016/j.ijggc.2018.07.005.

[132] P. Usubharatana, P. Tontiwachwuthikul, Enhancement factor and kinetics of CO2 capture by MEA-methanol hybrid solvents, Energy Proc. 1 (2009) 95–102, https://doi.org/10.1016/J.EGYPRO.2009.01.015.

[133] K.-S. Hwang, S.-W. Park, D.-W. Park, K.-J. Oh, S.-S. Kim, Absorption of carbon dioxide into diisopropanolamine solutions of polar organic solvents, J. Taiwan Inst. Chem. Eng. 41 (2010) 16–21, https://doi.org/10.1016/J.JTICE.2009.05.009.

[134] S. Park, J. Lee, B. Choi, J. Lee, Reaction Kinetics of Carbon Dioxide with Diethanolamine in Polar Organic Solvents, Sep. Sci. Technol. 40 (2005) 1885–1898, https://doi.org/10.1081/SS-200064536.

[135] Y.-S. Son, N.-H. Heo, S.-S. Lee, S.-W. Park, Absorption of Carbon Dioxide into Polar Solvents of 2-Amino-2-Methyl-1-Propanol, 2009.

[136] S. Dinda, A.V. Patwardhan, N.C. Pradhan, Kinetics of Reactive Absorption of Carbon Dioxide with Solutions of Aniline in Nonaqueous Aprotic Solvents, Ind. Eng. Chem. Res. 45 (2006) 6632–6639, https://doi.org/10.1021/ie060147k.

[137] S. Dinda, A.V. Patwardhan, S.R. Panda, N.C. Pradhan, Kinetics of reactive absorption of carbon dioxide with solutions of aniline in carbon tetrachloride and chloroform, Chem. Eng. J. 136 (2008) 349–357, https://doi.org/10.1016/j.cej.2007.04.037.

[138] K. Izutsu, Potentiometry in Non-Aqueous Solutions, in: Electrochem. Nonaqueous Solut., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, 2002: pp. 167–200. doi:10.1002/3527600655.ch6.

[139] K.K. Kundu, M.N. Das, Autoprotolysis Constants of Ethylene Glycol and Propylene Glycol and Dissociation Constants of Some Acids and Bases in the solvents at 30o C, J. Chem. Eng. Data. 9 (1964) 82–86, https://doi.org/10.1021/je60020a024.

[140] S. Kadiwala, A.V. Rayer, A. Henni, Kinetics of carbon dioxide (CO2) with ethylenediamine, 3-amino-1-propanol in methanol and ethanol, and with 1-dimethylamino-2-propanol and 3-dimethylamino-1-propanol in water using stopped-flow technique, Chem. Eng. J. 179 (2012) 262–271, https://doi.org/10.1016/j.cej.2011.10.093.

[141] C. Alvarez-Fuster, N. Midoux, A. Laurent, J.C. Charpentier, Chemical kinetics of the reaction of CO2 with amines in pseudo m–nth order conditions in polar and viscous organic solutions, Chem. Eng. Sci. 36 (1981) 1513–1518, https://doi.org/10.1016/0009-2509(81)85112-3.

[142] M.H. Oyevaar, R.W.J. Morssinkhof, K.R. Westerterp, The kinetics of the reaction between CO2 and diethanolamine in aqueous ethyleneglycol at 298 K: a viscous gas-liquid reaction system for the determination of interfacial areas in gas-liquid contactors, Chem. Eng. Sci. 45 (1990) 3283–3298, https://doi.org/10.1016/0009-2509(90)80220-9.

[143] Y. Jiru, D.A. Eimer, A study of mass transfer kinetics of carbon dioxide in (Monoethanolamine + water) by stirred cell, Energy Proc., Elsevier Ltd (2013) 2180–2187, https://doi.org/10.1016/j.egypro.2013.06.097.

[144] M. Garcia, H.K. Knuutila, U.E. Aronu, S. Gu, Influence of substitution of water by organic solvents in amine solutions on absorption of CO 2, Int. J. Greenh. Gas Control. 78 (2018) 286–305, https://doi.org/10.1016/j.ijggc.2018.07.029.

[145] C. Zheng, B. Zhao, K. Wang, G. Luo, Determination of kinetics of CO2 absorption in solutions of 2-amino-2-methyl-1-propanol using a microfluidic technique, AIChE J. 61 (2015) 4358–4366, https://doi.org/10.1002/aic.14972.

[146] M.-K. Kang, J.-H. Cho, J.-H. Lee, S.-S. Lee, K.-J. Oh, Kinetic Reaction Characteristics of Quasi-Aqueous and Nonaqueous Sorbents for CO2 Absorption Using MEA/H2O/Ethylene Glycol, Energy Fuels 31 (2017) 8383–8391, https://doi.org/10.1021/acs.energyfuels.7b00768.

