

## Performance of non-aqueous amine hybrid solvents mixtures for CO<sub>2</sub> capture: A study using a molecular-based model

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### ABSTRACT

We present here results regarding the chemisorption of CO<sub>2</sub> in non-aqueous hybrid solvents of mixtures of amines and physical solvents such as glycols or glymes as alternatives to aqueous amines for CO<sub>2</sub> capture and separation, using the molecular-based equation of state, soft-SAFT, as a modelling tool. The reactive nature of the CO<sub>2</sub> absorption process in non-aqueous amines was implicitly considered through the formation of CO<sub>2</sub>-amine physical aggregates bounded by strong and localised intermolecular interactions, with the effect of non-aqueous solvents on the reactivity included in these interactions. With such a modelling framework, only VLE data on the absorption of CO<sub>2</sub> in amine solvents is required, without any need for additional information such as speciation reactions or equilibrium constants, thus decreasing the number of adjustable parameters needed to accurately model the absorption process. Subsequently, the developed models were used to examine the CO<sub>2</sub> capture performance of these hybrid solvents in terms of absorption cyclic capacity and heat of regeneration as key performance indicators using a simple and short-cut estimation method. Results show that for the same total amine mass concentration, non-aqueous amine solvents possess a 30–40% decrease in total heat of regeneration compared to their aqueous counterparts at the expense of a 10–50% reduction in cyclic capacity. These results validate the reliability of the molecular modelling approach as an attractive and valuable tool for the screening of chemical solvents and process modelling.

### 1. Introduction

It is acknowledged that the increasing levels of anthropogenic CO<sub>2</sub> emissions is the primary contributor to global warming and climate change, requiring immediate mitigation and control [1–3]. With the emergence of stringent environmental legislations on climate change mitigation, significant efforts have been exerted to the development of CO<sub>2</sub> capture technologies that limit the degree of future climate change, deeming CO<sub>2</sub> capture as a global engineering project [4]. Although various strategies are available to curtail anthropogenic CO<sub>2</sub> emissions, Post-Combustion Carbon Capture (PCCC) is the most suitable choice for retrofitting existing fossil fuel combustion and power-generation facilities [1,3]. Among the wide variety of available PCCC technologies, the physical or chemical absorption of CO<sub>2</sub> from large-scale emission sources, such as power-generation facilities, are considered the most viable and close-to-market approaches to be deployed at a large industrial scale. More specifically, chemical solvents, mainly aqueous

solutions of amines, are regarded as the most technically proven and industrially feasible technology for carbon capture at large scale [4,5]. Since their emergence, as early as the 1930s, several amines have been developed and patented, owing to their selectivity for CO<sub>2</sub> over other species present in flue gases and ease of solvent regeneration through heating [5].

Aqueous solutions of amines, primarily monoethanolamine (MEA), are the most mature technology for CO<sub>2</sub> absorption due to their high affinity and reactivity with CO<sub>2</sub> and relatively low costs of production. Still, a significant barrier to their full-scale deployment or “Achilles’ heel” as dubbed by Heldebrant et al. [6], is the high energy requirement associated with solvent regeneration (usually done at high temperatures of 373–393 K) [7–12]. This energy penalty adds a parasitic load on power-generation facilities to burn more fossil fuels, resulting in more CO<sub>2</sub> emissions to compensate for the energy consumed for solvent regeneration, in addition to dropping overall efficiency of these facilities by approximately 30% [4,12]. The regeneration energy (reboiler,

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stripper) for a conventional 30 wt.% MEA aqueous solution is 60–65% of the total energy consumption of a CO<sub>2</sub> capture plant [7–12]. This excessive energy penalty of using aqueous amines hindering their full-scale commercialisation is primarily due to the large amount of water co-solvent present in the solution, with its high heat capacity and enthalpy of vaporisation relative to other physical co-solvents [13]. The estimated heat duty required to regenerate a conventional 30 wt.% MEA aqueous solution is approximately 180.3 kJ/mol of captured CO<sub>2</sub>, with 87.9 kJ required to desorb 1 mol of CO<sub>2</sub> absorbed into aqueous MEA, and an additional 92.4 kJ required to heat the solution and produce 2.1 mol of H<sub>2</sub>O steam to remove 1 mol of CO<sub>2</sub> from the aqueous MEA solution [4,14]. Hence, more than 50% of the total heat duty required for solvent regeneration is directed at water heating and vaporisation, due to its large amount in the solution and high thermal properties.

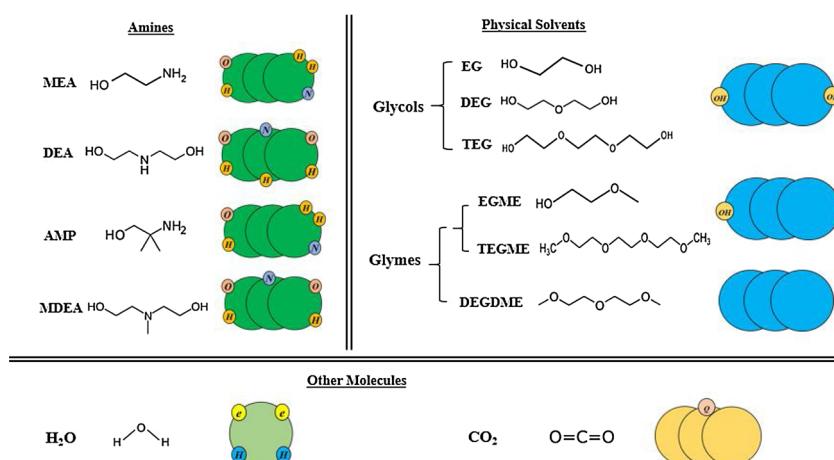
The reduction of this energy penalty can be accomplished through several strategies such as: process optimisation by adjusting stripper operating conditions; the use of alternative amines such as secondary, tertiary or sterically hindered amines with lower regeneration energy requirements or the use of amine blends, among others [9,10,15]. However, a drawback of all these systems is still the existence of high amounts of water as a co-solvent, which significantly contributes to the high regeneration energy requirement. This can be remedied by the usage of hybrid chemical-physical solvents such as non-aqueous amine solutions. These solvents fully replace water as a co-solvent with alternative physical solvents, forming chemical-physical absorbents when combined with amines [6,16,17]. Physical solvents candidates for this application are 1-alkanols [18], glycols [16,19,20], glymes [21,22], ionic liquids [23,24], and other polar solvents [25,26]. These solvents hold the promise of maintaining the chemical reactivity and selectivity of aqueous amines along with significant reductions in regeneration energy requirements [6], due to their lower heat capacity and enthalpy of vaporisation (almost half of that of water). In these hybrid solvents, most of the regeneration energy will be that required to reverse the chemical reaction (heat of absorption) and release the absorbed CO<sub>2</sub> rather than that needed to heat and evaporate the co-solvent [27]. For example, Yu et al. [28] reported that regeneration of a non-aqueous MEA + methanol solution can be achieved at a temperature lower than 373 K, resulting in a regeneration energy of 110 kJ/mol.CO<sub>2</sub> (2.3 GJ/ton CO<sub>2</sub>) which is lower than that needed for aqueous MEA in the range of 146–218 kJ/mol.CO<sub>2</sub> (3.0–4.5 GJ/ton CO<sub>2</sub>), marking a 24–49% reduction in the consumed regeneration energy. Rivas and Prausnitz [27] demonstrated that a mixed solvent of MEA + N-methyl pyrrolidone (NMP) has a lower absorption capacity compared to aqueous MEA, however, it can be regenerated far easier than aqueous MEA at lower temperatures. The implications of lower regeneration temperatures for non-aqueous amines reflects itself in requiring substantially less steam for solvent regeneration and smaller number of trays in the stripping column, significantly enhancing the techno-economic viability of the process [27]. Furthermore, it offers the possibility of using sources of energy at low temperature and pressure in the reboiler (e.g. hot water, condensates, etc.). Still, other performance parameters need to be considered such as solvent viscosity, volatility, CO<sub>2</sub> absorption capacity and absorption rate [9]. Although these hybrid solvents are quite promising, many of them are still in early development stages, lacking sufficient data required for rigorous modelling or large-scale projections with the current state of available modelling tools.

Thermodynamic modelling, integrated with rudimentary engineering calculations, can provide an efficient framework to assess the performance of hybrid solvents in terms of key performance indicators such as solvent regeneration requirements and absorption cyclic capacities. A simple and effective thermodynamic-based framework to screen and evaluate performance of emerging solvents can be developed using a single set of vapour-liquid equilibrium (VLE) data integrated with an appropriate and consistent thermodynamic model [29]. The available thermodynamic models such as empirical and semi-empirical, activity coefficient or excess Gibbs energy models, and those

based on classical equations of state (EoSs), have proved their ability in modelling the absorption of CO<sub>2</sub> in traditional aqueous amines. However, these models require considerable number of empirical parameters fitted to experimental data [30–32] and *a priori* knowledge of the reaction equilibria and reaction equilibrium constants of all relevant ionic species due to their rigours treatment that explicitly accounts for the chemical reactions occurring during the CO<sub>2</sub> absorption process. In highly non-ideal mixtures such as those encountered with the chemical absorption of CO<sub>2</sub>, it is challenging to find sufficient data to describe speciation reactions and interactions between molecules and ions in these reactive systems [29]. Thus, these models, though thermodynamically sound, are not apt to be applied to relatively new solvents or for solvent screening when such data are not available or insufficient [33,34].

Key to the development of a robust thermodynamic screening tool capable of describing the absorption process of CO<sub>2</sub> in new solvents, is envisioning a simpler modelling treatment for the reactive nature of the absorption process integrated with a molecular-based equation of state, primarily the Statistical Associating Fluid Theory (SAFT) [35–38]. Such a treatment of the absorption process has been successfully implemented in our previous works [33,34,39]. Wherein, the formation of reaction products from the reactions between acid gases (H<sub>2</sub>S or CO<sub>2</sub>) and amines in aqueous solutions have been modelled using soft-SAFT EoS [40,41] through emulating the chemical interactions by a physical aggregation process. The reaction products from the absorption of acid gases in aqueous amines were mimicked as physically aggregated acid gasamine complexes bounded by strong and specific interactions via association sites incorporated on the acid gas molecules. Although this approach is an oversimplification of the chemical absorption process, still it was capable of accurately representing the absorption of acid gases in aqueous amines without the need to specify all speciation reactions and their equilibrium constants. The predictive nature of this modelling approach hinges on the accurate representation of pure substances and their binary mixtures within the studied system, which suffice to represent the behaviour of these substances in multi-component systems, assuming data for all binary systems are available. The coupling of this modelling approach using soft-SAFT along with a single set of available VLE data for the ternary mixture (CO<sub>2</sub> + amine + co-solvent) is sufficient to describe a range of chemical data required for solvent screening such as solvent cyclic capacity, enthalpy of reaction and vaporisation, second order derivative properties and heat of regeneration. Up to our knowledge, this contribution marks the first attempt at developing a thermodynamic model for the absorption of CO<sub>2</sub> in non-aqueous amine solutions using a molecular-based EoS.

In this work, we investigate the feasibility of using soft-SAFT [40,41] for modelling the absorption of CO<sub>2</sub> in non-aqueous solutions of amines mixed with physical solvents. The studied non-aqueous solvents range from mixtures of amines such as, monoethanolamine (MEA), diethanolamine (DEA), methyl diethanolamine (MDEA), and amino-methyl propanol (AMP) with physical solvents of glycols (ethylene glycol (EG), diethylene glycol (DEG) and triethylene glycol (TEG)) and glymes (ethylene glycol monomethyl ether (EGME), triethylene glycol monomethyl ether (TEGME), and diethylene glycol dimethyl ether (DEGDME)), dictated by available literature data. This work belongs to a long-term project towards the development of a reliable and robust solvent screening tool for CO<sub>2</sub> capture and separation extendable to process modelling and simulation. In the next section, a description of the theoretical basis of soft-SAFT and the molecular models of the various pure substances investigated in this work are provided. Subsequently, the influence of physical solvents on the reactivity of amines with CO<sub>2</sub> and their main reactions are defined, along with the proposed soft-SAFT modelling approach. The developed modelling framework is then used to study the absorption of CO<sub>2</sub> in non-aqueous amine solutions over a range of temperatures and CO<sub>2</sub> partial pressures. Finally, the modelling framework is used to calculate solvent cyclic capacity and solvent regeneration energy, compared with those of aqueous



**Fig. 1.** The chemical structure of the pure substances examined in this work (amines, physical solvents of glycols and glymes, water and carbon dioxide) and their counterpart soft-SAFT molecular model representation.

amines highlighting its potential as a solvent screening tool for CO<sub>2</sub> capture.

