



Sustainability criteria as a game changer in the search for hybrid solvents for CO₂ and H₂S removal

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ABSTRACT

The appearance of hybrid solvents in recent years introduced a potential replacement for aqueous amines for acid gas removal in order to mainly overcome the high energy of regeneration. Yet, the assessment of solvent potentiality remains haphazard with limited information and assessment criteria. In this contribution, we develop and apply a multi-criteria assessment approach built on the use of a molecular-based equation of state, namely, polar soft-SAFT, in combination with sustainability indicators to examine the performance of hybrid solvents for acid gas removal (CO₂ and H₂S). The first stage of the approach relies on the robust development of the thermodynamic model with available experimental data. Subsequently, with assured fidelity, the model is used in a fully predictive manner to obtain relevant assessment criteria for technical performance evaluation. This is inclusive of standard key performance indicators such as cyclic capacity and energy of regeneration, along with key solvent properties at conditions representative of acid gas removal processes. Additionally, we examine the environmental, health and safety impact of the investigated solvents as a sustainability criteria to select them. This framework has been applied for the first time to six solvents for acid gas removal, including the benchmark solvents aqueous monoethanolamine (MEA) and aqueous diethanolamine (DEA), along with hybrid solvents formulated from chemical solvents such as MEA, or DEA, with physical co-solvents including N-methyl-2-pyrrolidone (NMP), or sulfolane (SFL). The results of the multi-criteria assessment demonstrate that among the six solvents investigated in this work, the overall best performer remains to be the benchmark aqueous MEA. Results also indicate the potentiality of MEA + NMP hybrid solvent in terms of an acceptable compromise between reduced absorption capability and reduced energy of regeneration, compared to aqueous MEA; however, the hybrid solvents fail when applying the sustainability metrics. This work clearly indicates that potential solvents for acid gas removal should be examined following a holistic approach, inclusive of their technical performance and environmental footprint.

1. Introduction

The utility of chemical solvents for gas absorption and separation has been continuously displayed since their development in the 1930 s [1,2]. Their initial application was solely focused on natural gas sweetening, for the removal of acid gases (CO₂ and H₂S) from raw natural gas feed. With time, the long-standing operation of this technology bequeathed it with sufficient technical knowledge and flexibility to facilitate its successful transition to other applications [3]. Table 1

On one front, the growing concerns over the effects of climate change and increased atmospheric CO₂ emissions have steered global efforts

towards increasing action to mitigate them and finding sustainable solutions for the transformation of CO₂ into value added products [4,5]. This resulted in the adoption of chemical absorption processes in the removal of CO₂ from flue gas generated from fossil fuel consumption [6], which is an integral stage within the carbon capture, utilization, and storage (CCUS) value chain in order to avoid its emissions into the atmosphere. On another front, the constant dread over depletion of available energy resources led to the emergence of “greener” alternative gaseous fuels such as syngas or biogas with the potential of achieving the UN’s sustainable development goals for availability of clean energy [4]. Yet again, chemical absorption processes found themselves in a new

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setting, *i.e.* syngas purification or biogas upgrading, for the removal of acid gas impurities to ensure higher product quality [7]. Irrespective of the metamorphing operational, environmental, or economic drivers for acid gas removal, the preferential utilization of chemical absorption processes persisted.

Among the large family of available chemical solvents for acid gas removal, aqueous amines are the most widely used, with monoethanolamine (MEA) being the industrial golden standard, owing to its high acid gas affinity and absorption capacity [3]. However, their major drawback remains their large parasitic energy load associated with solvent regeneration, significantly affecting the overall efficiency for systems integrated with aqueous amine-based absorption processes [8]. One of the primary precursors for the high solvent regeneration energy is the use of water as a co-solvent, with its high thermal properties compared to other co-solvents [9]. The estimated energy of regeneration for 30 wt% aqueous MEA, in the case of CO₂ absorption, revealed that more than 50% of the total energy was directed at heating and vaporizing the water co-solvent, while the remainder was expended on reversing the chemical reaction between MEA and CO₂ [1,10]. Accordingly, it was envisioned that either fully or partially replacing water with other organic diluents as co-solvents, effectively forming water-free/water lean hybrid solvents, can potentially reduce solvent regeneration energy, given that the replacement co-solvent has lower thermal properties as opposed to water [11–16]. In this manner, the regeneration energy will be more efficiently utilized to reverse acid gas chemisorption, as opposed to heating, and vaporizing the co-solvent as seen in the case of aqueous amines.

Hybrid water-free/water-lean solvents have been extensively examined in recent years mainly for their CO₂ capture applications, offering a wide variety of potentially attractive alternatives to conventional aqueous amines [8,17]. However, the assertion of their attractiveness is contested by two challenging areas. The first challenge is that scaling-up the reported success of these solvents from lab- to industrial-scale conditions has not been thoroughly explored; simply because a large number of required properties are yet unavailable. This is expected due to the taxing nature of experimental efforts, making it an impossible feat to extend experimental measurements for the wide range of thermo-physical and transport properties required for accurate and representative performance assessment at industrial-scale. The second challenge is that the demonstration of a potentiality of a particular solvent, whenever conducted at a lab-scale, is usually attested with a small number of criteria, particularly, high absorption capacity and low enthalpy of absorption [18–21]. Indeed, these two properties are of particular interest for chemical absorption processes; however, they remain insufficient to properly assess the potentiality of the examined solvents for their final application. The conclusions drawn from a simple assessment can be helpful in guiding the development of new generation solvents; however, still overlooking potential trade-offs between conflicting operational, economic, and environmental facets [22,23].

Nonetheless, tackling these challenges is possible, provided the availability of the right set of tools. For the first challenge, scaling data from lab to industry operating conditions can be remedied with the recent progress in thermodynamic modeling approaches and computational capabilities, by the application of molecular modeling techniques. Molecular equations of state (EoSs) based on the Statistical Associating Fluid Theory (SAFT) [24,25] stand out as the most attractive models for this purpose due to their firm theoretical basis, demonstrated accuracy for a wide range of complex systems and predictive capabilities. Furthermore, with these models, a holistic thermodynamic assessment of fluid systems is easily attainable in an accurate and rapid manner, inclusive of a variety of thermodynamic properties, such as phase equilibria, interfacial properties, heat capacities, speed of sound, and transport properties (once integrated with other theories). Among the available SAFT-based EoSs employed in the search for solvents for CO₂ capture, SAFT-VR [26,27], and SAFT- γ -Mie [28,29] have valuable contributions on examining an expansive range of aqueous amine

solvents [30,31], and phase change solvents for CO₂ capture [32]. However, their approach is limited by the reliance on a variety of regression models to obtain relevant solvent properties, while the application of the thermodynamic model was confined to obtaining CO₂ solubility in the examined solvents. A more apt application of a SAFT-based model in a similar context was done employing the soft-SAFT EoS [33,34]. The thermodynamic model was fully exploited to obtain all relevant thermodynamic information needed for screening and evaluating solvents for acid gas removal and CO₂ capture, such as conventional aqueous amines and their blends [35,36], novel water-free hybrid solvents [37,38], and task-designed solvents [39]. In addition to SAFT-type EoS, other modeling approaches are available such as quantitative-structure–property relationships (QSPR) based on the conductor-like Screening Model for Real Solvents (COSMO-RS); however, their successful application is more demonstrated for physical rather than chemical solvents [40,41]. Notwithstanding, the rigorous foundation of SAFT-based EoSs lends them sufficient flexibility to accurately model the chemisorption of acid gases in chemical solvents.

For the second abovementioned challenge, the demonstration of the potentiality of a selected solvent usually attested with a small number of criteria, the solution might seem rather intuitive, which is the inclusion of additional assessment criteria to the pre-existing standard key performance indicators (KPIs). However, such a decision is rather easier said than done, as information related to a particular criterion might not be available at the early design stages [42]. Limiting the search space among the wide array of available properties to include a limited set of representative criteria requires a basis to rationalize their inclusion or exclusion [30,31,43]. Typically, the impact of solvent properties on economic indicators such as overall capital cost (CAPEX) and operating cost (OPEX) serves as a rationalization basis. Mota-Martinez *et al.* [44], through rigorous process modeling of hypothetical solvents, managed to rank several solvent properties depending on their impact on the overall economics of the process. Recently, Leclaire and Heldebrant [45] have called for the incorporation of concepts drawn from green chemistry and engineering in tackling challenges in the development of CCUS technologies. The premise of their argument is that the application of the 12 + 12 principles of green chemistry and engineering [46] transcends their environmental driver, and indirectly provides an incentive to make chemical processes more efficient and economically attractive. In the same spirit, the inclusion of sustainability, and health and safety criteria can also be illuminating in assessing the potentiality of promising solvents for acid gas removal [47,48].

In this contribution, we assess the attractiveness of water-free hybrid solvents for the removal of acid gases (CO₂ and H₂S) using a multi-criteria assessment approach. The selected hybrid solvents are mixtures of chemical solvents such as MEA and diethanolamine (DEA), mixed with highly polar physical co-solvents such as N-methyl-2-pyrrolidone (NMP), and sulfolane (SFL) for which there is available experimental data. The molecular-based EoS, polar soft-SAFT EoS [49], is used to model the thermodynamic behavior of the examined hybrid solvents, where the available experimental data is used to assess the accuracy of the model. Subsequently, the model is used in a predictive manner, along with other tools, to evaluate the potentiality of these hybrid solvents compared to their aqueous counterparts in terms of technical performance, solvent properties, and sustainability criteria, highlighting the trade-offs in solvent evaluation. The evaluation of these solvents is done under typical operating conditions representative of post-combustion capture (PCC). To our knowledge, this is the first time a molecular-based EoS is used in conjunction with key performance indicators and sustainability criteria to provide an overall technical and environmental assessment for these types of emerging solvents.

2. Methods

In this section, we provide details on the methodology employed in the multi-criteria assessment of hybrid solvents for acid gas removal.

The assessment is carried out in two-stages, as depicted in Fig. 1, with the first stage hinging on the holistic thermodynamic modeling of the examined solvents using the molecular-based model, polar soft-SAFT [49]. The reliability and accuracy of the model is validated using available experimental data. In the second stage, the performance of the examined solvents is assessed depending on three different criteria categories, from solvent physico-chemical properties, standard key performance indicators (KPI), and sustainability metrics. Solvent properties and KPI are obtained from polar soft-SAFT predictions at industrially representative conditions, while the sustainability metrics include health and safety (HS) hazard assessment, and a cradle-to-gate life cycle assessment, following the procedures explained in this section. Collectively, the assessment criteria are employed to explore the trade-offs in evaluating the performance of these solvents relative to their aqueous counterparts.

2.1. Polar soft-SAFT equation of state (EoS)

The polar soft-SAFT EoS [49] computes the residual Helmholtz energy density (a^{res}) of a fluid by explicitly accounting for different microscopic contributions associated with different energetic and structural features, expressed as:

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

where a^{ref} is the reference term accounting for repulsive and dispersive interactions for Lennard-Jones (LJ) segments, a^{chain} designates the chain term accounting for chain formation from individual segments, a^{assoc} refers to the association term due to highly directional and strong interactions such as formation of hydrogen bonds, and lastly, a^{polar} is the polar contribution added to explicitly include the effect of dipolar and quadrupolar interactions. Once the Helmholtz energy is

known, the rest of the thermodynamic properties of the pure fluids and mixtures are obtained by the corresponding derivatives. The details of the theory are included elsewhere [33,34,49], and will not be repeated herein.