[147] S.K. Pal, M.M. Sharma, Solvay type processes: absorption of carbon dioxide in ammoniated aqueous and non-aqueous solutions of sodium nitrate, calcium nitrate, and potassium chloride, Ind. Eng. Chem. Process Des. Dev. 22 (1983) 76–79, https://doi.org/10.1021/i200020a014.

[148] J.E. Crooks, J.P. Donnellan, Kinetics of the formation of N, N-dialkylcarbamate from diethanolamine and carbon dioxide in anhydrous ethanol, J. Chem. Soc. Perkin Trans. 2 (1988) 191–194, https://doi.org/10.1039/P29880000191.

[149] R.A. Davis, O.C. Sandall, Kinetics of the reaction of carbon dioxide with secondary amines in polyethylene glycol, Chem. Eng. Sci. 48 (1993) 3187–3193, https://doi.org/10.1016/0009-2509(93)80204-4.

[150] S. Xu, Y.W. Wang, F.D. Otto, A.E. Mather, Kinetics of the reaction of carbon dioxide with 2-amino-2-methyl-1-propanol solutions, Chem. Eng. Sci. 51 (1996) 841–850, https://doi.org/10.1016/0009-2509(95)00327-4.

[151] A.V. Rayer, A. Henni, J. Li, Reaction kinetics of 2-((2-aminoethyl) amino) ethanol in aqueous and non-aqueous solutions using the stopped-flow technique, Can. J. Chem. Eng. 91 (2013) 490–498, https://doi.org/10.1002/cjce.21690.

[152] N. Zhong, H. Liu, X. Luo, M.J. AL-Marri, A. Benamor, R. Idem, P. Tontiwachwuthikul, Z. Liang, Reaction Kinetics of Carbon Dioxide (CO2) with Diethylenetriamine and 1-Amino-2-propanol in Nonaqueous Solvents Using Stopped-Flow Technique, Ind. Eng. Chem. Res. 55 (2016) 7307–7317. doi:10.1021/acs.iecr.6b00981.

[153] S. Chen, G. Hu, K.H. Smith, K.A. Mumford, Y. Zhang, G.W. Stevens, Kinetics of CO2 Absorption in an Ethylethanolamine Based Solution, Ind. Eng. Chem. Res. 56 (2017) 12305–12315, https://doi.org/10.1021/acs.iecr.7b02932.

[154] F.P.G. Duatepe, O.Y. Orhan, E. Alper, Kinetics of Carbon Dioxide Absorption by Nonaqueous Solutions of Promoted Sterically Hindered Amines, Energy Proc., Elsevier Ltd (2017) 57–65, https://doi.org/10.1016/j.egypro.2017.03.1147.

[155] C. Alvarez-Fuster, N. Midoux, A. Laurent, J.C. Charpentier, Chemical kinetics of the reaction of carbon dioxide with amines in pseudo m-nth order conditions in aqueous and organic Solutions, Chem. Eng. Sci. 35 (1980) 1717–1723, https://doi.org/10.1016/0009-2509(80)85006-8.

[156] S.H. Ali, S.Q. Merchant, M.A. Fahim, Kinetic study of reactive absorption of some primary amines with carbon dioxide in ethanol solution, Sep. Purif. Technol. 18 (2000) 163–175, https://doi.org/10.1016/S1383-5866(99)00064-7.

[157] H. Li, S. Shen, Kinetics of Carbon Dioxide Absorption into Water-Lean Potassium Prolinate/Ethylene Glycol, Solutions (2019), https://doi.org/10.1021/acs.iecr.9b01662.

[158] Y. Bian, H. Li, S. Shen, Reaction kinetics of carbon dioxide with potassium prolinate in water-lean solvents, Chem. Eng. Sci. 199 (2019) 220–230, https://doi.org/10.1016/j.ces.2019.01.027.

[159] D. Song, A.F. Seibert, G.T. Rochelle, Effect of Liquid Viscosity on Mass Transfer Area and Liquid Film Mass Transfer Coefficient for GT-OPTIMPAK 250Y, Energy Proc., Elsevier Ltd (2017) 2713–2727, https://doi.org/10.1016/j.egypro.2017.03.1534.

[160] C.L. Yaws, Transport Properties of Chemicals and Hydrocarbons, Elsevier Inc., 2009.