## 2. Theoretical background and methodology

### 2.1. soft-SAFT equation of state

The soft-SAFT molecular-based EoS [40,41], derived by Blas and Vega, is an accurate variation of the original SAFT [35–38], originating from Wertheim's first order thermodynamic perturbation theory (TPT1) [42–44]. Within the framework of soft-SAFT, the residual Helmholtz free energy of a fluid,  $a^{\text{res}}$ , is calculated as the sum of the various microscopic contributions to the total free energy of a fluid, attributed to different molecular effects, expressed as:

$$a^{\text{res}} = a^{\text{ref}} + a^{\text{chain}} + a^{\text{assoc}} \quad (1)$$

where  $a^{\text{ref}}$  refers to the contribution of the reference fluid to the Helmholtz free energy, owing to interactions occurring between individual segments forming the molecule,  $a^{\text{chain}}$  accounts for the contribution attributed to the connectivity of segments forming chains and  $a^{\text{assoc}}$  is the association forces contribution term accounting for short range localised attractive forces such as hydrogen-bonding.

The reference term in soft-SAFT uses a Lennard-Jones (LJ) intermolecular potential to account for the repulsive and attractive interactions between segments in a single expression as derived by Johnson et al. [45,46]. The expression for the chain and association terms, as resulting from Wertheim's theory (TPT1) [42–44], are similar in all SAFT equations. An additional term,  $a^{\text{polar}}$ , can be added to account for polar interactions arising from dipole or quadrupole moments. This term is computed based on the theory proposed by Gubbins and Twu [47,48], extended to chain fluids by Jog et al. [49].

The implementation of the soft-SAFT approach to molecular systems requires a set of molecular parameters describing the basic physical features of any pure substance. For non-associating substances, three molecular parameters are needed, namely: segment diameter ( $\sigma_i$ ), chain length ( $m_i$ ), and dispersive energy between segments, ( $\varepsilon_i$ ). In the case of associating molecules, two additional parameters are required related to the association volume ( $\kappa_{\alpha-\beta, ii}^{\text{HB}}$ ) and association energy ( $\varepsilon_{\alpha-\beta, ii}^{\text{HB}}$ ). Additionally, for quadrupolar fluids, the fraction of segments containing the polar moment ( $x_p$ ) and the effective quadrupolar moment ( $Q$ ) are considered in an explicit manner. The set of soft-SAFT molecular parameters are regressed simultaneously using liquid density and vapour pressure of pure substance and transferred for the description of the behaviour of the molecules in multicomponent mixtures.

Extending the computations of soft-SAFT to mixtures is straightforward for the chain and association terms as they are explicitly

written for mixtures. The reference term is extended to multicomponent mixtures by using the van der Waals one-fluid theory, which approximates the free energy of the mixture of fluids to that of a hypothetical pure fluid. The generalized Lorentz-Berthelot (LB) combining rules are used to calculate the crossed size,  $\sigma_{ij}$ , and energy,  $\varepsilon_{ij}$  for the mixture:

$$\sigma_{ij} = \eta_{ij} \frac{(\sigma_{ii} + \sigma_{jj})}{2} \quad (2)$$

$$\varepsilon_{ij} = \xi_{ij} \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \quad (3)$$

where  $\eta_{ij}$  and  $\xi_{ij}$  ( $\eta_{ij} = 1 - l_{ij}$  and  $\xi_{ij} = 1 - k_{ij}$  in classical EoS) are the adjustable size and energy binary parameters, respectively. Soft-SAFT is used in a fully predictive manner whenever the values of the binary parameters  $\eta_{ij}$  and  $\xi_{ij}$  are set to unity, without fitting to binary mixture data.

For mixtures of associating molecules, cross-association interactions between different molecules or different functional groups within the same molecules are computed using combining rules similar to those in Eq.s (2) and (3). The volume of cross-association is calculated by the mean arithmetic radius of the association site, while the energy of cross-association is calculated through the modified geometric average as follows:

$$\kappa_{\alpha-\beta, ij}^{\text{HB}} = \left( \frac{\sqrt[3]{\kappa_{\alpha-\beta, ii}^{\text{HB}}} + \sqrt[3]{\kappa_{\alpha-\beta, jj}^{\text{HB}}}}{2} \right)^3 \quad (4)$$

$$\varepsilon_{\alpha-\beta, ij}^{\text{HB}} / k_B = \alpha_{ij}^{\text{HB}} \sqrt{\varepsilon_{\alpha-\beta, ii}^{\text{HB}} / k_B \varepsilon_{\alpha-\beta, jj}^{\text{HB}} / k_B} \quad (5)$$

where  $\alpha_{ij}^{\text{HB}}$  is an added binary parameter that generalizes the energy of cross-association, fitted to binary mixture VLE data, if needed.

### 2.2. Molecular models of pure substances

An essential element to the utilization of molecular-based EoSs such as soft-SAFT is the choice of a representative coarse-grain molecular model of the molecule. The chosen molecular model should be simple yet representative of the basic physical features of the molecule. A graphical representation of the soft-SAFT molecular models for substances examined in this work is provided in Fig. 1. Soft-SAFT parameters and the molecular models chosen in this work describing the pure substances transferred from previous works or developed in this work as shown in Table 1.

Amines such as MEA, AMP, DEA, and MDEA were modelled as homonuclear LJ chains, representing their multifunctional groups (amines and hydroxyls) with a specific number of association sites for each functional group [39,50]. In each of the amine molecules, three,

**Table 1**

Soft-SAFT molecular parameters of examined pure substances.

Substance	<i>m</i>	$\sigma$ (Å)	$\varepsilon/k_B(K)$	Association Type				Ref.	
				NH <sub>2</sub> -NH <sub>2</sub> /NH-NH		OH-OH/ e-H			
				$\varepsilon^{HB}/k_B(K)$	$\kappa^{HB}(\text{\AA}^3)$	$\varepsilon^{HB}/k_B(K)$	$\kappa^{HB}(\text{\AA}^3)$		
MEA <sup>a</sup>	2.149	3.567	324.00	1695	2000	3387	2641	[39]	
DEA <sup>a</sup>	2.456	4.019	358.20	1600	2000	3387	2641	[50]	
AMP <sup>a</sup>	2.198	4.096	314.00	1695	2000	3450	2250	[50]	
MDEA	2.456	4.235	334.10	1500 <sup>c</sup>	565 <sup>c</sup>	3387	2641	[50]	
EG	1.751	3.668	326.05	—	—	4384	4195	[52]	
DEG	2.548	3.860	334.40	—	—	4384	4195	[52]	
TEG	3.190	4.010	340.58	—	—	4384	4195	[52]	
EGME	2.312	3.664	291.35	—	—	3976	2600 <sup>d</sup>	This work	
TEGME	3.671	4.006 <sup>d</sup>	341.80 <sup>d</sup>	—	—	3450 <sup>d</sup>	2600 <sup>d</sup>	This work	
DEGDME	3.300	3.955	308.15	—	—	—	—	[56]	
CO <sub>2</sub> <sup>b</sup>	1.571	3.184	160.20	—	—	—	—	[58]	
H <sub>2</sub> O	1.000	3.154	365.00	—	—	2388	2932	[59]	

<sup>a</sup> Cross-association parameters between different functional groups predicted directly using Eqs. (4) & (5).<sup>b</sup> The quadrupole moment of CO<sub>2</sub> was set to Q = 4.40 × 10<sup>-40</sup> C. m<sup>2</sup>.  $x_p$  was set to 1/3.<sup>c</sup> N-H cross-association interactions between MDEA molecules.<sup>d</sup> Transferred from Navarro et al. [56].

two, or one association sites were considered for the models of primary (-NH<sub>2</sub>), secondary (-NH), and tertiary (-N) amine functional groups, respectively. For the amine functional groups, sites of type *H* account for the hydrogen atom and sites of type *N* for the lone pair of electrons in the nitrogen atom. The corresponding volume and energy of association for the amine functional groups were transferred from those for ethylamine and diethylamine [39,50]. The hydroxyl functional group in all the amines was modelled analogues to that for 1-alkanols using 2B association scheme [51], with two association sites, one of type *O* and type *H* accounting for the two lone pairs of electrons on the oxygen atom, and for the hydrogen atom, respectively. Their corresponding association volume and energy were transferred from those used for ethanol and 1-propanol [51]. The model allows interactions between similar functions groups on two amine molecules (self-association, i.e. NH<sub>2</sub>-NH<sub>2</sub>, NH-NH, OH-OH), as reflected by their transferred association energy and volume parameters. Moreover, the model also allows interactions between different functional groups on two amine molecules (cross-association, i.e. NH<sub>2</sub>-OH, NH-OH), with the corresponding association energy and volume predicted directly from the combining rules (Eqs. (4) and (5), with  $\alpha_{ij}^{HB} = 1.0$ ). In the case of the tertiary amine MDEA, cross-association interactions occurring between two MDEA molecules were modelled as N-H interactions between the hydrogen atom of the hydroxyl group and the nitrogen atom, optimised from experimental vapour pressure and liquid density of pure MDEA.

Low molecular weight glycols such as ethylene glycol (EG), diethylene glycol (DEG) and triethylene glycol (TEG) were modelled as LJ chainlike molecules with two associating sites of type OH representing the two hydroxyl groups placed at each end group [52], demonstrating good transferability to poly(ethylene glycols) [53]. The sites are bipolar i.e., dual in nature (positive/negative), analogues to the 1A association scheme proposed for acid dimerization [37]. Additionally, the effect of the lone pair of electrons in each oxygen atom of the ethylene oxide groups (such as in DEG and TEG) is implicitly accounted for in the molecular parameters. The choice of modelling glycols with one bipolar associating site for the hydroxyl group rather than the 2B association scheme typically used for 1-alkanols is to allow for the higher degree of self-association exhibited by glycols compared to 1-alkanols [54,55].

Glymes were modelled based on previous work accounting for the different subfamilies in the glyme family such as monoalkyl ethers (one hydroxyl end group), and dialkyl ethers (no hydroxyl end group) [56]. Monoalkyl ethers such as ethylene glycol monomethyl ether (EGME) and triethylene glycol monomethyl ether (TEGME) were represented as

a chainlike molecule with one association site of type OH, for the hydroxyl end group. Conversely, dialkyl ethers such as diethylene glycol dimethyl ether (DEGDME) were modelled as a non-associating chainlike molecule due to the absence of the hydroxyl end group. In both subfamilies of glymes, the effect of the lone pair of electrons in each oxygen atom of the ethylene oxide groups were implicitly accounted for in the molecular parameters, similar to that for glycols [52].

Based on a previous work with glymes [56], ethylene glycol monomethyl ether (EGME) was modelled as a homonuclear LJ chain with one bipolar association site of type OH (for the hydroxyl end group), capable of forming associative interactions. As it is the first member of the family, similar to methanol for 1-alkanols, only the volume of association (i.e.,  $\kappa^{HB} = 2600 \text{ \AA}^3$ ) was transferred from those obtained for the rest of the family [56], while regressing the remaining molecular parameters to pure fluid liquid density and vapour pressure compiled in [57]. The results for the proposed model are shown in Figure S1 in the supporting information, with AAD of 0.64, and 3.6%, for liquid density and vapour pressure, respectively. Triethylene glycol monomethyl ether (TEGME) was modelled in a similar manner as it belongs to the same monoalkyl ether subfamily. Although the soft-SAFT molecular parameters for TEGME could be obtained from the correlation developed by Navarro et al. [56], this set of parameters resulted in large deviations for the vapour pressure (AADP = 21.3%). Deviations were significantly reduced by fine-tuning the chain length (*m*) while transferring the remaining molecular parameters from those obtained by the correlation for the monoalkyl ether subfamily. The new set of proposed molecular parameters for TEGME are provided in Table 1, with their performance depicted in Figure S1 in the supporting information, with AAD of 0.75, and 3.5%, for liquid density and vapour pressure, respectively. As previously highlighted, dialkyl ethers such as diethylene glycol dimethyl ether (DEGDME) were modelled as a non-associating homonuclear chainlike molecule. The soft-SAFT molecular parameters were directly transferred from our previous work [56].

Carbon dioxide was modelled as a flexible homonuclear chain-like molecule with explicit consideration of its quadrupolar moment [58]. Water was modelled as a single LJ sphere (*m* = 1.0), with four association sites, two of type *e* for the two lone pair of electrons on the oxygen atom and two of type *H* for the hydrogen atoms. The value of the dipolar moment of water was implicitly accounted for in the values of the molecular parameters [59].

In the case of binary mixtures of water and amines, interactions due

to cross-association between the water molecule and the different functional groups (NH<sub>2</sub>, NH, OH) of each amine molecule were permitted in the model. The corresponding association volume and energy parameters were either calculated directly from combining rules or transferred from binary mixtures of water with ethanol, 1-propanol, ethylamine and diethylamine [39,50]; the values are listed in **Table S1** in the supporting information. Moreover, for water and CO<sub>2</sub> binary mixtures, a binary size parameter ( $\eta_{ij}$ ) as a function of temperature was required to obtain a correct description of the phase equilibria of this binary system defined as [39]:

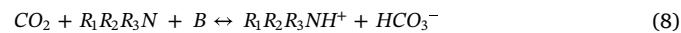
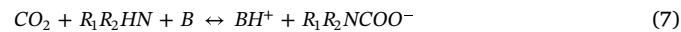
$$\eta_{ij} = -0.00031 \times T + 1.1854 \quad (6)$$

The binary interactions between physical solvents examined in this work with amines or CO<sub>2</sub> along with their absorption in non-aqueous amines are discussed and characterized in the subsequent sections of this contribution.