Applying polar soft-SAFT requires a set of molecular parameters descriptive of the main molecular characteristics of the pure fluids. The basic parameters for any fluid are the chain length (m_i), segment diameter (σ_i), and segment dispersive energy (ε_i). For associating fluids, two additional parameters are added which are the volume (κ^{HB}) and energy (ε^{HB}) of association. Similarly, for polar fluids, two additional parameters are included, namely, the dipole/quadrupole moment (μ/Q), and the fraction of polar segments (x_p). These parameters are obtained either from regression to pure fluid liquid density and vapor pressure or fixed *a priori* depending on a physical argument [33,34,49].

The extension of polar soft-SAFT to multicomponent systems requires the application of mixing rules only for the reference term, as the remainder of the terms are explicitly written for mixtures. Extending the reference term to mixtures is done using the generalized Lorentz-Berthelot (LB) combining rules to calculate the crossed size, σ_{ij} , and energy, ε_{ij} , as such:

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

$$\varepsilon_{ij} = \xi_{ij} \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \quad (2b)$$

where η_{ij} and ξ_{ij} ($\eta_{ij} = 1 - l_{ij}$ and $\xi_{ij} = 1 - k_{ij}$ in classical EoSs) are the binary interaction parameters for size and energy, respectively.

Additionally, mixing rules are needed in the case of association molecules to account for cross-association interactions either between different molecules or different functional groups within the same molecules, with the volume and energy of cross-association expressed

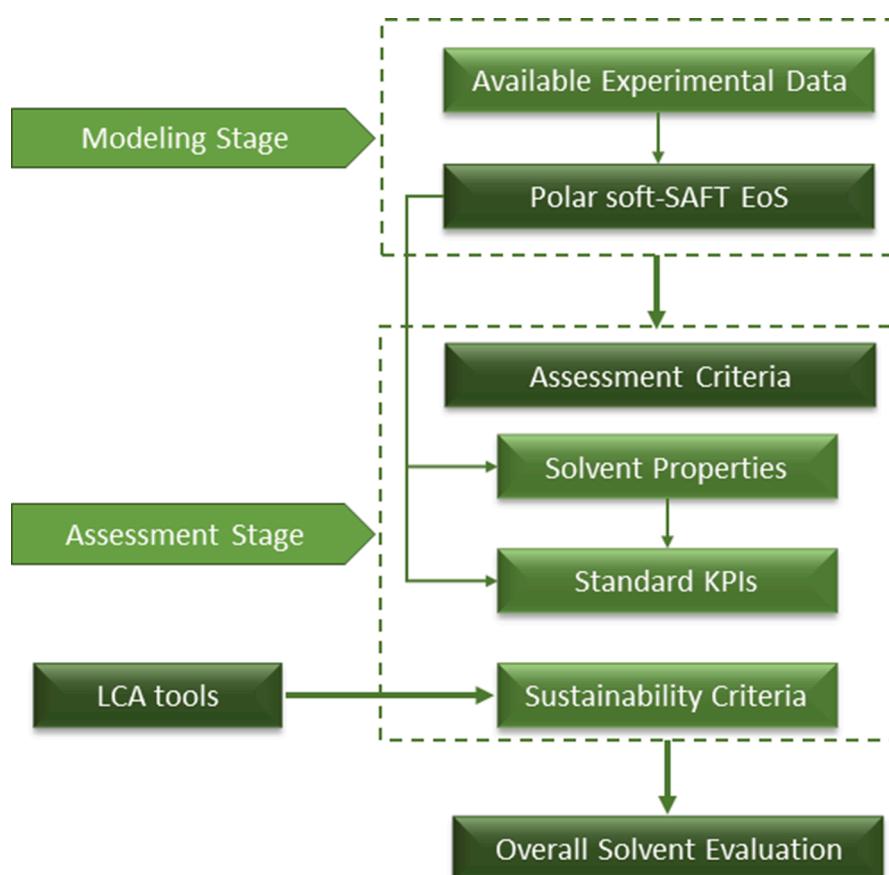


Fig. 1. Schematics of the multi-criteria assessment framework employed in this work to assess hybrid solvents for CO₂ and H₂S removal.

as:

$$\kappa_{ij}^{HB} = \left(\frac{\sqrt[3]{\kappa_{ii}^{HB}} + \sqrt[3]{\kappa_{jj}^{HB}}}{2} \right)^3 \quad (3a)$$

$$\varepsilon_{ij}^{HB} = \alpha_{ij}^{HB} \sqrt{\varepsilon_i^{HB} \varepsilon_j^{HB}} \quad (3b)$$

where α_{ij}^{HB} is a binary parameter that generalizes the energy of cross-association, fitted to binary mixture data if needed. The model is used in a fully predictive manner whenever the binary parameters (η_{ij} , ξ_{ij} , and α_{ij}^{HB}) are fixed to unity, without fitting to binary mixture data.

2.2. Free-Volume Theory (FVT)

The viscosity of pure fluids (μ) is modeled through combining polar soft-SAFT with the Free Volume Theory (FVT) [50], computed as:

$$\mu = \Delta\mu + \mu_0 \quad (4)$$

where, $\Delta\mu$ is the correction term used to account for the viscosity of the dense-state obtained using the expression of Allal and co-workers [50]. The additional term, μ_0 , for the viscosity of the dilute gas, can be excluded due to its small contribution to the total viscosity in the case of solvents with low vapor pressure, such as those included in this work [51]. The application of FVT for viscosity computations requires three adjustable parameters, α , B , and L_v , which are regressed using pure fluid viscosity data. The reader is referred to the original works for additional details on each FVT expression and application with soft-SAFT [52].

Calculating the viscosity of multicomponent mixtures is done in a predictive manner without additional parameters adjusted to mixture

viscosity data, through using linear compositional mixing rules for each FVT adjustable parameter [52], as:

$$\alpha_{mix} = \sum_i x_i \alpha_i \quad (5a)$$

$$B_{mix} = \sum_i x_i B_i \quad (5b)$$

$$L_{v,mix} = \sum_i x_i L_{v,i} \quad (5c)$$

2.3. Coarse-grain model and parameters of acid gases and solvents using polar soft-SAFT

Towards applying molecular-based EoSs, coarse-grain molecular models are needed to provide a simplified abstract representation of the real fluids, inclusive of their basic molecular features depending on governing molecular interactions and geometry. The polar soft-SAFT molecular models of pure fluids encountered in acid gas removal with water-free hybrid solvents examined in this work are highlighted below, with a graphical representation provided in Fig. 2.

Carbon dioxide (CO_2) was modeled as in previous works, as a LJ chainlike fluid model with explicit consideration of its quadrupolar moment, fixed to the experimental value [53]. Conversely, hydrogen sulfide (H_2S) was modeled as an associating fluid with three association sites, two sites for the two hydrogen atoms, and one site for the electronegativity of the sulfur atom [54].

The studied chemical solvents, MEA [55] and DEA [51], were modeled as associating chainlike fluids, accounting for their multifunctional groups with different association sites. Each hydroxyl group ($-OH$) (one for MEA, and two for DEA) was modeled with two

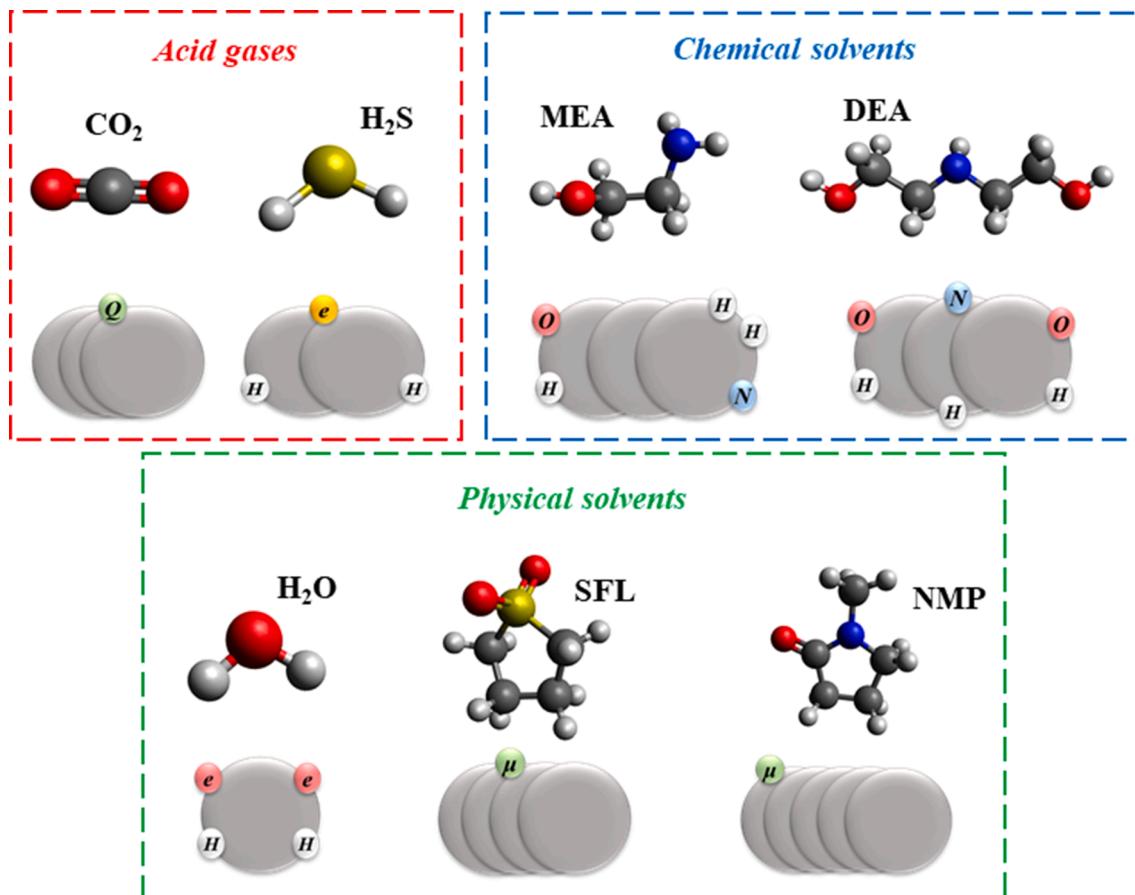


Fig. 2. Molecular structure and corresponding polar soft-SAFT coarse-grain molecular models for acid gases, chemical and physical solvents examined in this work.

associating sites, one positive for the hydrogen atom (H), and one negative for the lone pair of electrons on the oxygen atom (e), with its associating parameters transferred from ethanol [56]. Conversely, for amine groups each hydrogen was modeled as a single positive site (H), while the lone pair of electrons on the nitrogen were modeled as a single negative site (e). The number of sites depends on the type of amine groups, with the primary amine in MEA ($-NH_2$) modeled with three sites, two of type H , and one of type e , while the secondary amine group of DEA ($-NH$) was modeled with two sites, one of type H , and one of type e . The association parameters for the primary amine group, and secondary amine group were transferred from ethylamine [55] and diethylamine [51], respectively. Cross-association interactions between the hydroxyl and amine groups were allowed in the model, with the cross-association parameters directly predicted from mixing rules in Eq. (3).