[161] A. Henni, Y. Maham, P. Tontiwachwuthikul, A. Chakma, A.E. Mather, Densities and Viscosities for Binary Mixtures of N -Methyldiethanolamine + Triethylene Glycol Monomethyl Ether from 25 °C to 70 °C and N -Methyldiethanolamine + Ethanol Mixtures at 40 °C, J. Chem. Eng. Data. 45 (2000) 247–253, https://doi.org/10.1021/je9902140.

[162] F. Bougie, D. Pokras, X. Fan, Novel non-aqueous MEA solutions for CO2 capture, Int. J. Greenh. Gas Control. 86 (2019) 34–42, https://doi.org/10.1016/j.ijggc.2019.04.013.

[163] M.J.C. Esteves, M.J.E ., de, M. Cardoso, O.E. Barcia, A Debye−Hückel Model for Calculating the Viscosity of Binary Strong Electrolyte Solutions, Ind. Eng. Chem. Res. 40 (2001) 5021–5028, https://doi.org/10.1021/ie010392y.

[164] T.G. Amundsen, L.E. Øi, D.A. Eimer, Density and Viscosity of Monoethanolamine + Water + Carbon Dioxide from (25 to 80) °C, J. Chem. Eng. Data. 54 (2009) 3096–3100, https://doi.org/10.1021/je900188m.

[165] C. Wohlfarth, in: Selection and arrangement of static dielectric constants of pure liquid substances and their binary liquid mixtures, Springer, Berlin Heidelberg, 2015, pp. 1–2, https://doi.org/10.1007/978-3-662-48168-4_1.

[166] Y. Yuan, G.T. Rochelle, Lost work: A comparison of water-lean solvent to a second generation aqueous amine process for CO 2 capture, Int. J. Greenh. Gas Control. (2019) 82–90, https://doi.org/10.1016/j.ijggc.2019.03.013.

[167] F.J. Tamajón, E. Álvarez, F. Cerdeira, D. Gómez-Díaz, CO2 absorption into N-methyldiethanolamine aqueous-organic solvents, Chem. Eng. J. 283 (2016) 1069–1080, https://doi.org/10.1016/J.CEJ.2015.08.065.

[168] J. Gao, J. Yin, F. Zhu, X. Chen, M. Tong, W. Kang, Y. Zhou, J. Lu, Study on Absorption and Regeneration Performance of Novel Hybrid Solutions for CO2 Capture, China Pet. Process. Petrochemical Technol. 18 (2016) 66–72.

[169] Y. Yuan, G.T. Rochelle, CO2 absorption rate and capacity of semi-aqueous piperazine for CO2 capture, Int. J. Greenh. Gas Control. 85 (2019) 182–186, https://doi.org/10.1016/j.ijggc.2019.03.007.

[170] L. Zou, H. Gao, Z. Wu, Z. Liang, Fast screening of amine/physical solvent systems and mass transfer studies on efficient aqueous hybrid MEA/Sulfolane solution for postcombustion CO2 capture, J. Chem. Technol. Biotechnol. (2019) jctb.6246, https://doi.org/10.1002/jctb.6246.

[171] A. Liu, J. Li, B. Ren, X. Lu, Development of High-Capacity and Water-Lean CO2 Absorbents by a Concise Molecular Design Strategy through Viscosity Control, ChemSusChem 12 (2019) 5164–5171, https://doi.org/10.1002/cssc.201902279.

[172] H. Karlsson, H. Svensson, Rate of Absorption for CO2 Absorption Systems Using a Wetted Wall Column, Energy Proc., Elsevier Ltd (2017) 2009–2023, https://doi.org/10.1016/j.egypro.2017.03.1335.

[173] S. Shen, Y. Bian, Y. Zhao, Energy-efficient CO2 capture using potassium prolinate/ethanol solution as a phase-changing absorbent, Int. J. Greenh. Gas Control. 56 (2017) 1–11, https://doi.org/10.1016/j.ijggc.2016.11.011.

[174] Y. Bian, S. Shen, CO2 absorption into a phase change absorbent: Water-lean potassium prolinate/ethanol solution, Chin. J. Chem. Eng. (2018) 2318–2326, https://doi.org/10.1016/j.cjche.2018.02.022.

[175] J. Gervasi, L. Dubois, D. Thomas, Screening tests of new hybrid solvents for the post-combustion CO2 capture process by chemical absorption, Energy Proc., Elsevier Ltd (2014) 1854–1862, https://doi.org/10.1016/j.egypro.2014.11.193.

[176] S.W. Park, B.S. Choi, J.W. Lee, Influence of polyethylene oxide on absorption of carbon dioxide into aqueous N-methyldiethanolamine solution, Korean J. Chem. Eng. 24 (2007) 431–435, https://doi.org/10.1007/s11814-007-0074-y.