### 2.3. Reaction mechanisms for CO<sub>2</sub> absorption in amines

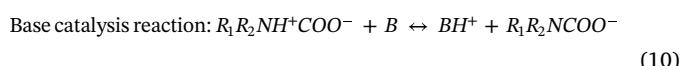
Understanding the underlying reaction mechanisms governing the chemisorption of CO<sub>2</sub> in non-aqueous amines, its similarities and differences with respect to CO<sub>2</sub> absorption in aqueous amines is vital for the accurate modelling of the absorption process in these hybrid solvents. This will guide the development of their equivalent representation within the soft-SAFT framework in a systematic procedure, as explained next.

There are different reaction mechanisms governing the absorption of CO<sub>2</sub> in aqueous amines depending on the type of amine involved in the absorption process. The overall reactions for the absorption of CO<sub>2</sub> in aqueous amines can proceed by the formation of two primary reaction products (*i.e.* carbamate (Eq. 7) and bicarbonate (Eq. 8)). Carbamate formation is more favourable for primary and secondary amines such as MEA and DEA, respectively [60,61]. In contrast, the absorption of CO<sub>2</sub> proceeds through the formation of bicarbonate for sterically hindered and tertiary amines such as AMP and MDEA, respectively [62].



where  $R_1R_2R_3N$  represents amine and, depending on the type of amine,  $R_1$ ,  $R_2$ ,  $R_3$  can be hydrocarbon groups or mobile protons, and  $B$  is amines or water in the solution.

In the case of non-aqueous amines, the absorption of CO<sub>2</sub> will primarily proceed through the formation of carbamate (Eq. 7), as the absence of water ( $B$ ) will prevent the formation of bicarbonate (Eq. 8). In this work, we are merely interested in equilibrium properties, however, examining the reaction mechanism governing the formation of carbamate is essential for understanding the effect of non-aqueous co-solvents on the absorption of CO<sub>2</sub> in amines. The formation of carbamate (Eq. 7), originally proposed by Caplow [60] and reintroduced by Danckwerts [61], proceeds by the instantaneous formation of a zwitterion intermediate (Eq. 9), that is stabilized by deprotonating the formed zwitterion through a base catalysis reaction (Eq. 10), leading to the formation of stable carbamate with the overall reaction shown in (Eq. 7).



These reactions are valid regardless of the reaction medium (aqueous or non-aqueous) [63–67], however, the type of reaction medium has an influence on the reactivity of the amine with CO<sub>2</sub>. As previously highlighted, a co-solvent “base”, which can be another amine molecule,

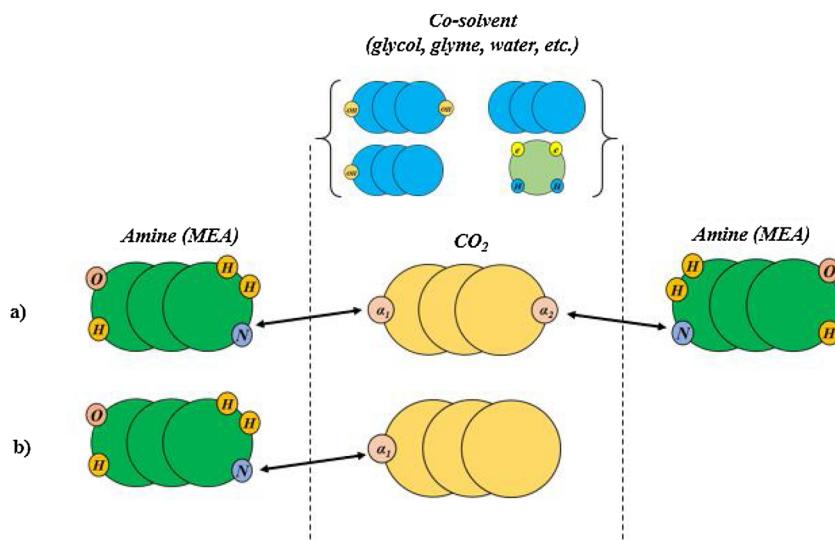
water or any other physical solvent, is required to deprotonate the reaction intermediate and stabilize the formation of the reaction products. This is directly linked to the dielectric constant of the solvent [68], by which solvents with high dielectric constant such as water will more easily deprotonate zwitterions before they revert back to amine and CO<sub>2</sub>, compared to co-solvents with lower dielectric constants. However, in turn, reversing the reaction to release of the absorbed CO<sub>2</sub> requires a higher temperature [68,69].

Researchers reported that dielectric constant of the co-solvent varies inversely with the reaction order, with the dielectric constant decreasing with increasing reaction order [66,70–73]. The reaction order with respect to MEA changed from unity (for water as co-solvent) to 2<sup>nd</sup> order reaction (for methanol, ethanol, 2-propanol) [66], or to a 3<sup>rd</sup> order reaction for (ethylene glycol) [72] in a reverse order of the solvent polarity. Similar observations were reported by Park et al. [70,71] for DEA and MDEA in a range of physical solvents such as alcohols, glycols and propylene carbonate. This change was interpreted through the zwitterion mechanism indicating that the rate of the deprotonation step (Eq. 10) decreases in the presence of non-aqueous solvents. This indicates that the formed zwitterion is less stable, and physical solvents are not able to fully ionize and deprotonate the zwitterion and produce it in a complete ionic form compared to water. Although such observations indicate that the absorption of CO<sub>2</sub> in non-aqueous amines will not be as efficient as aqueous amines in terms of absorption capacity, this will result in a lower regeneration temperatures, along with the lower enthalpy of vaporisation and heat capacity of physical solvents, leading to potential significant reductions in the energy of non-aqueous amines regeneration compared to aqueous amines [27,63,68]. Such a trade-off between solvent absorption capacity and energy of regeneration can be finely tuned through process optimisation to find the optimal process operating conditions.

### 2.4. Modelling strategy for CO<sub>2</sub> absorption in non-aqueous amines

As previously mentioned, the essence of modelling the process of CO<sub>2</sub> absorption in aqueous or non-aqueous amines depends on capturing the equilibrium relations between CO<sub>2</sub> and the formed reaction products (*i.e.* carbamate and bicarbonate). Following our previous work [33,34,39] the formation of reaction products from the main reactions in the absorption process were implicitly accounted for by the formation of CO<sub>2</sub>-amine physical aggregates connected through strong and highly directional association sites. The number of these association sites was dictated by the reaction stoichiometry of the amine with CO<sub>2</sub>, while the intermolecular interaction parameters (cross-association) were either transferred directly from previous works [39], or regressed only to experimental acid gas solubility in aqueous amines. These parameters are presented in **Table S2** of the supporting information.

As the main reaction for the absorption of CO<sub>2</sub> in amines are similar for aqueous and non-aqueous solvents, the methodology employed in our previous works was carried out in a consistent manner in this work for modelling CO<sub>2</sub> absorption in non-aqueous amines, as depicted in **Fig. 2** (with MEA as an example). Hence, one or two association sites, labelled as  $\alpha_1$  and  $\alpha_2$ , were placed on the CO<sub>2</sub> molecule and assumed to cross-associate only with the lone pair of electrons on the nitrogen atom in the amine, effectively emulating the reactions between CO<sub>2</sub> and each amine. The number of “reactive” association sites placed on the CO<sub>2</sub> molecule depends on the reaction stoichiometry with each of the examined amines. The overall stoichiometry of reactions with CO<sub>2</sub> for primary and secondary amines such as MEA and DEA, is 2 mol of amine per mole of CO<sub>2</sub>, therefore, two association sites (*i.e.*  $\alpha_1$  and  $\alpha_2$ ) were placed on the CO<sub>2</sub> molecule leading to the formation of [amine – CO<sub>2</sub>-amine] aggregates, through N- $\alpha_i$  cross-association interactions for both aqueous and non-aqueous amines. Instead, tertiary amines such as MDEA preferentially lead to the formation of bicarbonate in aqueous mediums with a stoichiometry of 1 mol of MDEA per mole of CO<sub>2</sub>, therefore only one association site was placed on the CO<sub>2</sub> forming a



N- $\alpha_1$  bond with the nitrogen atom in the tertiary amine. The same treatment was tested for non-aqueous tertiary amines, even with the knowledge that the formation of bicarbonate is not possible in the absence of water, to maintain the consistency of our modelling approach. Sterically hindered primary amines such as AMP, exhibit a theoretical stoichiometry of 1 mol of AMP per mole of CO<sub>2</sub>, suggesting that the absorption of CO<sub>2</sub> is done through the formation of bicarbonate similar to that of tertiary amines such as MDEA (Eq. 8). However, several reaction mechanisms suggest that the formation of carbamate in aqueous AMP is indeed viable, but it can be easily converted to bicarbonate and free-amine [74]. Based on that, and based on our previous work [34], two strategies were employed and tested to model the absorption of CO<sub>2</sub> in non-aqueous AMP depending on the number of active association sites placed on the CO<sub>2</sub> molecule: 1) one-site approach ( $\alpha_1$ ) similar to tertiary amines, 2) two-sites approach ( $\alpha_1$  and  $\alpha_2$ ) similar to primary and secondary amines.

Regardless of the type of amine, based on the previously described methodology, their interactions with CO<sub>2</sub> are characterized by specific cross-association parameters, which are the volume and energy of cross-association. In order to make the approach as predictive and robust as possible, most of the parameters were transferred from previous works, if available. The value for the cross-association volume was transferred directly from that regressed from the modelling of CO<sub>2</sub> absorption in aqueous amines (*i.e.*,  $\kappa_{N-\alpha_1}^{HB} = 500 \text{ \AA}^3$ ). The choice of such a value assumes localised short range interactions as found in chemical reactions, which reduces the number of adjustable parameters and focuses the strength of the intermolecular interactions between each amine and CO<sub>2</sub> in a single parameter *i.e.*, the energy of cross-association [34,39]. The cross-association energy between the reactive sites on CO<sub>2</sub> molecules with each amine was fitted to available data for the solubility of CO<sub>2</sub> in non-aqueous amines. The effect of the co-solvent on the stabilization of the reaction product from the reaction between CO<sub>2</sub> and non-aqueous amine as highlighted in Section 2.3, was implicitly accounted for in the value of the cross-association energy ( $\epsilon_{N-\alpha_1}^{HB}/k_B$ ). The choice of non-aqueous amines examined in this work was dictated by the availability of CO<sub>2</sub> absorption data in these hybrid solvents in order to validate the model. Short glycals and amine mixtures studied in this work include MEA + DEG, MEA + TEG, DEA + TEG, AMP + EG, AMP + DEG, and AMP + TEG. Hybrid solvents composed of mixtures of glycals and amines examined in this work include MEA + EGME, MEA + DEGDME and MDEA + TEGME.

### 3. Results & discussion

In this section, we present and discuss results pertaining to the

**Fig. 2.** Schematic representation of the chemical reaction between amine and CO<sub>2</sub> in aqueous and non-aqueous co-solvents using a) two site approach, and b) one site approach. Site N represents the lone pair of electrons on the nitrogen atom of MEA (as a representative amine), while sites  $\alpha_1$  and  $\alpha_2$  represent the reactive sites on the CO<sub>2</sub> molecule. The reaction/interaction between amine and CO<sub>2</sub> is influenced by the co-solvent, implicitly captured in the value of the cross-association energy,  $\epsilon_{N-\alpha_1}^{HB}/k_B$ .