The examined physical co-solvents include water (forming conventional aqueous amines), and polar aprotic solvents, namely, N-methyl-2-pyrrolidone (NMP), and sulfolane (SFL) (forming water-free hybrid solvents). Water was modeled as an associating LJ sphere ($m = 1$) with four association sites, two sites for the two hydrogen atoms, and two sites for the lone pair of electrons on the oxygen atom [57]. Conversely, aprotic dipolar fluids such as NMP,[58] and SFL, were explicitly modeled as dipolar fluids, accounting for their experimental dipole, and fixing their dipolar segments *a priori* based on the physical argument presented in previous contributions [49].

The molecular parameters for all studied pure fluids, except for SFL, were transferred from earlier contributions [51,53–55,57,58], while those for SFL were developed in this work using pure fluid saturated liquid density and vapor pressure, and are included in **Table S1 in the Supporting Information (SI)** for completeness. Additionally, FVT parameters for viscosity computations are included in **Table S2 in the SI**, with those for NMP and SFL developed in this work. The performance of polar soft-SAFT in characterizing the pure fluid behavior for SFL, and the viscosity of NMP and SFL using FVT treatment are shown in **Figure S1 in the SI**.

Notwithstanding, the most critical element in describing the chemisorption of acid gases in amine-based solvents using a molecular-based EoSs, is the development of a simplified modeling approach that implicitly transitions the chemical reactivity of amines towards acid gases to a physical-based model, such as polar soft-SAFT. This modeling approach has been successfully developed in our previous works for modeling the solubility of single and mixed acid gases (CO_2 and H_2S) in aqueous amines [35,36,55], and CO_2 absorption in water-free hybrid solvents using soft-SAFT EoS [37,38].

The application of this approach depends on understanding the main chemical reactions in acid gas absorption. It is generally accepted that the reaction mechanisms governing the absorption of CO_2 in primary and secondary amines, such as MEA and DEA, respectively, undergoes the formation of carbamate ($R_1R_2NCOO^-$) with a stoichiometric ratio of

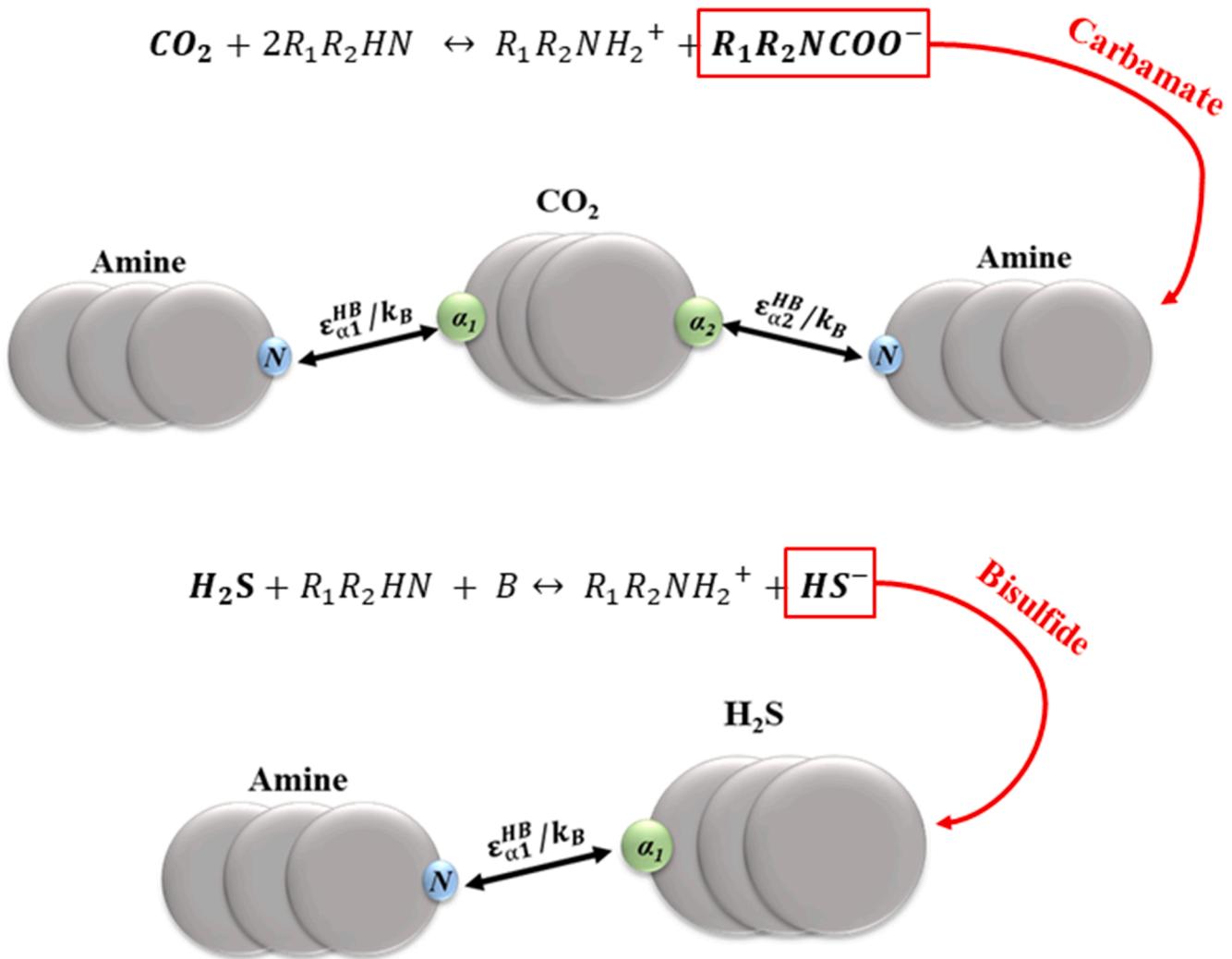


Fig. 3. Governing reactions for acid gas absorption in primary and secondary amines, highlighting the major reaction products, and their equivalent polar soft-SAFT representation.

2 mol amine for 1 mol CO₂ [59–62], while the chemisorption of H₂S undergoes the formation of bisulfide (HS⁻) with a stoichiometric ratio of 1 mol amine for 1 mol H₂S [63–65]. These reaction mechanisms are applicable irrespective of the co-solvent utilized, being aqueous or non-aqueous systems [66–70]. However, the co-solvent plays a major role in the progression of the reaction and stabilization of the resulting reaction product [71]. Mediating the formation of these reaction products using a physical based model such as polar soft-SAFT is implicitly mimicked through the formation of [acid gas-amine] molecular agglomerates connected through strong and highly directional association interactions, as shown in Fig. 3. This is done through adding specific association “reactive” sites in the acid gas molecule capable of only forming strong localized intermolecular interactions with the lone pair of electrons in the nitrogen atom in the amines, emulating the formation of the reaction product [35,37,38,55]. The number of association “reactive” sites depends on the reaction stoichiometry of the acid gas with the primary and secondary amines examined in this work, as such two sites, α_1 and α_2 , were added on CO₂ for the formation of carbamate, while one site, α_1 , was added on H₂S for the formation of bisulfide. The added reaction sites are characterized by cross-association parameters, with the cross-association volume fixed to a value representative of well-localized short-range interactions (*i.e.*, $\kappa_{N-\alpha_1}^{HB} = 500 \text{ A}^3$) [35,55], while the cross-association energy for each reactive site was fitted to available data for the solubility of acid gas in the examined amine solvents. This approach is used to model acid gas solubilities in solvents including aqueous MEA and aqueous DEA, along with hybrid solvents of MEA, or DEA chemical solvents mixed with NMP or SFL physical co-solvents.

2.4. Multi-criteria solvent evaluation framework

The implemented multi-criteria assessment accounts on solvent properties reflective of their potentiality for acid gas removal. These criteria are divided into three categories: (1) relevant solvent physico-chemical properties, (2) standard key performance indicators, and (3) sustainability metrics, and are applied to the hybrid solvents and their aqueous equivalents. The breakdown for each category, and assessment methods are summarized in Table 1.

2.4.1. Relevant solvent thermophysical and transport properties

In this category, a large set of properties of the solvents are included,

Table 1

Assessment criteria for solvent selection employed in this work along with their intended variation, and assessment method.

| Criteria | Variation | Assessment method |
|---|---------------|---|
| Category I: Relevant physico-chemical solvent properties | | |
| Solvent liquid density (ρ) | Maximized (+) | Polar soft-SAFT |
| Solvent viscosity (μ) | Minimized (-) | Polar soft-SAFT + FVT |
| Enthalpy of vaporization (ΔH^{vap}) | Minimized (-) | Polar soft-SAFT |
| Heat capacity (C_p) | Minimized (-) | Polar soft-SAFT |
| Category II: Standard key performance indicators | | |
| Acid gas cyclic capacity ($\Delta\alpha_{AG}$) | Maximized (+) | Polar soft-SAFT |
| CO ₂ ideal selectivity (S_{CO_2}) | Maximized (+) | Polar soft-SAFT |
| Solvent regeneration energy (Q_{reg}) | Minimized (-) | Polar soft-SAFT + shortcut method of Kim <i>et al.</i> [72] |
| Category III: Sustainability criteria | | |
| Health and safety hazards | Minimized (-) | Method of Koller <i>et al.</i> [73] |
| LCA indicators (Cumulative energy demand, Global warming potential, Eco-indicator 99) | Minimized (-) | FineChem Tool [74,75] |

which are obtained from polar soft-SAFT predictions at relevant conditions, once the models have been validated with available experimental data. For the investigated solvents (chemical solvent + physical co-solvent), the density and viscosity are of critical importance. The density of the solvent affects the sizing of the equipment within the process, solvent circulation rate, and pumping requirements, and should be maximized to reduce these processing aspects, and consequently, decrease the CAPEX and OPEX of the process. Alternatively, the viscosity of the solvent affects the mass transfer within the absorption column and the energy requirements for pumping, and should be minimized to reduce the associated CAPEX and OPEX of the process [44], respectively.

Heat of vaporization and heat capacity are two relevant properties for both chemical solvent and physical co-solvent. The heat of vaporization is one of the components affecting the total energy of regeneration, and is related to the amount of energy required to vaporize the physical co-solvent and provide required driving force within the regeneration column. Similarly, heat capacity contributes to the total regeneration energy, and affects the amount of energy required to increase the temperature of the solvent to that of the reboiler. Both properties should be minimized to reduce the total regeneration energy and consequently the OPEX of the process [72].