[177] S. Park, B. Choi, J. Lee, Chemical Absorption of Carbon Dioxide into Aqueous PEO Solution of Monoethanolamine, Sep. Sci. Technol. 40 (2005) 3261–3275, https://doi.org/10.1080/01496390500423623.

[178] J. Li, C. You, L. Chen, Y. Ye, Z. Qi, K. Sundmacher, Dynamics of CO2 Absorption and Desorption Processes in Alkanolamine with Cosolvent Polyethylene Glycol, Ind. Eng. Chem. Res. 51 (2012) 12081–12088, https://doi.org/10.1021/ie301164v.

[179] K. Sridharan, M.M. Sharma, New systems and methods for the measurement of effective interfacial area and mass transfer coefficients in gas-liquid contactors, Chem. Eng. Sci. 31 (1976) 767–774, https://doi.org/10.1016/0009-2509(76)80049-8.

[180] P.H. Lin, D.S.H. Wong, Carbon dioxide capture and regeneration with amine/alcohol/water blends, Int. J. Greenh. Gas Control. 26 (2014) 69–75, https://doi.org/10.1016/j.ijggc.2014.04.020.

[181] C.H. Yu, C.S. Tan, CO2 capture by aqueous solution containing mixed alkanolamines and diethylene glycol in a rotating packed bed, Energy Proc., Elsevier Ltd (2014) 758–764, https://doi.org/10.1016/j.egypro.2014.11.084.

[182] C. Li, X. Shi, S. Shen, Performance Evaluation of Newly Developed Absorbents for Solvent-Based Carbon Dioxide Capture, Energy Fuels 33 (2019) 9032–9039, https://doi.org/10.1021/acs.energyfuels.9b02158.

[183] K. Yogish, Absorption of CO2 in some hybrid solvents, Can. J. Chem. Eng. 68 (1990) 511–512, https://doi.org/10.1002/cjce.5450680324.

[184] G. Jing, F. Liu, B. Lv, X. Zhou, Z. Zhou, Novel Ternary Absorbent: Dibutylamine Aqueous-Organic Solution for CO2 Capture, Energy Fuels 31 (2017) 12530–12539, https://doi.org/10.1021/acs.energyfuels.7b02382.

[185] D. Gómez-Díaz, J. Grueiro, J.M. Navaza, C. Noval, CO2 absorption with tri-n-butylamine in GL and GLL systems, Energy. 153 (2018) 568–574, https://doi.org/10.1016/j.energy.2018.04.071.

[186] Y.E. Kim, J.H. Park, S.H. Yun, S.C. Nam, S.K. Jeong, Y. Il Yoon, Carbon dioxide absorption using a phase transitional alkanolamine-alcohol mixture, J. Ind. Eng. Chem. 20 (2014) 1486–1492, https://doi.org/10.1016/j.jiec.2013.07.036.

[187] H. Svensson, C. Hulteberg, H.T. Karlsson, Precipitation of AMP Carbamate in CO2 Absorption Process, Energy Proc. 63 (2014) 750–757, https://doi.org/10.1016/J.EGYPRO.2014.11.083.

[188] S. Zheng, M. Tao, Q. Liu, L. Ning, Y. He, Y. Shi, Capturing CO2 into the Precipitate of a Phase-Changing Solvent after Absorption, Environ. Sci. Technol. 48 (2014) 8905–8910, https://doi.org/10.1021/es501554h.

[189] J. Cheng, Y. Li, L. Hu, J. Liu, J. Zhou, K. Cen, Characterization of CO2 Absorption and Carbamate Precipitate in Phase-Change N-Methyl-1,3-diaminopropane/N,N-Dimethylformamide Solvent, Energy & Fuels. 31 (2017) 13972–13978, https://doi.org/10.1021/acs.energyfuels.7b02627.

[190] W. Zhang, X. Jin, W. Tu, Q. Ma, M. Mao, C. Cui, Development of MEA-based CO2 phase change absorbent, Appl. Energy. 195 (2017) 316–323, https://doi.org/10.1016/j.apenergy.2017.03.050.

[191] Z. Zhang, W. Zhao, J. Nong, D. Feng, Y. Li, Y. Chen, J. Chen, Liquid-Solid Phase-Change Behavior of Diethylenetriamine in Nonaqueous Systems for Carbon Dioxide Absorption, Energy Technol. 5 (2017) 461–468, https://doi.org/10.1002/ente.201600351.