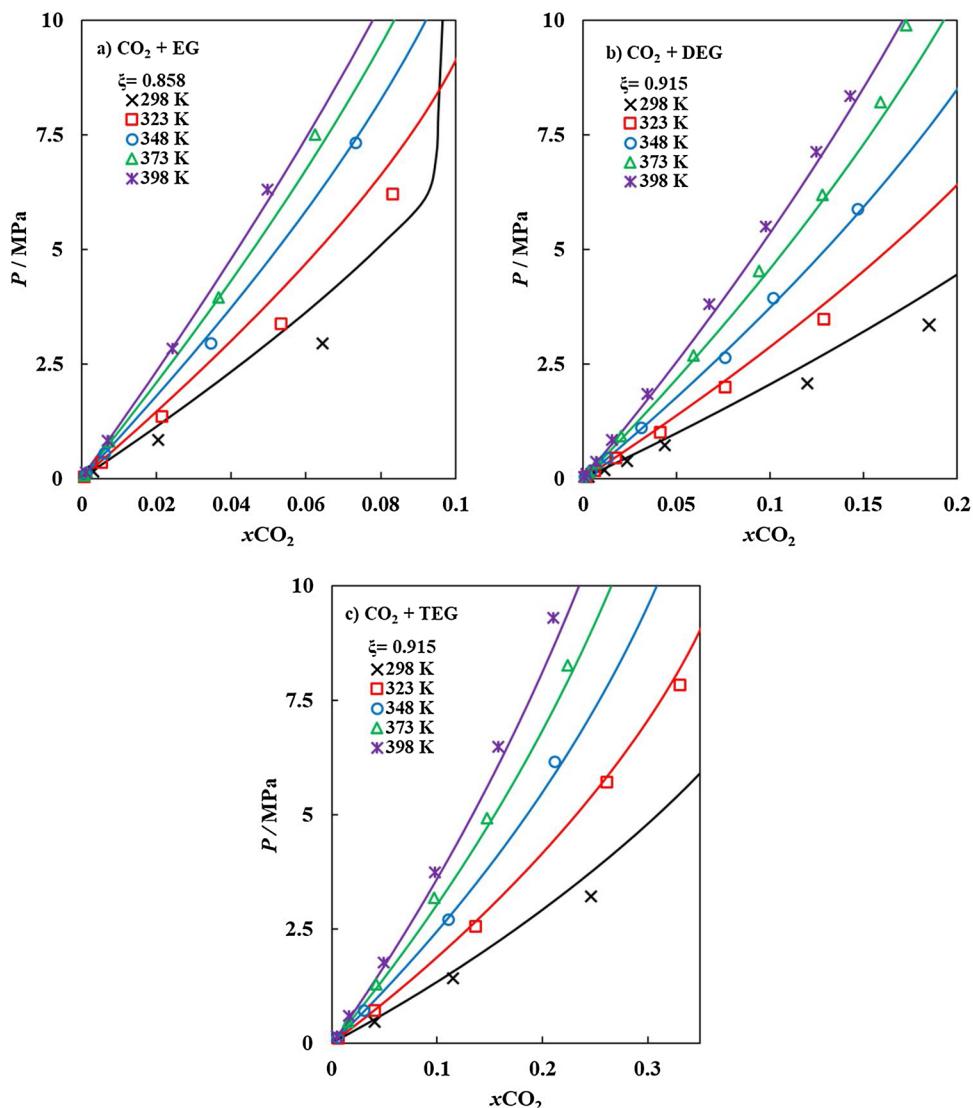
modelling of the absorption of CO<sub>2</sub> in non-aqueous amines using a molecular-based EoS (soft-SAFT) for the first time. As previously mentioned in Section 2, the absorption of CO<sub>2</sub> in non-aqueous amines is modelled in a consistent manner with our previous works on the acid gases absorption in aqueous amines [33,34,39]. This requires capturing the interactions in binary mixtures of CO<sub>2</sub> + physical solvents and amines + physical solvents, whenever experimental data are available. Subsequently, the absorption of CO<sub>2</sub> in non-aqueous amines is modelled employing the previously highlighted strategy. The developed models are then used to examine the performance of hybrid solvents using absorption cyclic capacity and heat of regeneration as key performance indicators.

#### 3.1. CO<sub>2</sub> + Physical solvents binary mixtures

In this section, the binary interactions between each of the examined physical solvents and CO<sub>2</sub> are characterized. The examined physical solvents are glycals such as EG, DEG and TEG, and glycals such as EGME, TEGME, and DEGDME. These mixtures have been studied with the molecular models and parameters presented in Section 2.1. Fitted binary interaction parameters obtained herein for the reported CO<sub>2</sub> + physical solvents binary mixtures are summarized in Table S3 in the supporting information.

##### 3.1.1. CO<sub>2</sub> + glycals binary mixtures

The low molecular weight glycals examined in this work were modelled as associating chainlike molecules as previously discussed. Initially, soft-SAFT was used in a predictive manner (*i.e.* binary interaction parameters in Eq.s (2) and (3) set to 1.0) to calculate the behaviour of the binary mixtures of glycals with CO<sub>2</sub> and results were compared to available experimental data [75–77]. Due to the high asymmetry of these binary mixtures, large deviations were observed between the models and the experiments. The description was considerably improved by using a single binary energy interaction parameter ( $\xi_{ij}$ ) for each glycal, fitted at an intermediate temperature (348 K) and transferred to the remaining temperatures. The solubility of CO<sub>2</sub> in glycals such as EG, DEG and TEG are shown in Figs. 3 (a) – (c) for temperatures up to 393 K and pressures up to 10 MPa, with values for  $\xi_{ij}$  of 0.858, 0.915 and 0.915 for EG, DEG, and TEG, respectively. The predictions with temperature independent binary parameter slightly deteriorate for low temperatures and high CO<sub>2</sub> concentration. Notice that better results can be obtained with a binary temperature dependent parameter; however, this will be at the expenses of losing transferability, which is one of the main purposes of developing this approach. We have considered, then, the use of one temperature independent



**Fig. 3.** Isotherms for the solubility of CO<sub>2</sub> in glycols with a temperature independent binary energy interaction parameter ( $\xi_{ij}$ ): a) CO<sub>2</sub> + EG with  $\xi_{ij} = 0.858$ , b) CO<sub>2</sub> + DEG with  $\xi_{ij} = 0.915$ , and c) CO<sub>2</sub> + TEG with  $\xi_{ij} = 0.915$ : soft-SAFT calculations (lines), and experimental data, EG [75], DEG [76], and TEG [77] (symbols).

binary parameter, which gives a trade-off between accuracy and transferability, demonstrating soft-SAFT ability in capturing the behaviour of these mixtures.

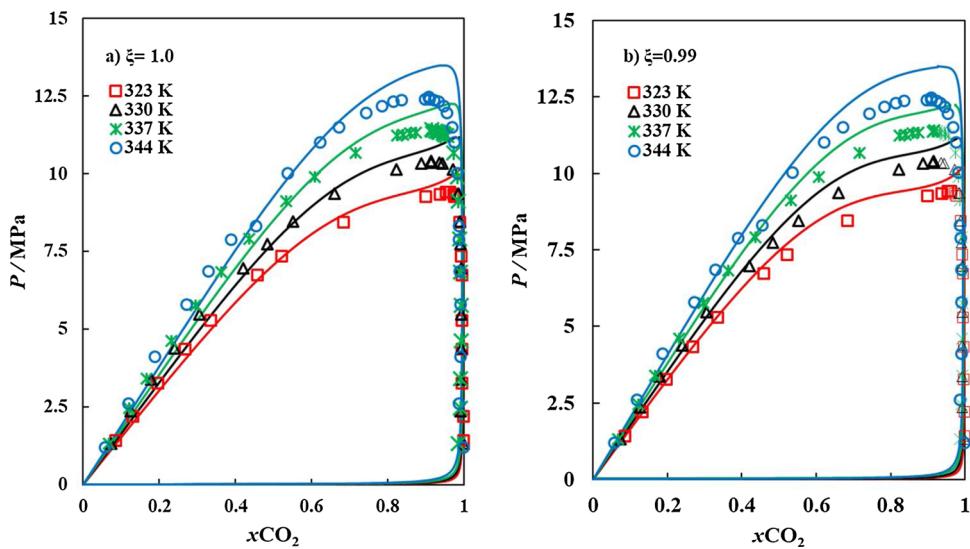
### 3.1.2. CO<sub>2</sub> + glymes binary mixtures

Monoalkyl ethers were modelled as association molecules, while dialkyl ethers were modelled as non-associating molecules, as previously explained. For binary mixture of CO<sub>2</sub> + EGME, soft-SAFT was able to predict the behaviour of this mixture in very good agreement with experimental data [78], without using any binary interaction parameters, as shown in Fig. 4(a). Slightly better agreement for higher temperatures can be obtained using a temperature independent binary energy interaction parameter  $\xi_{ij} = 0.99$ , which is close to unity, as shown in Fig. 4(b). In both cases, deviations near the critical region are expected as the original soft-SAFT is based on a mean-field approximation, not accounting for the effect of long-range interactions on density fluctuations, which can be captured by using the crossover treatment of soft-SAFT for the critical region [79], at the expenses of using slightly more computational time. As the performance of these models close to critical region is not of interest in this work, we have used here the original soft-SAFT EoS in order to save computational time, without compromising accuracy. Surprisingly, in spite of using its

classical, mean-field formulation, the model provides a good representation of the critical region (slightly overestimating it) even though this mixture is probably a type III binary system according to the van Krevelen and Rock classification, which are known to be difficult to be accurately modelled [80].

The available experimental data of the CO<sub>2</sub> + TEGME binary mixture is scarce. However, as shown in Fig. 5(a), pure predictions using soft-SAFT were able to represent the effects of pressure and temperature on the solubility of CO<sub>2</sub> in liquid TEGME. This is one of the key benefits of using a molecular based EoS with robust parameters, as it provides accurate trends for the mixtures. A better agreement with available experimental data [81] was obtained using a single temperature independent binary interaction parameter of  $\xi_{ij} = 1.03$ , relatively close to unity, as shown in Fig. 5(b). Notice that the available experimental data present a trend at CO<sub>2</sub> mole fraction less than 0.4 and at a temperature of 313 K, being inconsistent with the other isotherms; this behaviour could not be captured with the modelling approach, even when two binary parameters were used.

Finally, modelling the mixture CO<sub>2</sub> + DEGME using soft-SAFT have been previously reported in the literature by Amaral et al. [82], using two temperature independent binary interaction parameters close to unity of  $\eta_{ij} = 1.028$  and  $\xi_{ij} = 0.991$ , obtaining very good agreement



**Fig. 4.** Vapour-liquid equilibria of CO<sub>2</sub> and EGME as a function of temperature, with a) pure predictions  $\xi_{ij} = 1.0$ , and b) with a temperature independent binary parameter  $\xi_{ij} = 0.99$ . Calculations using soft-SAFT (lines), and experimental data [78] (symbols).

with experimental data, as shown in Fig. 6(a). Although such an approach is valid, still it is on the expense of the model's robustness with the additional fitted binary parameter, though temperature independent and transferable. Consistent with the other studied binary mixtures of CO<sub>2</sub> and physical solvents, a single binary energy interaction parameter independent of temperature has been used in this work to also model this binary mixture in a range of temperatures and pressures reported by the available experimental data [82,83], and results are depicted in Fig. 6 (b). As can be observed, both approaches, provide similar levels of accuracy in representing the behaviour of this binary mixture, while only one binary interaction parameter is used in this work, which is always desirable when building tools as predictive as possible.

### 3.2. Amines + physical solvents binary mixtures

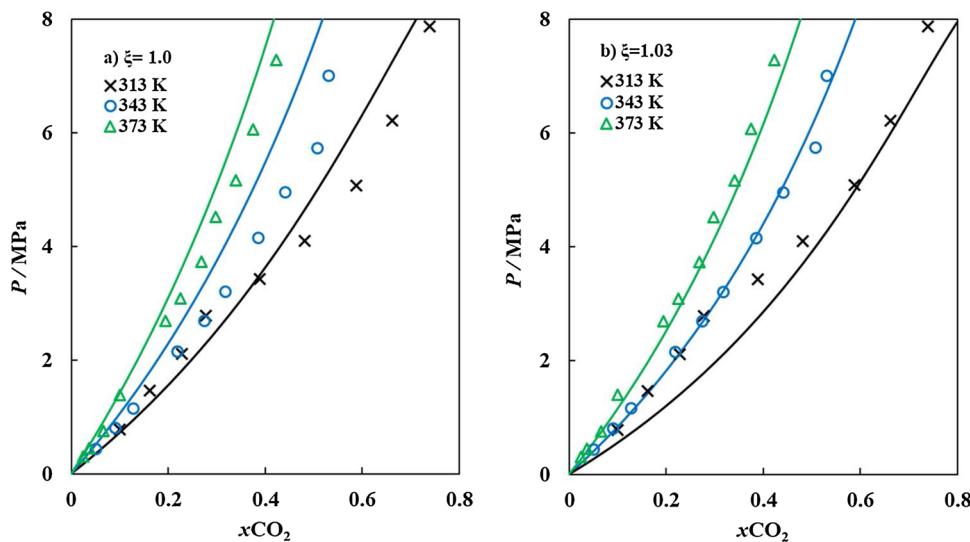
Examining the interactions between binary mixtures of amines and the studied physical solvents (glycols and glymes) is needed prior to characterizing the solubility of CO<sub>2</sub> in hybrid non-aqueous amine solvents. This is essential due to the multifunctional nature of amines with

the hydroxyl and amine groups capable of forming associative interactions either with themselves or with other associating molecules such as the ones studied in this work. As explained in section 2.2, glycols and glymes (mainly monoalkyl ethers) were modelled as associating molecules with sites of type OH dual in nature (positive/negative), hence these sites are able to cross-associate with both negative (O or N) and positive sites (H) in the functional groups of each amine.

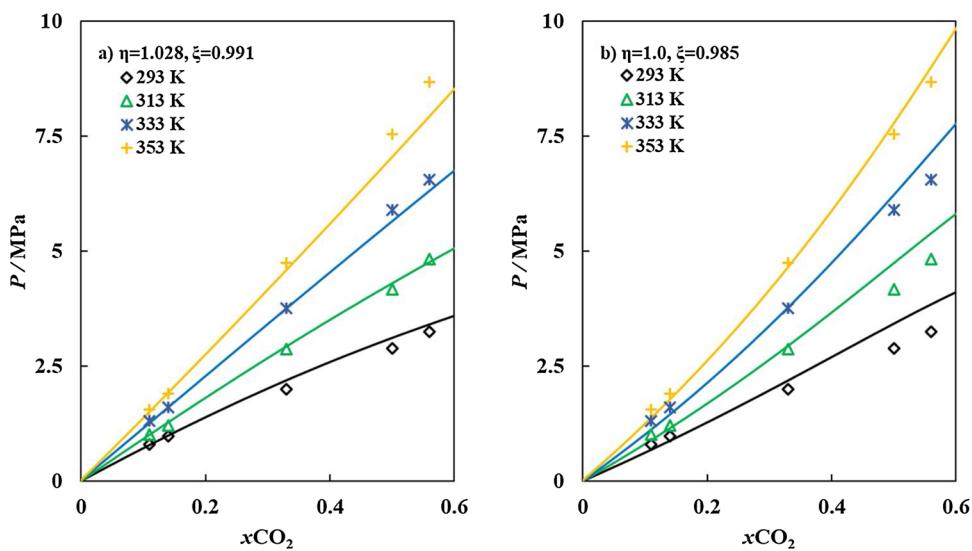
As the available experimental data for amines with physical solvents systems is very scarce or nonexistent, we have taken advantage of the molecular nature of the equation to propose predictive parameters for the cross-association between the different molecules and compare with the (few) available experimental data for mixtures in order to proceed with multicomponent mixtures.