2.4.2. Standard key performance indicators

This category includes acid gas cyclic capacity, CO₂ ideal selectivity, and solvent regeneration energy. The cyclic capacity ($\Delta\alpha_{AG}$) is defined as the amount of acid gas effectively removed from the feed gas stream, which has direct implications on all technical and economic aspects of the absorption process. The cyclic capacity for each acid gas is computed as the difference between the acid gas loading at absorption conditions (rich), and the acid gas loading at desorption conditions (lean) [76], as:

$$\Delta\alpha_{AG}(T, P) = \alpha_{AG,Rich}(T, P)_{\text{abs}} - \alpha_{AG,Lean}(T, P)_{\text{des}} \quad (6)$$

The cyclic capacity is inclusive of the acid gas absorption/desorption loadings (α_{AG}), which signifies the amount of acid gas (CO₂ or H₂S) in the solvent at absorption/desorption conditions, typically reported on the basis of moles of absorbed acid gas per mole amine, which is obtained using polar soft-SAFT predictions at representative absorption conditions.

Conversely, CO₂ ideal selectivity (S_{CO_2}) measures the maximum affinity of the solvent towards absorbing CO₂ rather than H₂S, which influences the design of the absorption column and required solvent regeneration energy. The CO₂ ideal selectivity, on the basis of moles of absorbed CO₂ per moles of absorbed H₂S, can be computed from polar soft-SAFT predicted acid gas loading at particular absorption conditions, as follows:

$$S_{CO_2}(T, P) = \frac{\alpha_{CO_2}(T, P)_{\text{abs}}}{\alpha_{H_2S}(T, P)_{\text{abs}}} \quad (7)$$

Lastly, solvent regeneration energy (Q_{reg}) is typically the focal point of solvent assessment which should be minimized due to its massive effect on the OPEX of the process. It is typically reported on the basis of MJ per ton of acid gas captured, and it is effectively related to the total amount of energy needed to remove the absorbed acid gas in the rich solvent, bringing it back to lean conditions, written as [77–79]:

$$Q_{\text{reg}} = Q_{\text{vap}} + Q_{\text{sen}} + Q_{\text{abs}} \quad (8)$$

where, Q_{vap} , is the latent energy required to vaporize the physical co-solvent which depends on the physical co-solvent enthalpy of vaporization, Q_{sen} , is the sensible energy required to increase the temperature of the solvent to that of the reboiler which depends on the heat capacities of the chemical solvent and physical co-solvents, while Q_{abs} , is the energy needed to reverse the absorption reaction and liberate the absorbed acid gas from the rich solvent which depends on the enthalpy of absorption. (ΔH_{abs}). The enthalpy of absorption, on basis of kJ per

mole of absorbed acid gas, is computed from polar soft-SAFT predicted solubility isotherms employing the following thermodynamic relation:

$$\Delta H_{abs} = R \left[\frac{\partial \ln P_{AG}}{\partial (\frac{1}{T})} \right]_{P, \alpha_{AG}} \quad (9)$$

where P_{AG} represents the pressure of the acid gas, T the temperature, R the ideal gas constant and α_{AG} the acid gas loading.

The total solvent regeneration energy is estimated using the shortcut method proposed by Kim *et al.* [72], in a manner consistent with our previous contributions [35,37,38]. The reader is referred to the original paper for additional details on the implementation of this method [72].

Preferred solvents are those with high cyclic capacity and CO₂ ideal selectivity, and low solvent regeneration energy due to their impact on increasing the efficiency of the process and reducing associated CAPEX and OPEX [72].

As previously highlighted, all required information to compute these criteria (using Eqs. (6) – (9)) are obtained directly from polar soft-SAFT predictions for the examined solvents (aqueous MEA/DEA, NMP + MEA/DEA, and SFL + MEA/DEA) once the developed models are validated with experimental data. Additionally, these criteria are affected by the choice of operating conditions of the absorption process such as, concentration of CO₂ and H₂S in the raw feed gas, absorber/reboiler temperatures, and absorber/ stripper operating pressures. It was assumed that the feed gas had equimolar composition of both acid gases ($P_{CO_2} = P_{H_2S}$), with their individual partial pressures changing in the range of 10 – 50 kPa, to examine the acid gas absorption capabilities of these solvents at conditions representative of different feed gas sources. The absorber temperature was fixed to $T_{abs} = 313$ K, while the absorber operating pressure was fixed to $P_{abs} = 100$ kPa. Conversely, the stripper was assumed to operate at a total pressure of 200 kPa, while the reboiler temperature in the stripper was allowed to change depending on the desorption temperature for each acid gas solubility in each solvent required to obtain 50% reduction in rich loading, and as such the cyclic capacity can be obtained as $\Delta\alpha_{AG} = 0.5\alpha_{AG,Rich}$, consistent with our previous works [35,37]. It should be noted that for the purpose of this work, the chosen conditions were those mimicking post-combustion capture, however, the approach developed in this work has sufficient flexibility to examine other conditions such as those encountered for natural gas processing, biogas upgrading, and syngas separation.

2.4.3. Sustainability assessment criteria

The inclusion of sustainability-related assessment criteria is usually overlooked, but highly needed as it provides insights on the associated environmental burdens with solvent production, along with required safety measures to ensure safe operation and handling of the utilized solvent [30,47,48]. In this work, the sustainability metrics included in the solvent assessment are divided into health and safety (HS) hazard assessment, and a cradle-to-gate life cycle assessment (LCA) on the cumulative environmental impact of solvent production.

The HS index represents the collective health hazards due to long-term effects on personnel, and safety hazards from accidental material or energy release. In the safety category, the properties include mobility, fire and explosion, and reaction/decomposition. In the health category, properties include acute toxicity, irritation, and chronic toxicity effects. The quantification of the associated HS indices was performed based on the methodology of Koller *et al.* [73] wherein a list of physical and chemical properties of the substances are used to estimate a comprehensive list of dangerous properties for each hazard category.

As mentioned, the LCA metrics included in this work are based on a cradle-to-gate life cycle for the production of the solvents, from extraction of raw material till solvent delivery to the process gate, excluding impact associated with the operation of the absorption process and any associated wastes. The chosen LCA metrics include the cumulative energy demand (CED), the global warming potential (GWP),

and the Eco-indicator 99 (EI-99). CED is a resource-oriented indicator reflecting the total primary energy demand during the solvent production cycle. GWP quantifies the effect of greenhouse gas emissions, considered here for a period of 100 years. Lastly, EI-99 provides an aggregated score for the end-point impact categories of human health, ecosystem quality and resource consumption. These metrics were obtained directly from the FineChem tool [74,75], using molecular descriptors for each pure substance in the examined hybrid solvents. It should be noted that a more detailed assessment is needed; however, this is too extensive for the purpose of an initial solvent assessment, and hence, it is out of the scope of this work.

3. Results and discussions

3.1. Polar soft-SAFT thermodynamic modeling for acid gas removal using hybrid solvents

As previously highlighted, polar soft-SAFT is the main element in obtaining the relevant thermodynamic properties to assess the potentiality of the examined hybrid solvents. Prior to using the model for the intended assessment, its accuracy and robustness has to be systematically validated with available experimental data from pure fluids (as already presented in Section 2.3), relevant binary mixtures, and finally, absorption of acid gases in the examined hybrid solvents.

3.1.1. Acid gas + physical co-solvent binary mixtures

The modeling accuracy of polar soft-SAFT in capturing the solubility of CO₂ and H₂S in pure physical co-solvents, NMP and SFL, was first examined and relevant results are presented here. This is needed to build the thermodynamic model for acid gas absorption in the investigated hybrid solvents formulated from the addition of these physical co-solvents. The highest modeling accuracy, with an average absolute deviation (AAD) of 1.5%, was obtained using a temperature independent binary energy interaction parameter, ξ (Eq. (2b)), for each binary mixture regressed to experimental data [80] at an intermediate isotherm, $T = 323$ K, and transferred to other isotherms, as shown in Fig. 4. The values for binary energy interaction parameters describing solubility of CO₂ in NMP and SFL were very close to unity indicating the ability of the model to accurately capture the molecular interactions governing acid gas physical solubility in these solvents. NMP is generally a better physical solvent than SFL due to its higher CO₂ and H₂S solubilities at similar conditions. Binary interaction parameters needed to describe the solubility of these acid gases in water co-solvent, for the formulation of aqueous amines, were transferred from previous works [35,36]. All binary interaction parameters for CO₂ and H₂S solubility in the examined physical co-solvents (NMP, SFL, and water) are included in Table S3 in the SI.

3.1.2. Chemical solvent + physical co-solvent binary mixtures

The thermodynamic behavior of the binary mixtures of the studied hybrid solvents MEA + NMP, MEA + SFL, DEA + NMP, and DEA + SFL was performed using the polar soft-SAFT approach and results are presented in the SI, where the modeling approach for the crossed interactions is also explained (see Figure S2 and associated comments in the SI). For the case of MEA + NMP, the highest modeling accuracy was obtained when the cross-association between NMP's carbonyl group with the hydrogen bond donor sites in either ethanol or MEA were accounted for in the model, with AADs of 1.2% and 0.9% for NMP + ethanol [83], and NMP + MEA [81], respectively, modeled with the same transferable cross-association energy correction factor of $\alpha_{ij}^{HB} = 1.075$ (see Eq. (3b)). The same approach was employed for binary mixture of NMP with DEA, using the cross-association parameters between NMP's carbonyl group and DEA's secondary group transferred from diethylamine [51].