[192] Y. Li, J. Cheng, L. Hu, J. Liu, J. Zhou, K. Cen, Phase-changing solution PZ/DMF for efficient CO2 capture and low corrosiveness to carbon steel, Fuel 216 (2018) 418–426, https://doi.org/10.1016/j.fuel.2017.12.030.

[193] F. Liu, G. Jing, X. Zhou, B. Lv, Z. Zhou, Performance and Mechanisms of Triethylene Tetramine (TETA) and 2-Amino-2-methyl-1-propanol (AMP) in Aqueous and Nonaqueous Solutions for CO2 Capture, ACS Sustain. Chem. Eng. 6 (2018) 1352–1361, https://doi.org/10.1021/acssuschemeng.7b03717.

[194] M. Tao, J. Gao, W. Zhang, Y. Li, Y. He, Y. Shi, A Novel Phase-Changing Nonaqueous Solution for CO2 Capture with High Capacity, Thermostability, and Regeneration Efficiency, Ind. Eng. Chem. Res. 57 (2018) 9305–9312, https://doi.org/10.1021/acs.iecr.8b01775.

[195] L. Wang, S. Yu, Q. Li, Y. Zhang, S. An, S. Zhang, Performance of sulfolane/DETA hybrids for CO2 absorption: Phase splitting behavior, kinetics and thermodynamics, Appl. Energy. 228 (2018) 568–576, https://doi.org/10.1016/j.apenergy.2018.06.077.

[198] Y.J. Lin, G.T. Rochelle, Optimization of advanced flash stripper for CO2 capture using piperazine, Energy Proc., Elsevier Ltd (2014) 1504–1513, https://doi.org/10.1016/j.egypro.2014.11.160.

[199] R.R. Wanderley, H.K. Knuutila, Mapping Diluents for Water-Lean Solvents: A Parametric Study, Ind. Eng. Chem. Res. 59 (2020) 11656–11680, https://doi.org/10.1021/acs.iecr.0c00940.

[200] F. Liu, M. Fang, N. Yi, T. Wang, Q. Wang, Biphasic behaviors and regeneration energy of a 2-(diethylamino)-ethanol and 2-((2-aminoethyl)amino) ethanol blend for CO2 capture, Sustain. Energy Fuels. 3 (2019) 3594–3602, https://doi.org/10.1039/c9se00821g.

[201] C.L. Yaws, The Yaws Handbook of Physical Properties for Hydrocarbons and Chemicals: Physical Properties for More Than 54,000 Organic and Inorganic Chemical Compounds, Coverage for C1 to C100 Organics and Ac to Zr Inorganics: Second Edition, Elsevier Inc., 2015.

[202] V. Svoboda, M. Zábranský, M. Bárta, Molar heat capacities of 2-methoxyethanol, 2-ethoxyethanol, and 2-propoxyethanol in the temperature range from 298 K to 330 K, J. Chem. Thermodyn. 711–712 (1991).

[203] M.N. Islam, M.M. Islam, M.N. Yeasmin, Viscosity of aqueous solutions of 2-methoxyethanol, 2-ethoxyethanol, and ethanolamine, J. Chem. Thermodyn. 36 (2004) 889–893, https://doi.org/10.1016/j.jct.2004.06.004.

[204] Y.J. Lin, G.T. Rochelle, Heat Transfer Enhancement and Optimization of Lean/Rich Solvent Cross Exchanger for Amine Scrubbing, Energy Proc., Elsevier Ltd (2017) 1890–1903, https://doi.org/10.1016/j.egypro.2017.03.1320.

[205] K. Okada, M. Ono, T. Tomimura, T. Okuma, H. Konno, S. Ohtani, Design and heat transfer characteristics of new plate heat exchanger, Heat Transf. - Japanese Res. 1 (1972) 90–95.

[206] F.A. Tobiesen, H.F. Svendsen, Study of a Modified Amine-Based Regeneration Unit, Ind. Eng. Chem. Res. 45 (2006) 2489–2496, https://doi.org/10.1021/ie050544f.

[207] P. Usubharatana, A. Veawab, A. Aroonwilas, P. Tontiwachwuthikul, Mass transfer performance of CO2 capture by aqueous hybrid MEA-methanol in packed absorber, in: 2006: pp. 1–7. doi:10.1109/EICCCC.2006.277215.

[208] J.T. Yeh, H.W. Pennline, K.P. Resnik, Study of CO2 Absorption and Desorption in a Packed Column, Energy Fuels 15 (2001) 274–278, https://doi.org/10.1021/ef0002389.