#### 3.2.1. Amines + glycols binary mixtures

No experimental data for binary mixtures of amines with glycols such as EG, DEG and TEG, have been found in the open literature to validate the cross-association interactions for these binary mixtures. Hence, cross-association interactions between amines with glycols were calculated in a fully predictive manner using Eq.s (4) and (5). The sets



**Fig. 5.** Solubility of CO<sub>2</sub> and TEGME as a function of temperature, with a) pure predictions  $\xi_{ij} = 1.0$ , and b) with a temperature independent binary energy interaction parameter  $\xi_{ij} = 1.03$ : calculations using soft-SAFT (lines), and experimental data [81] (symbols).



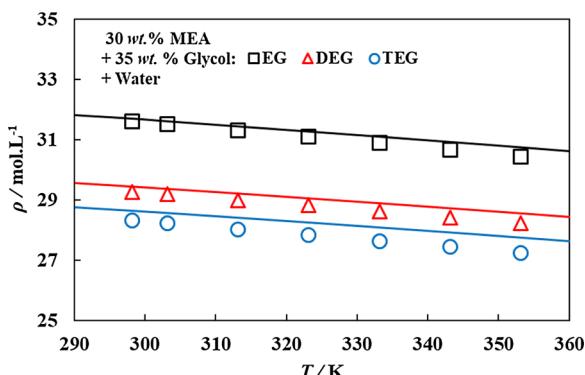
**Fig. 6.** Solubility of CO<sub>2</sub> in DEGDME as a function of temperature, with a)  $\eta_{ij} = 1.028$  and  $\xi_{ij} = 0.991$  [82], and b) with  $\xi_{ij} = 0.985$ : calculations using soft-SAFT (lines), and experimental data [82] (symbols).

of data available for ternary mixtures comprising MEA + Glycol + H<sub>2</sub>O was used to validate the model's predictions for cross-association interactions between MEA and glycols. In a similar manner, the cross-association interaction parameters between water and each of the glycols were calculated directly from combining rules in Eqs. (4) and (5). As shown in Figures S2 (a) –(c), soft-SAFT was capable of accurately representing the VLE behaviour of binary mixtures of glycols such as EG, DEG, and TEG with water [84], using a single binary energy interaction parameter fitted at an intermediate pressure and transferred to the remaining isobars. The fitted values for  $\xi_{ij}$  are 1.05, 1.09, and 1.125, for binary mixtures of water with EG, DEG and TEG, respectively.

The previously acquired binary parameter values were used to predict the behaviour of ternary mixtures of MEA + glycols + water to test the validity of the cross-association interaction parameters between MEA and glycols calculated from the combining rules. Depicted in Fig. 7, are soft-SAFT predictions for the ternary mixture's density as a function of temperature which are in good agreement with the reported experimental data [85]. The relative deviations of soft-SAFT predictions from experimental data were 0.6, 0.8 and 1.4% for ternary mixtures of MEA with water and EG, DEG, and TEG, respectively.

### 3.2.2. Amines + Glymes binary mixtures

Hybrid solvents studied in this work for mixtures of amines and glymes include MEA + EGME, MEA + DEGDME, and MDEA + TEGME.



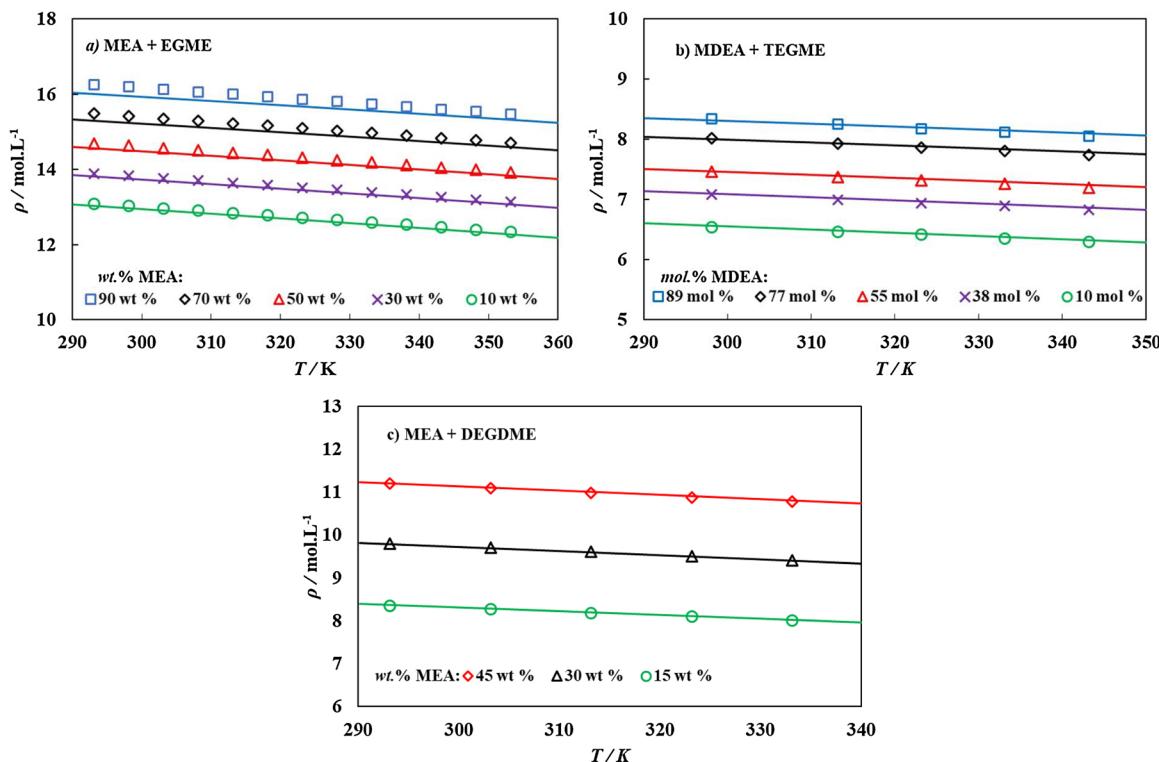
**Fig. 7.** Density-temperature diagram of 30 wt.% MEA + 35 wt.% H<sub>2</sub>O + 35 wt.% (EG, DEG, or TEG). Predictions using soft-SAFT (lines), and experimental data [85] (symbols).

The proposed interactions between amines and glymes were assessed using available data for density of the binary mixture as a function of temperature. In the case of associating glymes (monoalkyl ethers) such as EGME, and TEGME, cross-association between the amine functional groups and the hydroxyl group on the monoalkyl ethers was calculated using the combining rules in Eqs. (4) and (5), in a fully predictive manner. Dialkyl ethers such as DEGDME are non-associating molecules, hence the comparison with the experimental data will show the ability of the model in properly capturing the behaviour of the MEA + DEGDME binary mixture.

As shown in Figs. 8(a) – (c), soft-SAFT accurately predicts the density of binary mixtures of MEA + EGME and MDEA + TEGME as a function of temperature and amine concentration, without the need for any fitted parameters. The agreement between available experimental data [22,85,86] and soft-SAFT predictions is excellent with an AAD of 0.78%, 0.58%, and 0.18% for MEA + EGME, MDEA + TEGME, and MEA + DEGDME binary mixtures, respectively. This confirms that the proposed sets of molecular parameters characterizing the pure components were adequate for capturing the volumetric effects of these binary mixtures. Ideally, energetic effects should also be assessed, however, in the absence of VLE data of these binary mixtures, as previously highlighted, such an assessment could not be carried out.

### 3.3. CO<sub>2</sub> absorption in non-aqueous amines

The soft-SAFT modelling for CO<sub>2</sub> absorption in non-aqueous amines was done based on the framework developed in our previous contributions for the absorption of acid gases in aqueous amines [33,34,39]. This is a robust approach, which only requires characterizing the cross-association energy of the N- $\alpha_i$  bonds between each amine and the CO<sub>2</sub> molecule. This implicitly accounts for the effect of the co-solvent on the chemical absorption process. Molecular parameters of pure substances were transferred from previous works or developed in this work as explained in Section 2.2, while binary interaction parameters for binary mixtures of physical solvents with either CO<sub>2</sub> or amines have been proposed in this work, as described in Sections 3.1 and 3.2. Regardless of the type of co-solvent (aqueous or non-aqueous), the main reactions for the absorption of CO<sub>2</sub> in amines were described via the formation of physical molecular aggregates composed by a single CO<sub>2</sub> molecule with either one (one site) or two amine molecules (two sites), depending on the type of amine. For the two-sites modelling approach, the energy of cross-association of the two sites were assumed to be either symmetric ( $\epsilon_{N-\alpha_1}^{HB}/k_B = \epsilon_{N-\alpha_2}^{HB}/k_B$ ) or



**Fig. 8.** Density-temperature diagram of a) MEA + EGME, b) MDEA + TEGME, and c) MEA + DEGDME. Soft-SAFT predictions with cross-association interactions calculated using Eq.s (4) and (5) when needed (lines), and experimental data [22,86,87], (symbols). See text for details.

asymmetric ( $\varepsilon_{N-\alpha_1}^{HB}/k_B \neq \varepsilon_{N-\alpha_2}^{HB}/k_B$ ). Only the cross-association energy was fitted to solubility data of CO<sub>2</sub> in non-aqueous amines, while the cross-association volume was fixed as previously highlighted, thus reducing the number of fitted parameters.

Results for the absorption of CO<sub>2</sub> using soft-SAFT for a fixed temperature and amine concentration compared to experimental data [16,17,22,86,88,89] are shown in Fig. 9 for amines + glycols, and in Fig. 10 for amines + glymes. For all soft-SAFT calculations, the binary interaction parameters for energy ( $\xi_{ij}$ ) and size ( $\eta_{ij}$ ) between each amine and CO<sub>2</sub> and were set equal to 1.0, in a predictive manner. The optimised soft-SAFT parameters for cross-association energy for the N- $\alpha_i$  interactions are provided in Table S4 in the supporting information for a fixed temperature and amine concentration.