In the case of binary mixtures of MEA or DEA with SFL, due to the

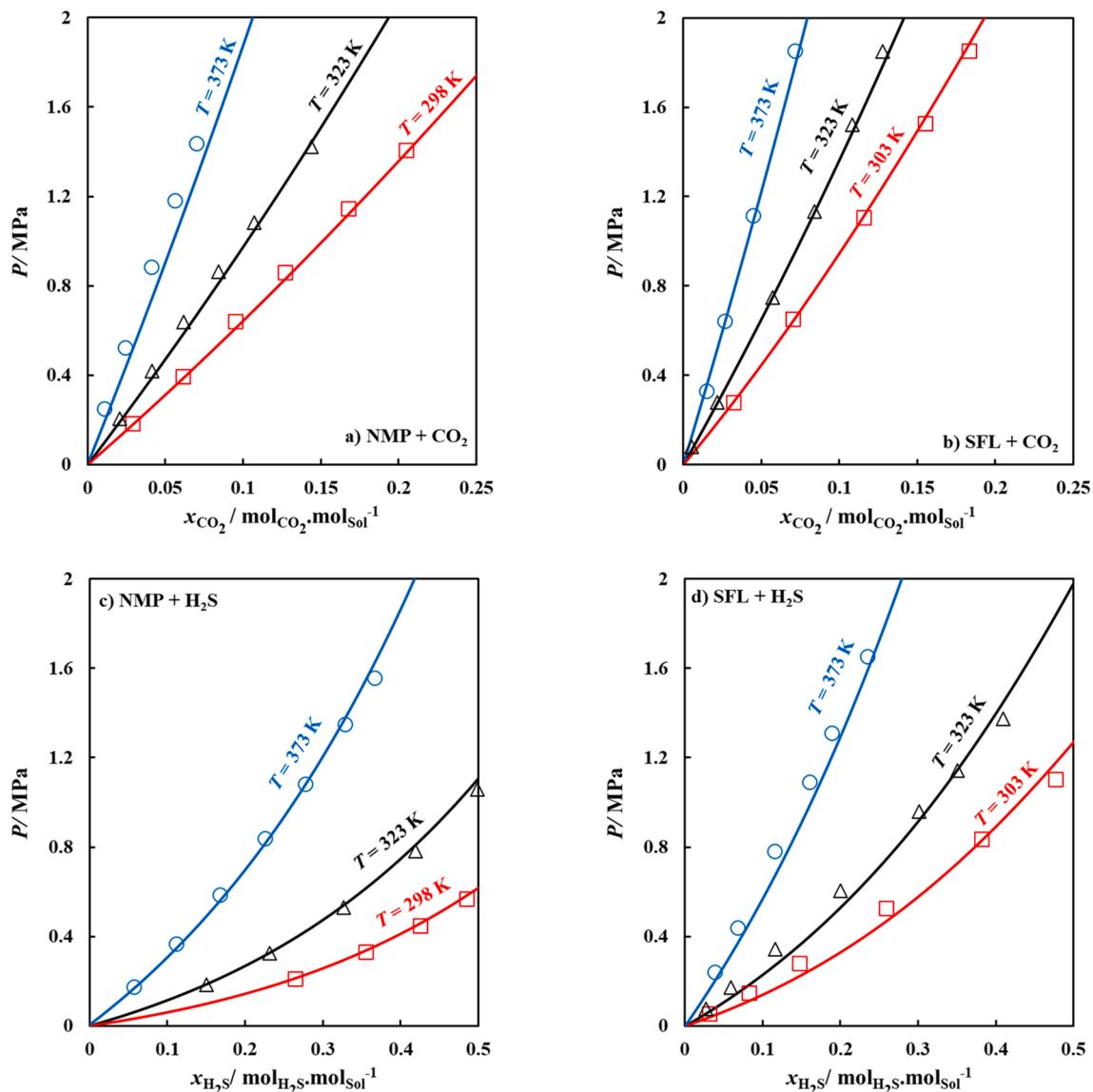


Fig. 4. Solubility of acid gases in pure physical co-solvent at different conditions, with a) CO₂ + NMP, b) CO₂ + SFL, c) H₂S + NMP, and d) H₂S + SFL, modeled using binary interaction parameters shown in Table S3 in the SI. Polar soft-SAFT calculations (lines) compared to experimental data [80].

steric hindrance of SFL, each SFL carbonyl group was modeled with one association site. Employing the same approach, cross association between SFL's carbonyl groups with the amine groups from MEA and DEA were transferred from ethylamine and diethylamine, respectively. Conversely, cross-association between SFL's carbonyl groups and the hydroxyl groups of MEA and DEA were transferred from those fitted for binary mixtures of SFL + ethanol with a cross-association energy correction factor, $\alpha_{ij}^{HB} = 1.045$, fitted to experimental VLE data [81], in a manner consistent with that for NMP + ethanol. The VLE behavior of SFL + ethanol binary mixture is included in Figure S3 in the SI, along with cross-association parameters for chemical + physical co-solvents provided in Table S4 in the SI, with those for aqueous amines transferred from earlier works [51,55].

With the cross-association interactions developed for the examined hybrid solvents, polar soft-SAFT was used to estimate other thermodynamic properties such as molar liquid density and viscosity, highlighted in Fig. 5. The quantitative agreement between predictions from the model and experimental data [82], with an AAD of 2.5% for all mixtures, for both properties further attest the accuracy of the model in evaluating the thermodynamic behavior of the investigated systems.

3.1.3. CO₂ absorption in hybrid solvents

Modeling the chemisorption of CO₂ in the examined hybrid solvents was done based on the modeling framework from our previous contributions [35–38,55] as explained in Section 2.4. The most feasible approach, consistent with previous works [35,37], was regressing asymmetrical cross-association energies for both sites ($\varepsilon_{N-\alpha_1}^{HB}/k_B \neq \varepsilon_{N-\alpha_2}^{HB}/k_B$) to available CO₂ solubility isotherms in the studied solvents, with the energy for one site fixed to a constant value, while the energy for the other site was allowed to change as a function of temperature. The optimized cross-association energy parameters for N- α_1 interactions for the hybrid solvents, along with those for aqueous amines transferred from earlier contribution [35], are provided in Table S5 in the SI.

Highlighted in Fig. 6 are polar soft-SAFT calculations for the solubility of CO₂ in hybrid solvents of MEA or DEA as chemical solvents, with NMP or SFL as physical co-solvents, for 30 wt% amine, and DEA + SFL with 50 wt% DEA (Fig. 6d), depending on the available experimental data. The model computations were consistently capable of capturing the shape of the CO₂ solubility isotherm exhibited by the experimental data for each hybrid solvent [83–86]. It should be noted that for MEA-based hybrid mixtures, a loss of modeling accuracy was

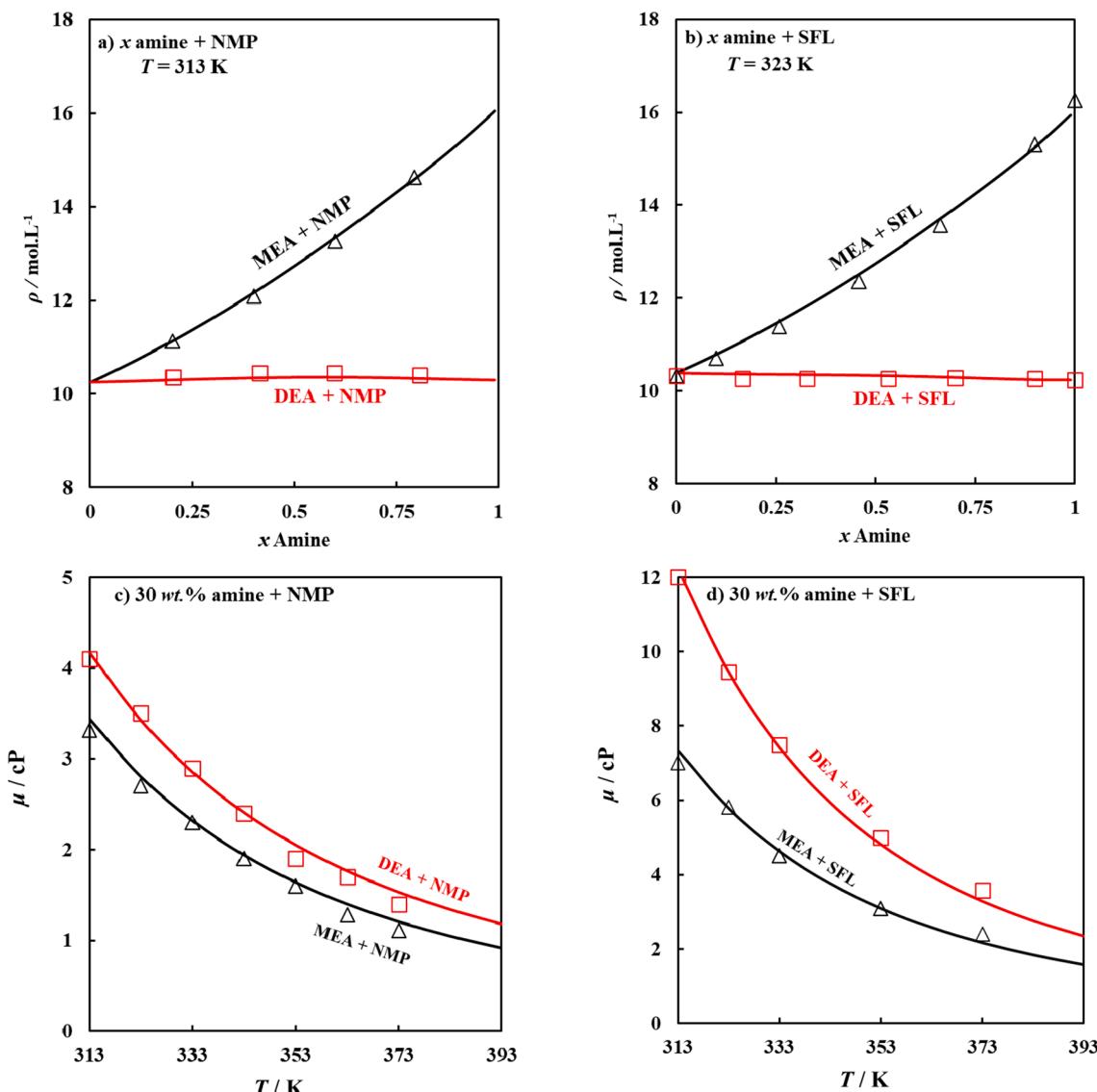


Fig. 5. a) Liquid density of MEA + NMP (black) and DEA + NMP (red) hybrid solvents, b) liquid density of MEA + SFL (black) and SFL + DEA (red) hybrid solvents, c) viscosity of NMP-hybrid solvents, and d) viscosity of SFL-hybrid solvents. Polar soft-SAFT predictions (solid lines), compared to experimental data [82] (symbols).

observed at CO₂ loading higher than the theoretical equilibrium loading, 0.5 mol_{CO₂}.mol_{Amine}⁻¹, as the model does not explicitly account for the formation of bicarbonate.

3.1.4. H₂S absorption in hybrid solvents

The chemisorption of H₂S in the examined hybrid solvents was done employing the same modeling approach provided in **Section 2.4**. The cross-association energies for the single reactive sites governing H₂S chemisorption in MEA + NMP and DEA + NMP hybrid solvents were optimized to available experimental H₂S solubility isotherms in these solvents [85–87], as provided in **Table S6 in the SI**. In the case of SFL-based hybrid solvents, an additional site was added to H₂S to model its solubility in these hybrid solvents, requiring two symmetrical temperature dependent sites ($\epsilon_{N-a_1}^{HB}/k_B = \epsilon_{N-a_2}^{HB}/k_B$) for H₂S chemisorption in MEA + SFL, while two asymmetrical sites ($\epsilon_{N-a_1}^{HB}/k_B \neq \epsilon_{N-a_2}^{HB}/k_B$) were needed to model H₂S solubility in DEA + SFL, also included in **Table S6 in the SI**. Provided in **Fig. 7** is the comparison between experimental data [85–87] and polar soft-SAFT calculations for H₂S solubility in the examined hybrid solvents at different temperatures as a function of H₂S molar composition, in excellent agreement with each other, attesting the accuracy of the modeling approach. It should be noted that all examined

hybrid solvents were at an amine concentration of 30 wt%, except for MEA + NMP, which was at 15 wt% MEA, depending on the availability of experimental data. Additionally, it was previously shown that the transferability of these parameters was still preserved if the amine concentration is within acceptable limits, ± 15 wt% of the concentration used in parameter optimization [36]. The prime advantage of molecular-based models is that they offer sufficient flexibility to predict the behavior of these solvents at conditions not included in the fitting, facilitating assessing the performance of these solvents at conditions of industrial relevance.

3.2. Multi-criteria assessment of hybrid solvents for acid gas removal

After developing and validating the polar soft-SAFT thermodynamic models for the concerned hybrid solvents using available experimental data, the solvents were assessed based on the multi-criteria approach explained in **Section 2.4** and **Table 1**. The solvents are ranked based on their performance in a stepwise assessment separately for each category. Subsequently, the ranking from each category is examined to determine the overall potentiality of hybrid solvents compared to their aqueous counterparts for acid gas removal.