[209] Y.S. Yu, H.F. Lu, T.T. Zhang, Z.X. Zhang, G.X. Wang, V. Rudolph, Determining the Performance of an Efficient Nonaqueous CO $_2$ Capture Process at Desorption Temperatures below 373 K, Ind. Eng. Chem. Res. 52 (2013) 12622–12634, https://doi.org/10.1021/ie400353f.

[210] I. von Harbou, S. Hoch, H.P. Mangalapally, R. Notz, G. Sieder, H. Garcia, O. Spuhl, H. Hasse, Removal of carbon dioxide from flue gases with aqueous MEA solution containing ethanol, Chem. Eng. Process. Process Intensif. 75 (2014) 81–89, https://doi.org/10.1016/j.cep.2013.11.004.

[211] H. Ghanbarabadi, B. Khoshandam, D.A. Wood, Simulation of CO2 removal from ethane with Sulfinol-M+AMP solvent instead of DEA solvent in the South Pars

phases 9 and 10 gas processing facility, Petroleum. 5 (2019) 90–101, https://doi.org/10.1016/j.petlm.2018.06.004.

[212] M.T. Angaji, H. Ghanbarabadi, F.K.Z. Gohari, Optimizations of Sulfolane concentration in propose Sulfinol-M solvent instead of MDEA solvent in the refineries of Sarakhs, J. Nat. Gas Sci. Eng. 15 (2013) 22–26, https://doi.org/10.1016/j.jngse.2013.08.003.

[213] T. Zhang, Z. Zhang, Computational study of CO2 absorption in aqueous and non-aqueous solutions using MEA, Energy Proc., Elsevier Ltd (2014) 1347–1353, https://doi.org/10.1016/j.egypro.2014.11.144.

[214] G.T. Rochelle, Conventional amine scrubbing for CO2 capture, in: Absorption-Based Post-Combustion Capture of Carbon Dioxide, Elsevier Inc., 2016: pp. 35–67. doi:10.1016/B978-0-08-100514-9.00003-2.

[215] G.T. Rochelle, Y. Wu, E. Chen, K. Akinpelumi, K.B. Fischer, T. Gao, C.T. Liu, J. L. Selinger, Pilot plant demonstration of piperazine with the advanced flash stripper, Int. J. Greenh. Gas Control. 84 (2019) 72–81, https://doi.org/10.1016/j.ijggc.2019.03.014.

[216] U. Shoukat, G. Fytianos, H.K. Knuutila, Thermal stability and corrosion studies of amines for combined acid gas removal and hydrate control for subsea gas treatment systems, in: Techno-Ocean 2016 Return to Ocean., Institute of Electrical and Electronics Engineers Inc., 2017: pp. 176–180. doi:10.1109/Techno-Ocean.2016.7890641.

[217] U. Shoukat, E. Baumeister, D.D.D. Pinto, H.K. Knuutila, Thermal stability and corrosion of tertiary amines in aqueous amine and amine-glycol-water solutions for combined acid gas and water removal, J. Nat. Gas Sci. Eng. 62 (2019) 26–37, https://doi.org/10.1016/j.jngse.2018.11.025.

[218] U. Shoukat, Combined subsea hydrate control and H2S removal, Norwegian University of Science and Technology, 2019.

[219] K.K. Høisæter, H.K. Knuutila, Degradation potential of aqueous and water-lean MEA (2019) 1–21 (accessed December 12, 2019), https://az659834.vo.msecnd.net/eventsairwesteuprod/production-ieaghg-public/8b35e3179849420384cc66fc8223bbf3.

[220] S. Chen, S. Chen, Y. Zhang, H. Chai, M. Cui, Role of SO2 in Non-aqueous Solution of Blended Monoethylethanolamine and Diethylethanolamine for CO2 Capture from Power Plant Flue Gas Streams, Energy Fuels 30 (2016) 8520–8528, https://doi.org/10.1021/acs.energyfuels.6b01562.

[221] A.T. Zoghi, M. Shokouhi, M. Abbasghorbani, M. Vahidi, M. Zare, S. Daripour, Investigation of Sulfolane Degradation in Aqueous Alkanolamine Solutions Under the Stripping Operational Condition, Int. J. Thermophys. 41 (2020) 124, https://doi.org/10.1007/s10765-020-02707-7.

[222] W.G. Lloyd, F.C. Taylor, Corrosion by and Deterioration of Glycol and Glycol-Amine Solutions, Ind. Eng. Chem. 46 (1954) 2407–2416, https://doi.org/10.1021/ie50539a054.

[223] S. Srinivasan, A. Veawab, A. Aroonwilas, Screening and Evaluating Environmentally-Friendly Corrosion Inhibitors for Amine-Based CO2 Absorption Process, in: Corros. Inhib. Princ. Recent Appl., InTech, 2018. doi:10.5772/intechopen.72752.