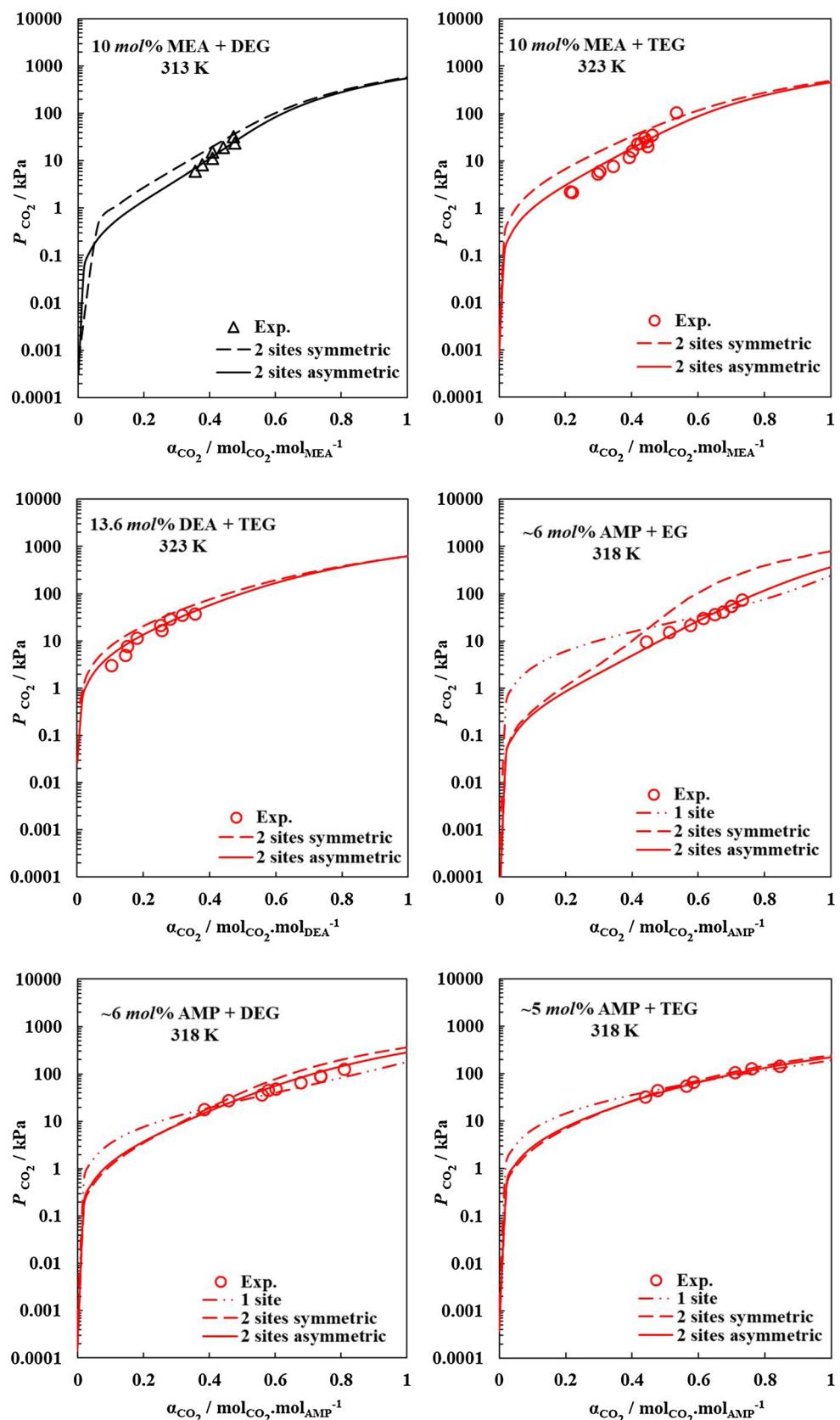
As shown in Fig. 9, for amines such as the primary MEA and the secondary DEA with glycols such as DEG or TEG, asymmetric cross-association energy parameters better represent the available experimental data [88] in contrast to symmetric cross-association energy, especially at CO<sub>2</sub> loadings lower than 0.5 mol<sub>CO<sub>2</sub></sub>, mol<sub>Amine</sub><sup>-1</sup>. The use of two asymmetric association sites has been previously adopted for the absorption of CO<sub>2</sub> in aqueous solutions of MEA and DEA [34]. For the absorption of CO<sub>2</sub> in mixtures of AMP with EG or DEG, the use of a one-site model seems incapable of capturing the shape of the absorption isotherm. However, good agreement with experimental data [16,17] for these hybrid solvents was obtained using two asymmetrical sites. In contrast, experimental solubility of CO<sub>2</sub> in AMP + TEG [17] seems to be captured well by all proposed modelling approaches, even the one-site model. Deviations in the behaviour of soft-SAFT calculations were observed at lower loading capacities, with no available data in those regions to confirm the behaviour at lower CO<sub>2</sub> partial pressures in order to make a definitive choice of the number of reactive sites in the CO<sub>2</sub> molecule. Hence, for simplicity, the use of a one-site model was adopted for AMP + TEG hybrid solvent. Notice that we have expressed the concentration in molar terms, for the equivalence of these solvents with the aqueous amines.

Soft-SAFT results for the absorption of CO<sub>2</sub> in mixtures of amines

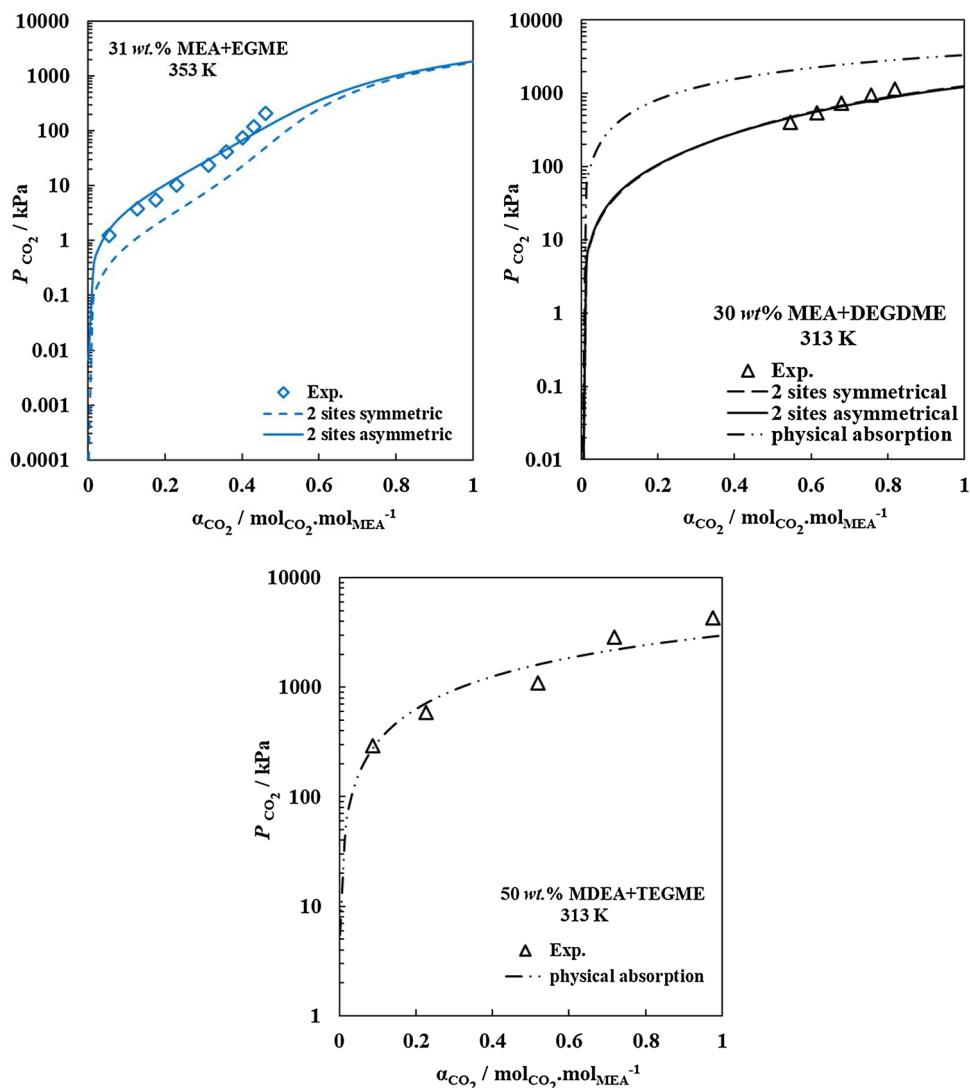
and glymes are presented in Fig. 10. In the case of CO<sub>2</sub> absorption in mixtures of MEA + EGME, the shape of the experimental solubility isotherm [86] is better captured using asymmetrical energies for the reactive sites, consistent with the previously obtained results for MEA + glycols. For MEA + DEGDME, both symmetric and asymmetric cross-association energies provide similar level of agreement with experimental data [22]. Hence, to reduce the number of fitted parameters for this mixture, the two symmetric sites approach was used. It should be noted that for this hybrid solvent the shape of the calculated solubility isotherm with the available data is in better agreement with that of a physical absorption process rather than a chemical one [10], as the soft-SAFT predicted absorption capacity at low CO<sub>2</sub> partial pressures are extremely smaller than those acquired for aqueous amines, or the ones with glycols or EGME. This was further supported by the values obtained for the cross-association energy of the reactive sites, which were far lower than those used for other non-aqueous and aqueous amines. Nonetheless, the occurrence of a chemical absorption for this hybrid solvent cannot be fully refuted, as experimental data for the absorption at low partial pressures are not available.

During preliminary trial calculations for the absorption of CO<sub>2</sub> in non-aqueous tertiary amine (MDEA + TEGME), it was observed that better agreement with experimental data [89] was obtained with a small value for the cross-association energy of the reactive site, approaching zero. This indicated that the CO<sub>2</sub> absorption in non-aqueous MDEA is a physical process ( $\varepsilon_{N-\alpha_1}^{HB}/k_B = 0$ ) rather than a chemical one. This is supported by both the shape of the solubility isotherm and range of CO<sub>2</sub> partial pressures. The interpretation of the results of this mixture shows a controversy in the literature. Versteeg and van Swaaij [65] established that CO<sub>2</sub> absorption in MDEA + methanol was entirely physical without the occurrence of any chemical reaction with CO<sub>2</sub>, contradicting the findings of Sada et al. [90] that maintained the occurrence of a chemical reaction upon the absorption of CO<sub>2</sub> in another tertiary amine (triethanolamine) and methanol hybrid solvent.

Further performance analysis of hybrid solvents such as mixtures of MDEA + TEGME and MEA + DEGDME were not conducted in this



**Fig. 9.** Fixed temperature solubility of CO<sub>2</sub> in non-aqueous solutions of MEA, DEA and AMP with glycols (EG, DEG and TEG) represented as partial pressure of CO<sub>2</sub> and CO<sub>2</sub> loading capacity, with the number of active association sites in CO<sub>2</sub> molecules. Soft-SAFT calculations (lines) and experimental data [16,17,88] (symbols).



**Fig. 10.** Fixed temperature solubility of CO<sub>2</sub> in non-aqueous solutions of MEA, and MDEA with glymes (EGME, DEGDME and TEGME) represented as partial pressure of CO<sub>2</sub> and CO<sub>2</sub> loading capacity, with the number of active association sites in CO<sub>2</sub> molecules. Soft-SAFT calculations (lines), experimental data [22,86,89], respectively (symbols).

**Table 2**

Values for N- $\alpha_i$  interactions' cross-association volume and energy extended to a range of temperature within the soft-SAFT framework. The energy and size binary interaction parameters,  $\xi_{ij}$ , and  $\eta_{ij}$  between each amine and CO<sub>2</sub> were kept equal to 1.0.

CO <sub>2</sub> +	$\kappa_{N-\alpha}^{HB} (\text{\AA}^3)$ <sup>a</sup>	$\varepsilon_{N-\alpha_1}^{HB}/k_B$ (K)	$\varepsilon_{N-\alpha_2}^{HB}/k_B$ (K) <sup>c</sup>	T range (K)	Ref.
MEA + TEG	500	- 5.011 × T + 6115	4400	303–343	[88]
DEA + TEG	500	- 2.498 × T + 4956	4000	303–343	[88]
AMP + TEG <sup>b</sup>	500	- 2.421 × T + 5328	-	303–353	[17]
AMP + DEG	500	- 6.027 × T + 6620	4000	303–353	[17]
AMP + EG	500	- 6.027 × T + 7120	4000	303–353	[16]
MEA + EGME	500	- 9.001 × T + 7347	4300	313–393	[86]
MEA + DEGDME	500	3200	3200	293–333	[22]

<sup>a</sup> Transferred from Lloret *et al.* [39].

<sup>b</sup> One-site model for CO<sub>2</sub>.

<sup>c</sup> Values optimised at a fixed temperature.

work, as the focus of it is on solvents showing chemical absorption of CO<sub>2</sub> at low pressures. Nevertheless, these results demonstrate the validity of the modelling approach in implicitly accounting for the effect of the co-solvent on the absorption of CO<sub>2</sub> in amines. The inclusion of the temperature-dependency of the absorption of CO<sub>2</sub> in non-aqueous amines is needed in any modelling framework, as equilibrium constants

and reaction rates governing the solubility of CO<sub>2</sub> are dependent on temperature. Moreover, the overall performance of solvent regeneration is affected by its ability to desorb CO<sub>2</sub> with changes in temperature. In our proposed models, such effect for each amine was included through optimising the values for the cross-association energy at each temperature rather than transferring the previously optimised

parameters at a fixed temperature. This resulted in better representation of experimental data over a wide range of temperatures, except for MEA + DEG and MDEA + TEGME solvents, due to the absence of additional solubility data at other temperatures. It should be noted that for the two asymmetric site approach, except for AMP + TEG, the values of the cross-association energy for N- $\alpha_1$  interactions were obtained as a function of temperature, while those for N- $\alpha_2$  were fixed to those optimised at a fixed temperature (Table S4), in an effort to maintain the robustness of the model. The new cross-association parameters for the examined hybrid solvents, extendable to a range of temperatures are provided in Table 2.

For each amine + CO<sub>2</sub> pair, a linear decreasing trend is observed for the values of cross-association energy for N- $\alpha_1$  bonds as a function of increasing temperature ( $R^2 > 0.98$ ). This is in agreement with the exothermic nature of the chemisorption process of CO<sub>2</sub> in aqueous amines. However, describing the absorption of CO<sub>2</sub> in MEA + DEGDME with transferred cross-association parameters fitted at a fixed temperature to other temperatures provided good agreement with experimental data. The decision to transfer the energy parameters for this mixture was done due to observed minimal changes in the values fitted at each isotherm.

Comparing the values of the cross-association energy for both aqueous (Table S2) and non-aqueous amines (Table 2), it is observed that the values for aqueous amines [34] are higher than those for non-aqueous solutions obtained in this work. This is consistent with experimental observations on the weaker ability of physical solvents in stabilizing formed reaction products between CO<sub>2</sub> and amines, in contrast to water. This highlights the legitimacy of our modelling strategy for the absorption of CO<sub>2</sub> in non-aqueous amines, as in the absence of water, physical solvents cannot stabilize reaction products as strongly as water, resulting in weaker N- $\alpha_i$  than those obtained for aqueous amines [34]. The weakest interactions among the non-aqueous amines examined in this work was obtained for MEA + DEGDME hybrid solvent. The low values of the cross-association energy falls in the region of physical association rather than strong energetic chemical intramolecular interactions, postulating that the absorption of CO<sub>2</sub> in this solvent is physical rather than chemical, as discussed earlier.