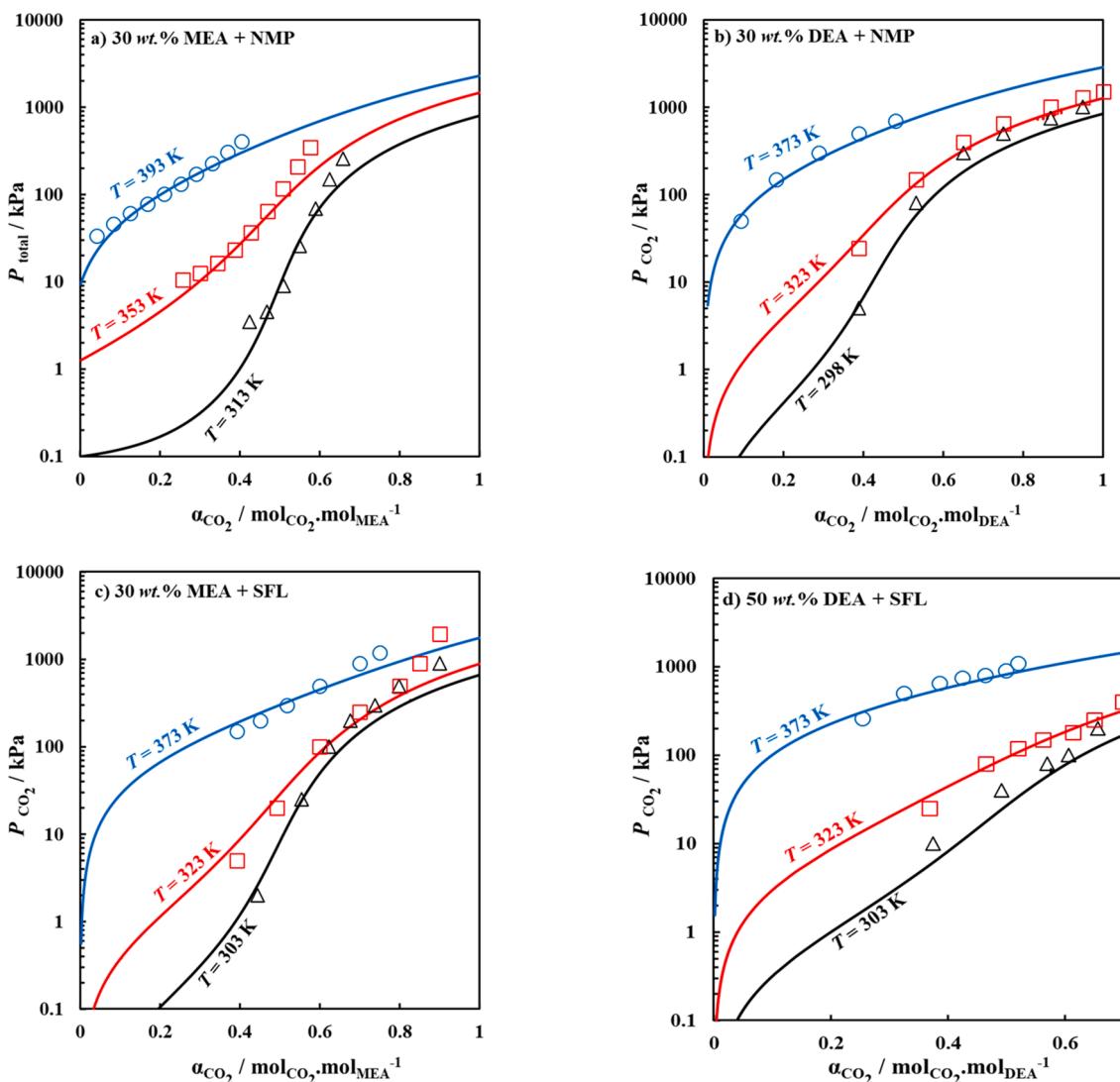


Fig. 6. CO_2 loading at different temperatures in hybrid solvents of a) MEA + NMP, b) DEA + NMP, c) MEA + SFL, and d) DEA + SFL. Calculations using polar soft-SAFT with parameters from Table S5 in the SI (solid lines), compared to experimental data [83–86] (symbols).

3.2.1. Assessment based on relevant solvent properties

The first criteria category, namely, relevant physico-chemical properties of the examined solvents, includes solvent density and viscosity, along with heat capacity and enthalpy of vaporization of chemical solvents and physical co-solvents. Once the robustness of the polar soft-SAFT performance was assessed (see Figs. 4–7), the model was used to predict these properties at typical processing conditions, for the different solvents with 30 wt% amine.

The trends for the mass liquid density and viscosity of the hybrid solvents at 30 wt% amine, shown in Fig. 8a and 8b, are consistent with the type of chemical solvents and physical co-solvents. In terms of chemical solvents, DEA-based solvents had higher liquid density and viscosity compared to MEA-based solvents. In terms of physical co-solvents, the descending order for both properties depends on the physical co-solvent, as SFL > NMP > H_2O . The trade-off between both properties is directly observed, that solvents with higher mass liquid density tend to have higher viscosity. The work of Mota-Martinez *et al.* [44] highlighted the significant contribution of solvent viscosity (from sensitivity analysis for properties of 30 wt% aqueous MEA) to the overall economics of the absorption process, being of higher order of importance compared to liquid density. As such, the observed increase in liquid density for hybrid solvents over their aqueous benchmarks will have a marginal effect on reducing the CAPEX of the process (roughly

5% reduction). Conversely, the large increase in viscosity for hybrid solvents will have a larger contribution to the CAPEX of the process with CAPEX increasing at least by 20%. Per se, judging solely based on solvent viscosities, aqueous amines had the lowest viscosities, promising more efficient mass transfer among the solvents studied here, which translates to lower CAPEX associated with the height of the absorption column, and lower OPEX due to less energy requirements for solvent pumping.

The solvent thermal properties, *i.e.*, heat capacity and enthalpy of vaporization, depicted in Fig. 8c and 8d, reveal that among both chemical solvents, DEA has lower heat capacity and enthalpy of vaporization than MEA. Similarly, for physical co-solvents, the benefit of using alternative organic diluents is clearly asserted with NMP and SFL having more than 80% lower heat capacity, and more than 60% lower enthalpy of vaporization, as compared to water. This clearly demonstrates the potential of water-free hybrid solvents in reducing solvent regeneration energy, due to the lower thermal properties of alternative physical co-solvents. This reduction should be manifested in the sensible and latent energy components of the solvent regeneration energy (Eq. (8)), with expected reductions in OPEX.

Provided in Fig. 9 is a comparative ranking of the four solvent properties highlighted earlier, with the ranking obtained based on polar soft-SAFT predicted properties at $T = 313$ as shown in Fig. 8. This

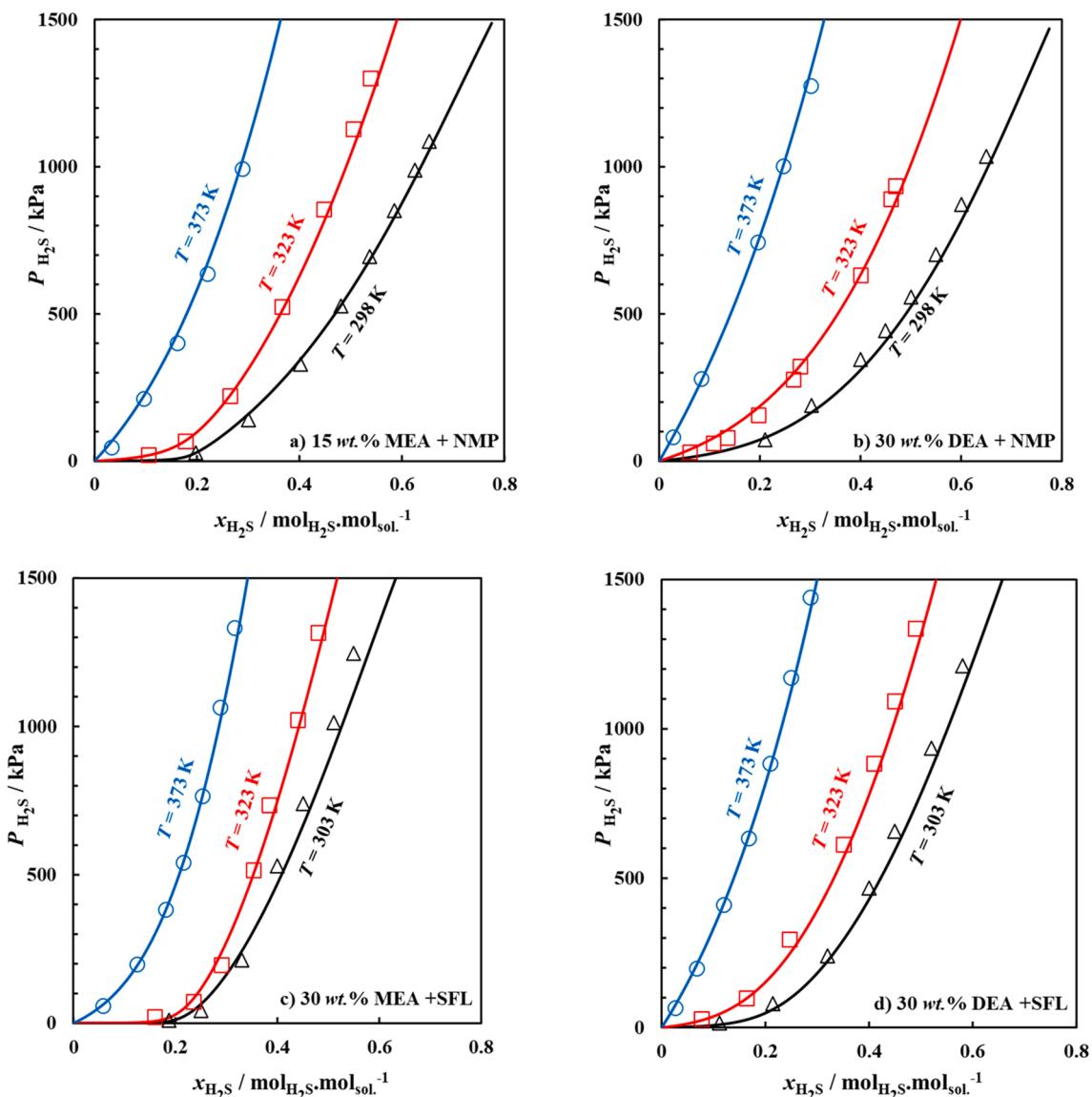


Fig. 7. H₂S solubility at different temperatures in hybrid solvents of a) MEA + NMP, b) DEA + NMP, c) MEA + SFL, and d) DEA + SFL. Calculations using polar soft-SAFT with parameters from Table S6 in the SI (solid lines), compared to experimental data [85–87] (symbols).

ranking reveals the advantage of aqueous solvents in terms of solvent viscosity, with the lowest obtained for aqueous MEA and DEA, while the highest was obtained using SFL as a co-solvent. Conversely, hybrid solvents using NMP or SFL as co-solvents are more beneficial in terms of lower thermal properties, and higher densities. Considering these diverging tendencies, the best compromise for solvent properties would be with NMP-based hybrid solvents, as they promise significant reduction in solvent regeneration energy due to the reduced thermal properties of the co-solvent, albeit on the expense of increased solvent viscosity (double that of aqueous amines) which could potentially increase the CAPEX of the process by 20%. This is still better than employing SFL as a physical co-solvent, as it increases the viscosity of the solvent almost 4 times higher than its aqueous equivalent, which could potentially result in doubling the capital cost of the absorption process [44] and making it unpractical from the operational point of view. Notwithstanding, these general properties are often overlooked from the selection of solvents for acid gas removal, particularly, solvent viscosities, but still remain indecisive, on their own, to determine an optimal solvent for such an application.