[224] F. Barzagli, F. Mani, M. Peruzzini, Efficient CO2 absorption and low temperature desorption with non-aqueous solvents based on 2-amino-2-methyl-1-propanol (AMP), Int. J. Greenh. Gas Control. 16 (2013) 217–223, https://doi.org/10.1016/j.ijggc.2013.03.026.

[225] F. Barzagli, M. Di Vaira, F. Mani, M. Peruzzini, Improved Solvent Formulations for Efficient CO2 Absorption and Low-Temperature Desorption, ChemSusChem 5 (2012) 1724–1731, https://doi.org/10.1002/cssc.201200062.

[226] F. Barzagli, F. Mani, M. Peruzzini, Novel water-free biphasic absorbents for efficient CO2 capture, Int. J. Greenh. Gas Control. 60 (2017) 100–109, https://doi.org/10.1016/j.ijggc.2017.03.010.

[227] F. Barzagli, S. Lai, F. Mani, CO2 Capture by Liquid Solvents and their Regeneration by Thermal Decomposition of the Solid Carbonated Derivatives, Chem. Eng. Technol. 36 (2013) 1847–1852, https://doi.org/10.1002/ceat.201300225.

[228] F. Barzagli, F. Mani, M. Peruzzini, A Comparative Study of the CO2 Absorption in Some Solvent-Free Alkanolamines and in Aqueous Monoethanolamine (MEA), Environ. Sci. Technol. 50 (2016) 7239–7246, https://doi.org/10.1021/acs.est.6b00150.

[229] S. Yamamoto, H. Yamada, T. Higashii, Development of Chemical CO2 Solvent For High Pressure CO2 Capture (2): Addition Effects of Non-aqueous Media on Amine Solutions, Energy Proc. 63 (2014) 1963–1971, https://doi.org/10.1016/J.EGYPRO.2014.11.209.

[230] S. Yamamoto, H. Machida, Y. Fujioka, T. Higashii, Development of chemical CO2 solvent for high-pressure CO 2 capture, in, Energy Proc., Elsevier Ltd (2013) 505–517, https://doi.org/10.1016/j.egypro.2013.05.137.

[231] J. Tanthana, A.V. Rayer, V. Gupta, P.D. Mobley, M. Soukri, J. Zhou, M. Lail, Experimental Study of a Hydrophobic Solvent for Natural Gas Sweetening Based on the Solubility and Selectivity for Light Hydrocarbons (CH4, C2H6) and Acid Gases (CO2 and H2S) at 298–353 K, J. Chem. Eng. Data. 64 (2019) 545–556, https://doi.org/10.1021/acs.jced.8b00735.

[232] M. Lail, J. Tanthana, L. Coleman, Non-Aqueous Solvent (NAS) CO2 Capture Process, Energy Proc. 63 (2014) 580–594, https://doi.org/10.1016/J.EGYPRO.2014.11.063.

[233] P.G. Jessop, D.J. Heldebrant, X. Li, C.A. Eckert, C.L. Liotta, Reversible nonpolar-to-polar solvent, Nature. 436 (2005) 1102–1102. doi:10.1038/4361102a.

[234] D.J. Heldebrant, P.K. Koech, J.E. Rainbolt, F. Zheng, CO2-binding organic liquids, An integrated acid gas capture system, in, Energy Proc., Elsevier Ltd (2011) 216–223, https://doi.org/10.1016/j.egypro.2011.01.044.

[235] D.J. Heldebrant, P.K. Koech, M.T.C. Ang, C. Liang, J.E. Rainbolt, C.R. Yonker, P. G. Jessop, Reversible zwitterionic liquids, the reaction of alkanol guanidines, alkanol amidines, and diamines with CO2, Green Chem. 12 (2010) 713–721, https://doi.org/10.1039/b924790d.

[236] F. Zheng, D.J. Heldebrant, P.M. Mathias, P. Koech, M. Bhakta, C.J. Freeman, M.D. Bearden, A. Zwoster, Bench-Scale Testing and Process Performance Projections of CO2 Capture by CO2–Binding Organic Liquids (CO2 BOLs) with and without Polarity-Swing-Assisted Regeneration, Energy & Fuels. (2016) acs.energyfuels.5b02437. doi:10.1021/acs.energyfuels.5b02437.

[237] D.J. Heldebrant, P.K. Koech, J.E. Rainbolt, F. Zheng, T. Smurthwaite, C. J. Freeman, M. Oss, I. Leito, Performance of single-component CO2-binding organic liquids (CO2BOLs) for post combustion CO2 capture, Chem. Eng. J. 171 (2011) 794–800, https://doi.org/10.1016/j.cej.2011.02.012.