Depicted in Figs. 11 and 12 are soft-SAFT calculations by our proposed models for hybrid solvents of amines with glymes or glycols using the cross-association energy parameters in Table 2. Soft-SAFT accurately describes the reported experimental CO<sub>2</sub> loading capacity over a broad range of temperatures [16,17,22,86,88]. The soft-SAFT models developed herein capture the temperature dependency of CO<sub>2</sub> solubility

in non-aqueous amines hybrid solvents, which can be used to extrapolate the solubility of CO<sub>2</sub> in temperatures not included in the fitting.

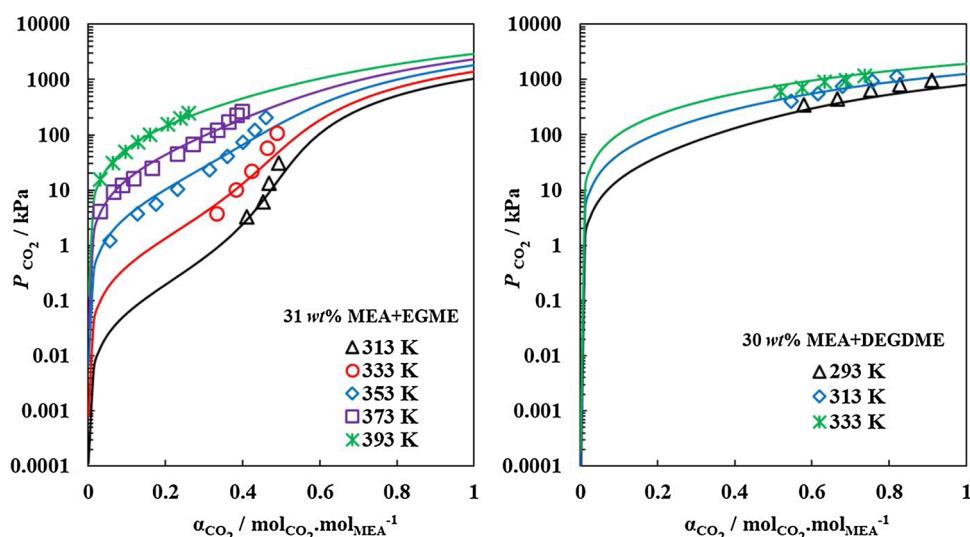
Ideally, further validation for the robustness of the developed models would require examining the transferability of the cross-association parameters for predicting CO<sub>2</sub> absorption at different amine concentrations. However, experimental data to facilitate such examinations are not available in the literature. Nevertheless, soft-SAFT predictions for each of the examined solvents, especially for amines with glycols, have been obtained at 30 wt.% amine concentration as shown in Figure S3 in the supporting information. This amine concentration was chosen as representative of typical concentration used in industry for aqueous amines. This will allow for process performance comparison of these solvents and aqueous ones under the same processing conditions.

In summary, the proposed models for the absorption of CO<sub>2</sub> in non-aqueous amines with glycols or glymes using soft-SAFT are capable of accurately representing the chemisorption process, using no more than two adjustable parameters, for a range of temperatures, CO<sub>2</sub> loading capacities and partial pressures. This showcases the efficiency of the proposed modelling treatment for the absorption process, yielding a robust and consistent modelling framework that can act as a solvent screening tool, merely using CO<sub>2</sub> absorption VLE data, the performance of these solvents for CO<sub>2</sub> capture is presented and discussed next.

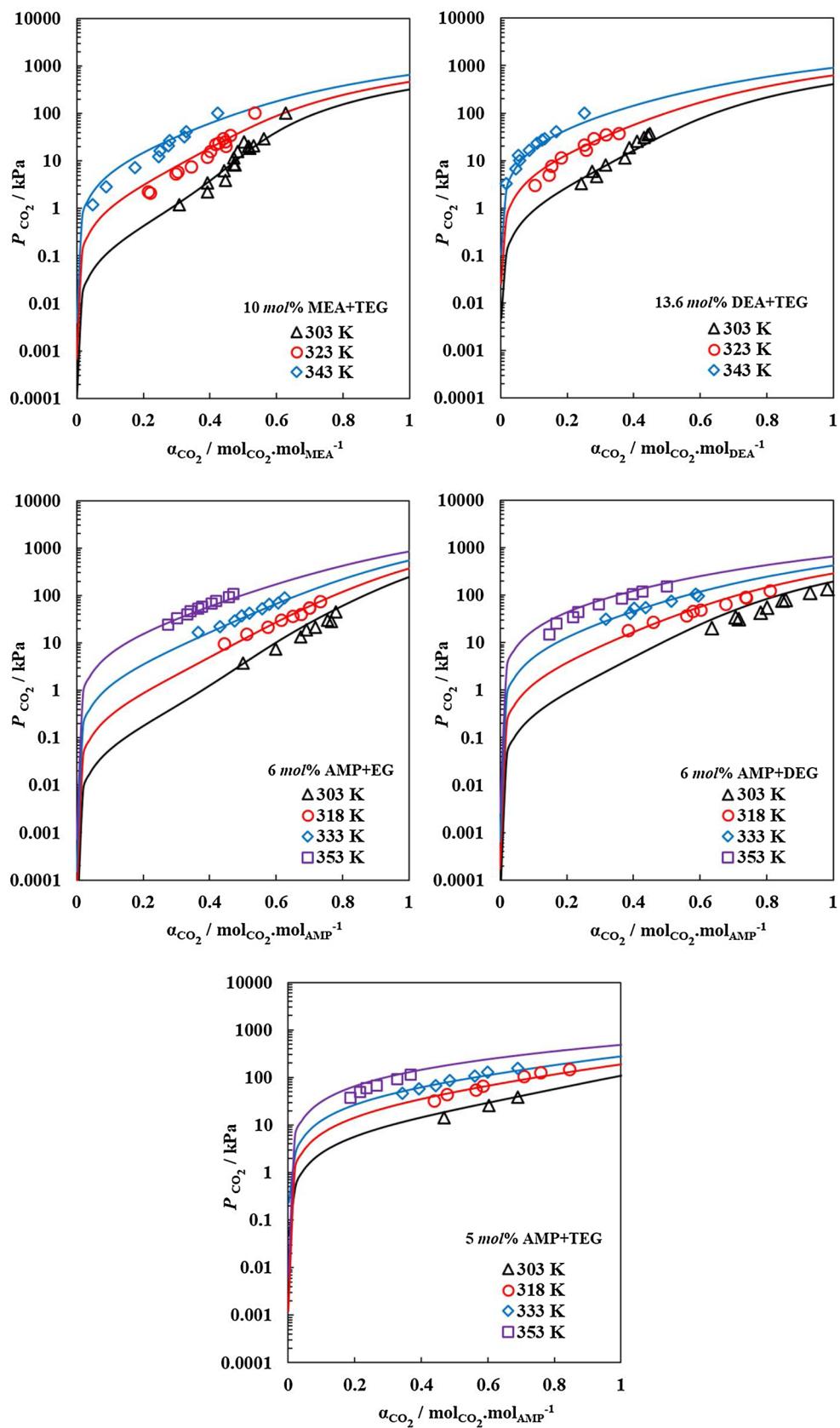
### 3.4. Performance evaluation of non-aqueous amine solutions for CO<sub>2</sub> capture

There is a plethora of available solvents (aqueous and non-aqueous) for the chemical absorption of CO<sub>2</sub>. The development of cost and energy effective carbon capture processes depends on the selection of optimum solvents through a robust screening of the available ones. Most efforts on optimum solvent development has focused on reducing the heat of absorption and enhancing the CO<sub>2</sub> absorption capacity [15,91]. Thus, the performance of chemical solvents is characterized by cyclic capacity and energy of regeneration for CO<sub>2</sub> desorption. The cyclic capacity of chemical solvents (Eq. 11) is the difference between the concentration of absorbed CO<sub>2</sub> at rich conditions (absorber temperature and pressure) and the concentration of CO<sub>2</sub> in the regenerated solvent after regeneration at lean conditions (stripper pressure and temperature) [92]. This is a measure of solvent performance in effectively removing and capturing CO<sub>2</sub> from the incoming feed gas.

$$\Delta\alpha_{CO_2}(T, p) = \alpha_{CO_2, Rich}(T, P)_{Absorber} - \alpha_{CO_2, Lean}(T, P)_{Stripper} \quad (11)$$



**Fig. 11.** Solubility of CO<sub>2</sub> in non-aqueous solutions of MEA with glymes (EGME and DEGDME) at different temperatures represented as partial pressure of CO<sub>2</sub> as a function of CO<sub>2</sub> loading capacity. Calculations using soft-SAFT with parameters from Table 2 (lines), experimental data [22,86] (symbols).



**Fig. 12.** Solubility of CO<sub>2</sub> in non-aqueous solutions of MEA, DEA and AMP with glycols (EG, DEG, and TEG) at different temperatures represented as partial pressure of CO<sub>2</sub> as a function of CO<sub>2</sub> loading capacity. Calculations using soft-SAFT with parameters from Table 2 (lines), experimental data [16,17,88] (symbols).

Solvent regeneration energy ( $Q_{reg}$ ) is the amount of energy needed to remove the CO<sub>2</sub> captured in the rich solvent, bringing it back to lean conditions, written as:

$$Q_{reg} = Q_{vap} + Q_{sen} + Q_{abs} \quad (12)$$

This energy (Eq. 12) can be decomposed into three primary contributions [12,93,94]:

- 1) Heat of vaporisation ( $Q_{vap}$ ), which is the heat required to vaporise the co-solvent (water or physical solvents) if needed, producing stripping steam that overcomes the pressure drop in the stripping column. This depends on the partial pressure of CO<sub>2</sub> and the co-solvent in equilibrium with the liquid phase in the stripping column, and the heat of vaporisation of the co-solvent. It is worth noting that non-aqueous solvents considered in this study might have low vapour pressure and the co-solvent might not vaporize in the current regeneration system. Therefore, there is a need to modify the design of current stripper column to ensure a better heat transfer [6,95–97], which is beyond the current scope of the current work.
- 2) Sensible heat ( $Q_{sen}$ ), which is the heat required to increase the temperature of the solvent to that of the reboiler, overcoming heat losses due to heat exchange between the lean and rich solvents. This depends on the heat capacities of the amine and the co-solvent.
- 3) Heat of absorption ( $Q_{abs}$ ), which is the heat required to reverse the absorption reaction and desorb CO<sub>2</sub> from the rich solvent. This depends on the type of amine solvent used and is directly linked to the desired CO<sub>2</sub> loading in the lean solvent.

Ideally, high cyclic capacity is preferred as it will reduce the circulation flow rate of the solvent [2]. A solvent with high cyclic capacity requires a high absorption capacity at rich conditions and high ability to easily desorb CO<sub>2</sub> at lean conditions. Reducing the heat of regeneration requires overcoming the three heat contributions, vaporisation, sensible and absorption, described earlier. Reducing the heat needed to reverse the absorption process and desorb the captured CO<sub>2</sub> requires an amine with a low heat of absorption, such as tertiary amines (MDEA) [12,15]. In contrast, reducing both heat of vaporisation and sensible heat can be achieved by using a less-energy demanding co-solvent, with low heat of vaporisation and heat capacity, such as water-lean or non-aqueous hybrid solvents [6].

We have assessed the effect of using non-aqueous amines compared to conventional aqueous amines in terms of solvent cyclic capacity and regeneration heat. The performance of aqueous amines was calculated using soft-SAFT parameters transferred from our previous work [34], while those for non-aqueous amines were developed in this work, as provided in Table 2. The solvents are compared under similar typical process conditions such as 30 wt.% amine + co-solvent solution (based on results from Fig. 11 and Figure S3). As highlighted earlier, the scope of this work is mainly focused on solvents for the chemical absorption of CO<sub>2</sub>, thus based on the results presented earlier, non-aqueous solvents such as MEA + DEGDME and MDEA + TEGME are excluded from this analysis.

The estimation of solvent cyclic capacity can be directly obtained from VLE data, using Eq. 11, provided that rich and lean conditions are known. The conditions for rich loading for the absorption process were defined at a CO<sub>2</sub> partial pressure of 15 kPa and a temperature of 313 K. The regeneration of CO<sub>2</sub> rich solvent takes place in the regeneration column typically under a pressure higher than atmospheric pressure and with a typical reboiler temperature of 393 K, depending on the type of amine and co-solvent. Lean conditions for the desorption process were chosen as those needed to achieve a 50% reduction in the rich loading,  $\Delta\alpha_{CO_2} = 0.5\alpha_{CO_2, Rich}$ , and assuming a stripper pressure of 0.2 MPa, both consistent with our previous work [34]. It should be noted that the cyclic capacity is heavily biased by the rich conditions (absorption), thus solvents with higher absorption capacity at rich conditions will have a higher cyclic capacity. Regarding the lean

conditions, the desorption temperature depends on the specific solvent, however, the temperatures obtained from the procedure used in this work were not optimized to be the best for each one of them, as these calculations are for screening purposes.