3.2.2. Assessment based on standard key performance indicators

As previously highlighted, the criteria in this category include acid gas cyclic capacity, CO₂ ideal selectivity, and solvent regeneration energy, which are typical metrics to evaluate the potential of solvents. The most promising solvent is the one with high acid gas cyclic capacity, high CO₂ ideal selectivity, and low solvent regeneration energy. All required properties to evaluate these criteria were predicted directly from polar soft-SAFT under the same conditions, along with using thermodynamic relations from Eqs. (6) – (9).

Polar soft-SAFT was used to predict CO₂ and H₂S absorption capacity in the selected solvents (aqueous and hybrid) as a function of acid gas partial pressure were done at $T = 313$ K, and 30 wt% amine, as shown in Fig. 10. As inferred from the figure, irrespective of the absorbed acid gas, hybrid solvents have a higher absorption capacity than their aqueous counterparts at high acid gas partial pressures greater than 100 kPa, hinting at their aptness for high pressure absorption rather than low pressure, similar to those encountered in pre-combustion capture, or natural gas sweetening. Conversely, aqueous amines are more effective for low pressure absorption, such as that encountered for post-combustion capture. Under the imposed acid gas partial pressures (see Section 2.4.2), in the range of 10 – 50 kPa, CO₂ absorption, irrespective

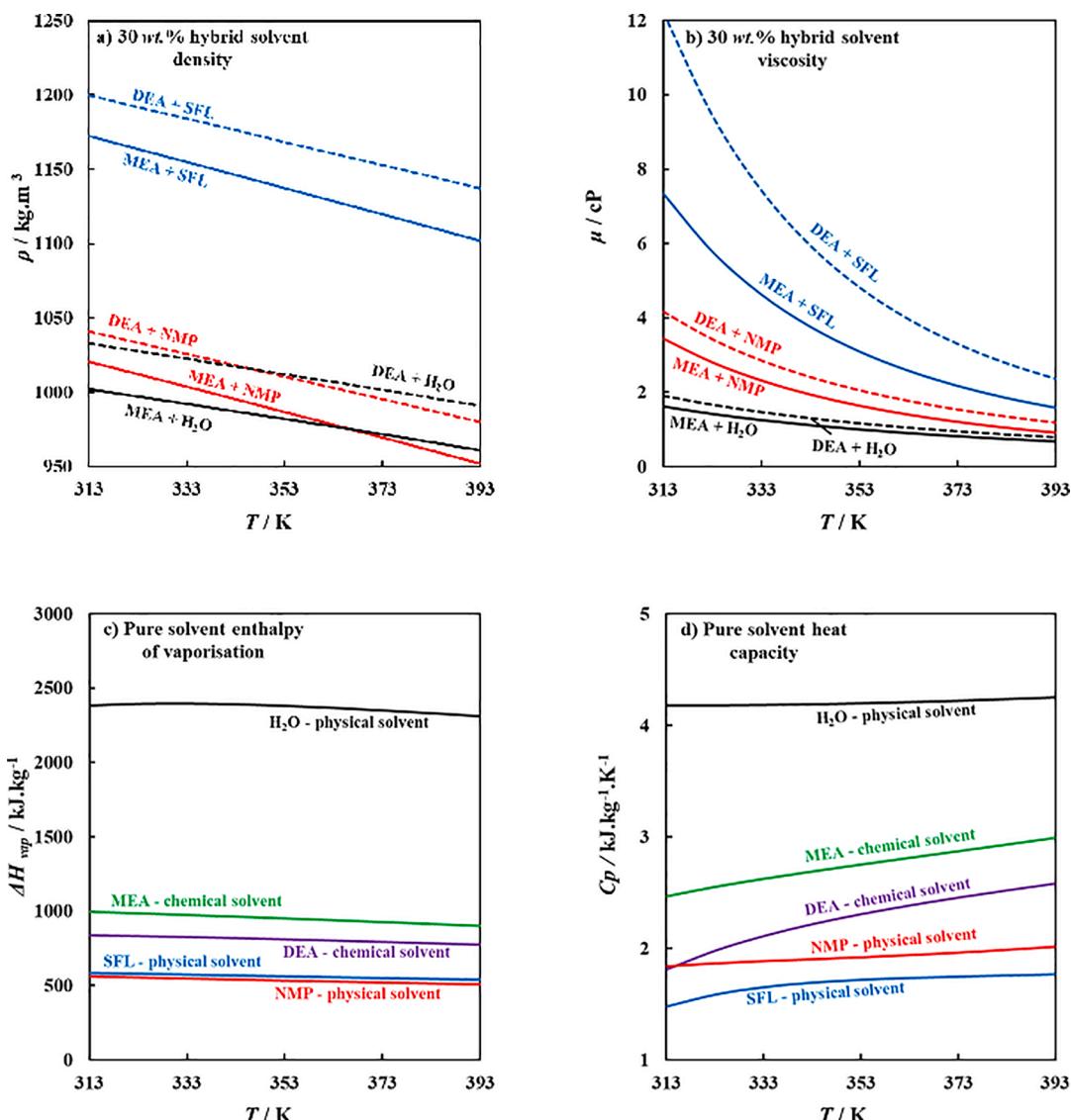


Fig. 8. Polar soft-SAFT predicted thermodynamic properties of aqueous and water-free solvents included in this work, for a) mass liquid density of solvent at 30 wt% amine, b) viscosity of solvent at 30 wt% amine, c) pure fluid enthalpy of vaporization, and d) pure fluid heat capacity.

of the amine, is in the order of $\text{H}_2\text{O} > \text{NMP} > \text{SFL}$ co-solvents. Conversely, for H_2S absorption, the highest absorption was obtained for aqueous amines, while the lowest obtained for MEA + SPL , and DEA + NMP .

The other criteria examined in this category is the CO_2 ideal selectivity, shown in Fig. 11, obtained using Eq. (7) from polar soft-SAFT predicted absorption isotherms shown in Fig. 10. As mentioned in Section 2.4.2, the feed gas was assumed to have equimolar composition of both CO_2 and H_2S , with their individual partial pressure varying in the range of 10 – 50 kPa, with an absorber total pressure of 100 kPa. Of course, this is one particular condition, and the results obtained herein can be different depending on the imposed absorption conditions, however, this is done to showcase the capabilities of the predictive thermodynamic model in obtaining such information for the assessment of solvents for acid gas removal. Additionally, the CO_2 selectivity can be lower than the ones reported herein in the case of examining mixed acid gas absorption. It can be seen that for MEA-based solvents, shown in Fig. 11a, the CO_2 ideal selectivity is below 1.0, which indicates that these solvents have a slightly higher affinity towards H_2S than CO_2 absorption. Increasing acid gas partial pressures, has a higher impact on reducing the CO_2 ideal selectivity in the case of MEA + NMP , with H_2S

absorption becoming more favorable. Conversely, the reduction in CO_2 ideal selectivity with aqueous MEA and MEA + SPL , is marginal shifting to almost plateau with increased acid gas concentrations. It can be generally inferred that the order of CO_2 ideal selectivity for MEA-based solvents is with $\text{SFL} > \text{NMP} > \text{H}_2\text{O}$.

Similar tendencies are observed with DEA-based solvents (provided in Fig. 11b); however, the order of CO_2 ideal selectivity is more consistent with the change in acid gas concentration, with $\text{NMP} > \text{SFL} > \text{H}_2\text{O}$. These general trends indicate that water-free amines have a higher maximum affinity to CO_2 compared to their aqueous counterparts, at the examined conditions.

The absorption enthalpy for each acid gas, illustrated in Fig. 12, were assessed based on the thermodynamic relation shown in Eq. (9), using the predicted solubility isotherms depicted in Fig. 10. The relevance of this criteria relies on the fact that absorption enthalpy contributes to the total solvent regeneration energy (see Eq. (8)). Irrespective of the solvent, increasing the acid gas loading decreases the absorption enthalpy for the solvent. Regardless of the absorbed acid gas, MEA-based solvents consistently had higher absorption enthalpies compared to DEA-based solvents. Additionally, aqueous solvents had the higher absorption enthalpy compared to their hybrid counterparts, except in the case of

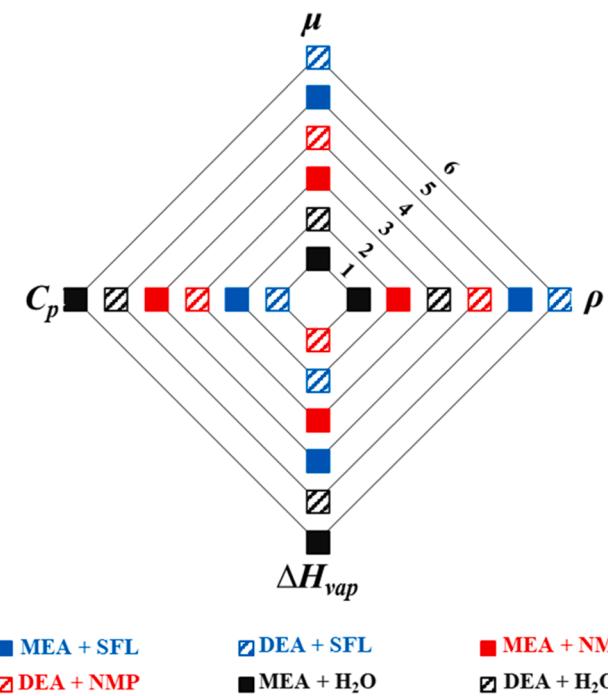


Fig. 9. Solvent thermodynamic properties comparative assessment of aqueous (black symbols for water co-solvent) and hybrid solvents (red symbols for NMP co-solvent, and blue symbols for SFL co-solvent) for acid gas removal, with 1–6 denoting increased value for the property.

H₂S absorption in aqueous MEA. Focusing solely on CO₂, the order of absorption enthalpy in terms of utilized physical co-solvents is H₂O > NMP > SFL, for both MEA and DEA chemical solvents, which is consistent with their absorption capacities at low CO₂ partial pressure, shown in Fig. 10a and 10b. Conversely, for H₂S absorption in MEA-based solvents, the highest enthalpy was observed for MEA + SFL, while the lowest was for MEA + NMP, up to H₂S loading of 0.6 mol_{H2S}.mol_{Amine}⁻¹, consistent with the inflection point observed in H₂S absorption in MEA-based solvents, depicted in Fig. 10c. Contrary to that, the highest H₂S absorption enthalpy in DEA-based solvents was for aqueous DEA, while the lowest was for DEA + NMP.