[238] D.C. Cantu, D. Malhotra, P.K. Koech, D.J. Heldebrant, R. Zheng, C.J. Freeman, R. Rousseau, V.A. Glezakou, Integrated Solvent Design for CO2 Capture and Viscosity Tuning, Energy Proc., Elsevier Ltd (2017) 726–734, https://doi.org/10.1016/j.egypro.2017.03.1215.

[239] G.A. Whyatt, C.J. Freeman, A. Zwoster, D.J. Heldebrant, Measuring Nitrous Oxide Mass Transfer into Non-Aqueous CO2BOL CO2 Capture Solvents, Ind. Eng. Chem. Res. 55 (2016) 4720–4725, https://doi.org/10.1021/acs.iecr.6b00390.

[240] D.J. Heldebrant, P.K. Koech, R. Rousseau, V.A. Glezakou, D. Cantu, D. Malhotra, F. Zheng, G. Whyatt, C.J. Freeman, M.D. Bearden, Are Water-lean Solvent Systems Viable for Post-Combustion CO2 Capture? Energy Proc., Elsevier Ltd (2017) 756–763, https://doi.org/10.1016/j.egypro.2017.03.1218.

[241] P.K. Koech, J.E. Rainbolt, M.D. Bearden, F. Zheng, D.J. Heldebrant, Chemically selective gas sweetening without thermal-swing regeneration, Energy Environ. Sci. 4 (2011) 1385–1390, https://doi.org/10.1039/c0ee00839g.

[242] R.P. Cabral, D.J. Heldebrant, N. Mac Dowell, A Techno-Economic Analysis of a Novel Solvent-Based Oxycombustion CO2 Capture Process, Ind. Eng. Chem. Res. 58 (2019) 6604–6612, https://doi.org/10.1021/acs.iecr.9b00305.

[243] D. Malhotra, J.P. Page, M.E. Bowden, A. Karkamkar, D.J. Heldebrant, V.-A. Glezakou, R. Rousseau, P.K. Koech, Phase-Change Aminopyridines as Carbon Dioxide Capture Solvents, Ind. Eng. Chem. Res. 56 (2017) 7534–7540, https://doi.org/10.1021/acs.iecr.7b00874.

[244] G.A. Whyatt, A. Zwoster, F. Zheng, R.J. Perry, B.R. Wood, I. Spiry, C.J. Freeman, D.J. Heldebrant, Measuring CO2 and N2O Mass Transfer into GAP-1 CO2 –Capture Solvents at Varied Water Loadings, Ind. Eng. Chem. Res. 56 (2017) 4830–4836, https://doi.org/10.1021/acs.iecr.7b00193.

[245] P.M. Mathias, K. Afshar, F. Zheng, M.D. Bearden, C.J. Freeman, T. Andrea, P. K. Koech, I. Kutnyakov, A. Zwoster, A.R. Smith, P.G. Jessop, O.G. Nik, D. J. Heldebrant, Improving the regeneration of CO2-binding organic liquids with a polarity change, Energy Environ. Sci. 6 (2013) 2233–2242, https://doi.org/10.1039/c3ee41016a.

[246] N. Brown, G. Heller, G. Staab, T. Silverman, R. Kupfer, R. Brown, A. Brown, Novel Advanced Solvent-based Carbon Capture Pilot Demonstration at the National Carbon Capture Center, Energy Proc., Elsevier Ltd (2017) 1075–1086, https://doi.org/10.1016/j.egypro.2017.03.1260.

[247] S.J. Zhou, J. Tanthana, P. Mobley, A. Rabindran, V. Gupta, M. Lesemann, M. Soukri, M. Lail, A. Tobiesen, T. Mejdell, U. Aronu, A. Grimstvedt, K. Hjarbo, L. Hovdahl, Pilot Testing of a Non-Aqueous Solvent (NAS) CO2 Capture Process, in: 14th Greenh. Gas Control Technol. Conf. Melb. 21-26 Oct. 2018, 2018.

[248] M. Iijima, T. Nagayasu, T. Kamijyo, S. Nakatani, MHI's Energy Efficient Flue Gas CO 2 Capture Technology and Large Scale CCS Demonstration Test at Coal-fired Power Plants in USA, 2011.

[249] K. Stéphenne, Start-up of world's first commercial post-combustion coal fired ccs project: Contribution of shell cansolv to saskpower boundary dam iccs project, Energy Proc., Elsevier Ltd (2014) 6106–6110, https://doi.org/10.1016/j.egypro.2014.11.642.