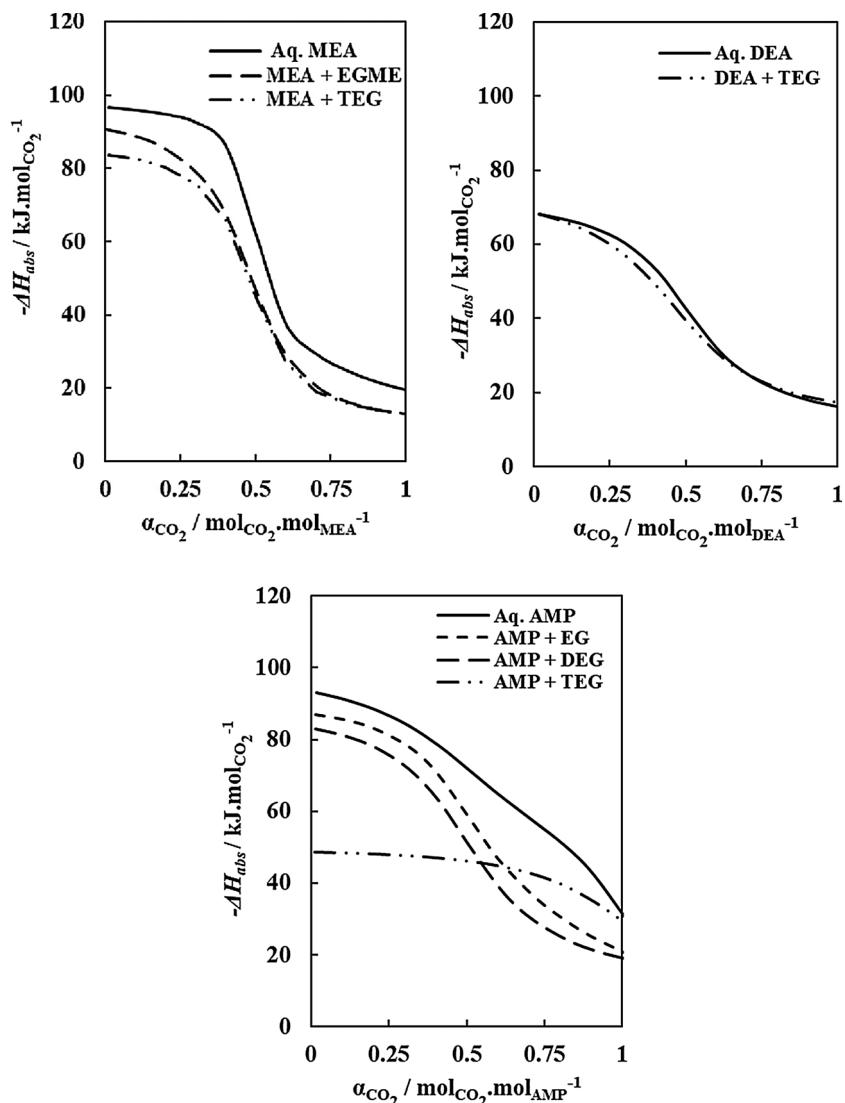
The heat of regeneration for the examined solvents was estimated using the shortcut method proposed by Kim et al. [98] due to its valid yet simple formulation, producing estimates comparable to those obtained from ASPEN simulations. More information on this estimation methodology can be found in the original paper [98]. Again, as already stressed-out these conditions are not the optimised conditions for each solvent. Furthermore, according to the authors, the method relies on the key assumption that amines volatility can be neglected when compared to that of water; this, in turn, might not hold true when applying the method to non-aqueous solvents with low vapour pressures. In a subsequent work, Kim and Lee [97] applied their shortcut method to the energetic evaluation of hypothetical water-lean and non-aqueous amines, yielding results consistent with expected trends from the use of non-aqueous solvents, while also neglecting the effect of amine volatility and stripper configuration on estimation for regeneration energy. One should be conscious of these limitations when using this method.

The enthalpy of vaporisation of water and physical solvents examined in this work were obtained from soft-SAFT enthalpy calculations for each pure substance, as shown in Figure S4 in the supporting information with high accuracy (AAD less than 1%) compared to correlated data from DIPPR database [57] as a function of temperatures. The heat capacities of physical solvents, amines, CO<sub>2</sub> and water were obtained from those available in the literature [57], provided in Table S5 in the supporting information, and assumed to be constant with pressure and temperature. The heat of absorption for the chemisorption of CO<sub>2</sub> in aqueous and non-aqueous amines was calculated by the Gibbs-Helmholtz thermodynamic relation, using calculated VLE data of CO<sub>2</sub> and each non-aqueous solvent from the developed soft-SAFT models:

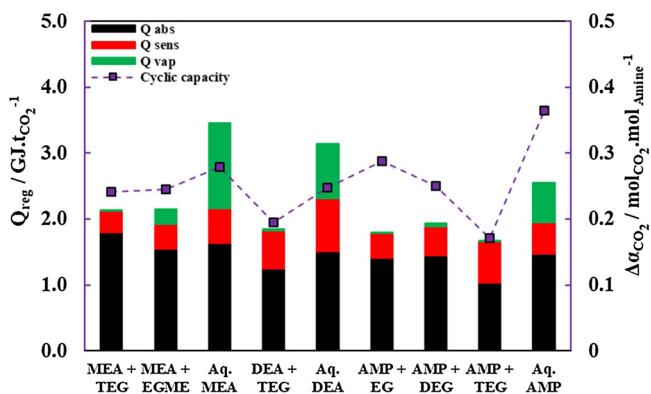
$$\Delta H_{abs} = R \left[ \frac{\partial \ln P_{CO_2}}{\partial (\frac{1}{T})} \right]_{P, \alpha_{CO_2}} \quad (13)$$

where  $P_{CO_2}$  is the predicted partial pressure of CO<sub>2</sub> using soft-SAFT at a given CO<sub>2</sub> loading, pressure and temperature. Depicted in Fig. 13 are the calculated heats of absorption for non-aqueous amines using (Eq. 13) and CO<sub>2</sub> solubility data obtained with the soft-SAFT models compared to those obtained for aqueous amines, previously validated against experimental data in our previous work [34]. As inferred from the figure, all the examined amine solvents, except for AMP + TEG, present a similar trend for the heat of absorption with CO<sub>2</sub> loading. Moreover, the values obtained for non-aqueous amines are lower than those for aqueous solvents, highlighting their weaker CO<sub>2</sub> absorption strength. The lowest heat of absorption was acquired for non-aqueous AMP + TEG solvent, indicating that their interaction might approach that of physical absorption rather than a chemical one, as previously discussed.

The estimated solvent cyclic capacity and heat of regeneration based on the previously mentioned conditions are shown in Fig. 14. It can be seen that, aqueous amines have a higher molar cyclic capacity than non-aqueous ones, which is consistent with the weaker effect of physical co-solvents on the stabilization of reaction products compared to water. However, it can be observed that non-aqueous amine solvents resulted in a lower energy of regeneration compared to their aqueous counterparts, mainly in the form of lower heat of vaporization and sensible heat. This is associated with the lower thermal properties of physical solvents compared to water (on a mass basis), and their ease of regeneration at lower temperatures related to the strength of interaction between CO<sub>2</sub> and amines in physical solvents, as previously highlighted. The estimated values for the temperature of regeneration



**Fig. 13.** Calculated enthalpy of absorption as a function of CO<sub>2</sub> loading for aqueous and non-aqueous amines (using Eq. 13). Lines represent the soft-SAFT calculations for each mixture.



**Fig. 14.** Solvent cyclic capacity (squares) and contribution to total heat of regeneration (absorption, sensible, vaporization) for 30 wt% aqueous and non-aqueous amine solutions estimated for CO<sub>2</sub> partial pressure of 15 kPa. The dashed line is a guide to the eyes.

for each solvent mixture at the lean conditions examined in this work are provided in Table S6 in the supporting information. It can be seen that with non-aqueous amines the required temperature for solvent

regeneration is lower than for their aqueous counterparts. One should bear in mind, as already mentioned, that the values presented in Table S6 were not obtained at their optimal conditions, and a modification to the stripper configuration is required to truly demonstrate the lower temperature of regeneration for each hybrid solvents separately.

For the benchmark 30 wt.% MEA, the use of non-aqueous solvents of EGME or TEG, resulted in a relatively similar molar cyclic capacity of 0.25 mol $CO_2 \cdot mol_{amine}^{-1}$ , marking a 12% reduction in cyclic capacity compared to conventional aqueous MEA with a molar cyclic capacity of 0.28 mol $CO_2 \cdot mol_{amine}^{-1}$  [34]. However, this decrease in cyclic capacity is accompanied with approximately 38% reduction in total energy of regeneration for non-aqueous MEA solvents compared to that for aqueous MEA. Similar trends are obtained for solutions of DEA with a reduction in both cyclic capacity and energy of regeneration of 20% and 40%, respectively.

In the case of solutions to AMP, the use of glycol co-solvents resulted in a reduction in cyclic capacity in the range of 20–50%, with the highest reduction for AMP + TEG solvent. This reduction using TEG as a co-solvent is far greater than that obtained using alkanolamines such as MEA and DEA. Such a behaviour might be attributed to the steric hindrance in AMP molecules, making it difficult for a bulky molecule as TEG to approach the shielded lone pairs on the nitrogen atom in the AMP molecule to ionize it. The use of smaller glycals such as EG and

DEG resulted in a better cyclic capacity compared to TEG co-solvents. In terms of energy of regeneration, the use of non-aqueous AMP solvents resulted in approximately 25–35% reduction in total energy of regeneration compared to aqueous AMP. Moreover, the estimated regeneration temperature

The simple analysis implemented in this work provides the general trade-offs associated with the use of non-aqueous amine solutions mainly in terms of cyclic capacity and heat of regeneration, allowing a systematic comparison for initial solvent screening. Nonetheless, more rigorous process modelling for these solvents, once screened for the most promising ones, are required for a more holistic understanding of their performance compared to aqueous solvents, which are outside the scope of the current work. For example, it should be noted that the process conditions or regeneration configuration chosen for this general assessment are not the optimal ones but were chosen for comparison purposes under the same conditions. A more rigorous approach for optimization should obtain the value of the lean loading that maximizes the cyclic capacity and minimizes the heat of regeneration for each of them. Moreover, other considerations are required such as the effect of their lower enthalpy of absorption on the maximum CO<sub>2</sub> recovery, solvent circulation rates and pumping requirements. In addition, other thermophysical properties such as viscosity and surface tension and others relevant to process design and simulation should be included. Their addition would complement the analysis in terms of cyclic capacity and energy of regeneration due to their effects of overall mass transfer, but such an assessment is limited by the available experimental data required for further model development.

Nonetheless, the soft-SAFT model developed in this work based on a systematic study for the absorption of CO<sub>2</sub> in amines, showcased its capabilities of acting as a robust solvent screening tool extendable to new solvents and for implementation in engineering simulators for process simulation and design.

#### 4. Conclusions

In this work, a robust thermodynamic-based model using a molecular-based EoS (soft-SAFT) was developed and applied for the assessment and screening of non-aqueous amine hybrid solvents for carbon capture. The soft-SAFT molecular models of the pure substances (amines, physical solvents, and CO<sub>2</sub>) were either taken from previous works or developed in this work, demonstrating the transferability of the molecular parameters and models. Specific interactions of CO<sub>2</sub> + physical solvents, and amine + physical solvents, were either directly predicted from combining rules or regressed in this work to available experimental data of these binary mixtures. Based on the robust modelling framework developed for CO<sub>2</sub> absorption in conventional aqueous amines, the formation of reaction products from the reactions between CO<sub>2</sub> and amines in non-aqueous physical co-solvents and the effect of the physical solvent on amine reactivity were implicitly accounted for in the developed models, in a consistent manner. With this simple yet robust framework, the absorption of CO<sub>2</sub> in non-aqueous hybrid solvents of amines such as MEA, DEA, MDEA and AMP with physical solvents of glycols (EG, DEG, and TEG) or glymes (EGME, TEGME, and DEGDME), were successfully modelled and validated against available experimental data, using only two adjustable parameters.

Furthermore, the models developed in this work were used to evaluate the performance of non-aqueous amine solvents in terms of the energy of regeneration and absorption cyclic capacity. The obtained results revealed that the use of non-aqueous amines for low pressure CO<sub>2</sub> capture is associated with a 10–50% decrease in solvent cyclic capacity compared to aqueous amines owing to the influence of organic solvents on the amine reactivity with CO<sub>2</sub>. However, this is accompanied with a 30–40% reduction in overall energy of regeneration for non-aqueous amines due to their lower heat capacity and heat of vaporisation associated with regeneration occurring at lower reboiler

temperature compared to that for aqueous amines. These results demonstrate the potential advantage of using non-aqueous amines and their impact on the techno-economic feasibility of carbon capture, mainly in the required energy of solvent regeneration. The results obtained in this work confirm the viability of the proposed model based on soft-SAFT, with its simplified treatment for the chemical reaction process, as a robust and effective tool for the screening of conventional and new solvents for carbon capture.

#### Declaration of Competing Interest

The authors declare no conflict of interest in the publication of this work.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jcou.2019.09.010>.

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