Towards effectively assessing the potentiality of hybrid solvents for acid gas removal, the trade-offs between the three standard KPIs, namely, acid gas cyclic capacity, CO₂ ideal selectivity, and solvent regeneration energy as shown in Fig. 13, was assessed based on the previously obtained results shown in Figs. 10–12, and by using Eqs. (6)–(8). For acid gas absorption, increasing the partial pressure of the acid gas in the incoming feed gas, irrespective of the solvent, makes the absorption process more efficient, in terms of increased cyclic capacity, and decreased regeneration energy. Additionally, for both MEA and DEA-based solvents, the aqueous solvents demonstrated higher cyclic capacity, but on the expense of higher solvent regeneration energy. Contrary to that, the hybrid solvents demonstrated reduced cyclic capacities, however, they are associated with much higher reduction in regeneration energy. In terms of CO₂ ideal selectivity, all the solvents demonstrated relatively similar selectivity towards CO₂, except for DEA + NMP which had a higher affinity to absorb CO₂ compared to H₂S.

The incremental change for each KPI for the hybrid solvents with respect to their aqueous counterparts, are relatively large at low acid gas partial pressures, however, these differences slowly diminish with increased acid gas partial pressure. Judging based on incremental changes, the highest gain (reduced regeneration energy) compared to the lowest loss (reduced cyclic capacity and CO₂ ideal selectivity) is obtained using NMP as a physical co-solvent compared to water in the case of CO₂ and H₂S absorption. This is due to the inherent compromise

between reducing the absorption energy and increasing the cyclic capacity. As such, it can be seen that the most promising solvent based on these KPIs would be the MEA + NMP hybrid solvent.

3.2.3. Assessment based on sustainability metrics

In addition to the technical performance previously explained, the solvents were also assessed using sustainability metrics, including HS index based on the work of Koller *et al.* [73], along with LCA metrics obtained from FineChem tool [74,75]. The estimated values for each solvent, chemical and physical are included in Table S7 in the SI. The solvents were ranked based on aggregated performance in each metric assuming 30 wt% amine, with the goal of minimizing environmental, health, and safety impacts as included in Fig. 14.

Among the examined solvents, the sustainability performance of aqueous amines is far greater than their hybrid equivalents, this mainly due to the type of physical co-solvents, *i.e.*, water, with its more benign and environmentally friendly production and handling, as water is the greenest available solvent. The picture is completely changed with the use of other physical co-solvents such as NMP and SFL, resulting in increased safety and health hazards, along with larger environmental impact with solvent production. Focusing solely on both physical co-solvents, NMP outperforms SFL as a co-solvent in terms of GWP associated with solvent production, and its health index, due to its higher dosage limits for acute toxicity and irritation. Conversely, SFL can be deemed better than NMP in terms of lower CED for solvent production, better safety index due to its higher boiling point, flash point, and auto-ignition temperature, which are precursors for hazards such as mobility, fire and explosion, and reaction decomposition. Exploring opportunities for “greener” organic diluents such as alcohols or ketones might be noteworthy [88], albeit their performance in the other assessment categories. For the examined chemical solvents, the use of DEA as opposed to MEA presented better overall performance with the imposed sustainability metrics. Notwithstanding, the results of this simplified analysis, though carrying some level of errors, still can help guide the synthesis of new emerging solvents and shed light on an extremely under-examined solvent selection criterion.

3.2.4. Overall comparison and assessment

In this session we present and discuss the ranking of the solvents based on their performance in each of the three categories. For the sake of simplicity, all criteria were given an equal contribution, and ranked accordingly. Please, notice that the results will be completely different if different weights were given to each contribution (for instance, double weight to technical performance versus HS, or other options), however, this is the first approach on considering all these categories to rank solvents for acid gas removal.

For simplicity, the solvent ranking based on solvent properties was limited to viscosity due to its higher contribution to CAPEX and OPEX compared to density. Additionally, the effect of thermal properties such as heat capacity and enthalpy of vaporization were implicitly accounted for in computing the solvent regeneration energy, which is one of the standard KPIs. The solvents ranking per each category is presented in Fig. 15. The hybrid solvents MEA + NMP and MEA + SFL were the best performing solvents in terms of standard KPIs for CO₂ and H₂S absorption, due to the trade-off between the slight reduction in cyclic capacity as compared to the larger reduction in solvent regeneration energy. Conversely, aqueous amines had the best performance in terms of solvent properties, in particular, due to their lower viscosities. With this taken into account, the intermediate viscosity of MEA + NMP along with its best performance in terms of KPIs for acid gas removal might deem this solvent as a potential replacement for aqueous MEA.

Albeit that, the inclusion of sustainability metrics was a game changer that altered the entire ranking of the solvents, with MEA + NMP being the most hazardous in terms of environmental, health and safety factors, while aqueous MEA is one of the most environmentally benign solvents. However, the addition of these metrics shed a light on an

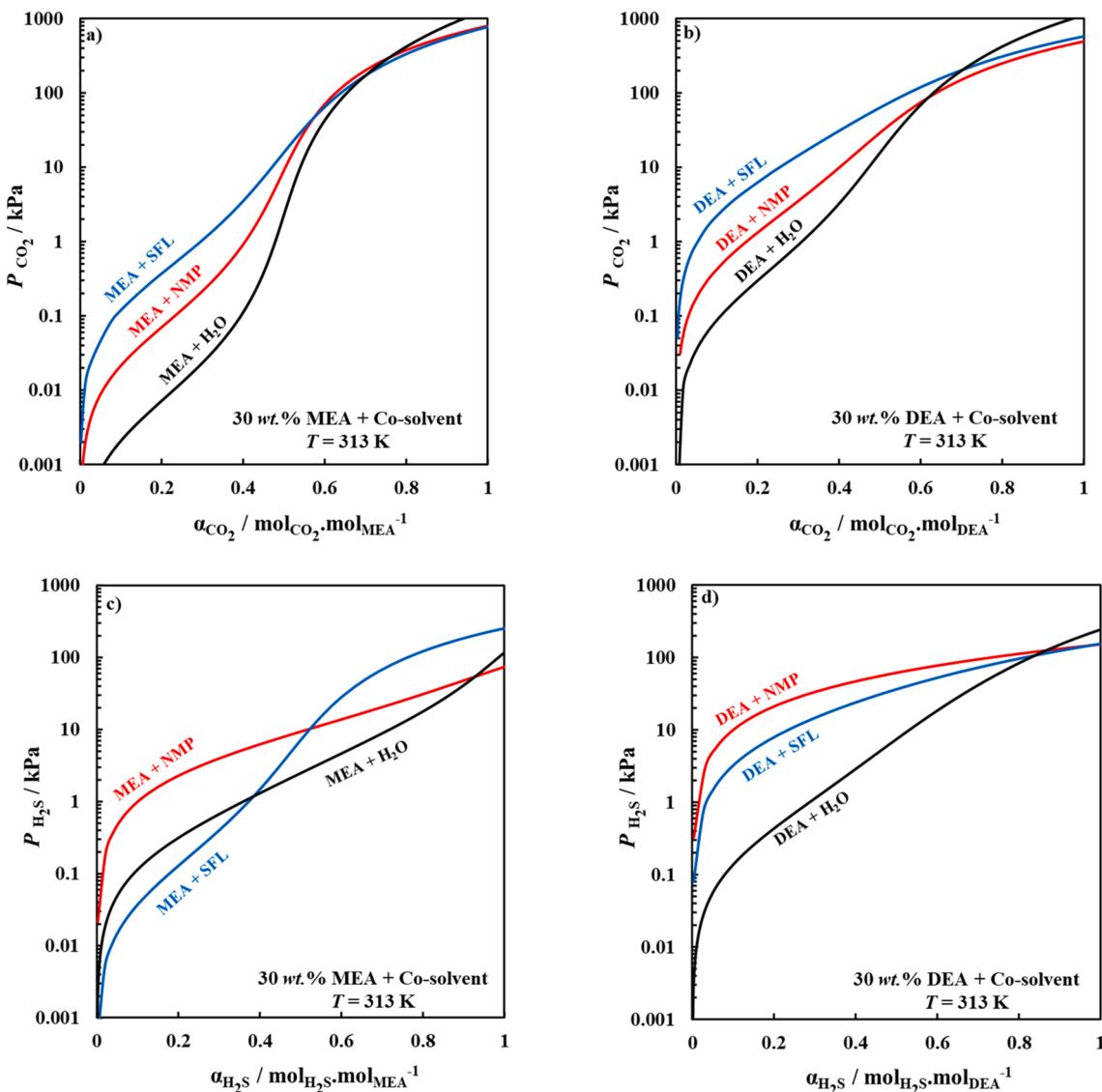


Fig. 10. Absorption capacity of acid gases in aqueous and hybrid solvents at $T = 313\text{ K}$ and 30 wt% amine for a) CO_2 absorption in MEA-based solvents, b) CO_2 absorption in DEA-based solvents, c) H_2S absorption in MEA-based solvents, and d) H_2S absorption in DEA-based solvents, as predicted from polar soft-SAFT (solid lines).

additional trade-off that is typically overlooked in the selection of solvents for CO_2 and H_2S removal, as such the benchmark aqueous MEA remains to be the one with the most acceptable trade-offs between all selection criteria. This is somehow expected, being water an environmentally friendly solvent, but the approach offers a path to take into account sustainability metrics when searching for alternative solvents.

Hence, the question remains to the actual importance regarding the inclusion of sustainability metrics. The current trend in choosing solvents for acid gas removal reduces all of the possible metrics to a single value, being the unit cost of acid gas removal based on techno-economic assessment. One can argue that the importance of sustainability metrics can be restricted to limited stages throughout the acid gas removal value chain, mainly during solvent production, along with any possible emissions or wastes during process deployment. However, such considerations are still needed as they can dictate the design of safety layers for process operation, waste disposal, and other aspects that can detract from the possible benefits of deploying these alternative solvents.

With this, the inclusion of sustainability metrics should be enforced even during solvent selection stages, and the search for “greener” co-solvents might open the path for finding promising hybrid solvents capable of usurping the golden standard, aqueous MEA.

4. Conclusions

In this work, a multi-criteria assessment framework, considering technical performance and sustainability metrics, has been employed to assess the potentiality of hybrid solvents for acid gas removal. The examined solvents were formed from the combination of chemical solvents, such as MEA and DEA, with physical co-solvents, such as NMP and SFL. Polar soft-SAFT was used a thermodynamic model, validated using available experimental data in a systematic manner from pure fluids, relevant binary mixtures, and acid gas (CO_2 and H_2S) absorption in the investigated hybrid solvents, and used to predict the required thermo-physical properties at process separation conditions. Subsequently, the performance of the selected hybrid solvents and their aqueous equivalents were assessed for acid gas removal in terms of three general categories, (1) solvent properties, (2) standard key performance indicators, and (3) sustainability metrics. The solvent assessment was carried out stepwise for each category, revealing trade-offs between the different criteria.

For solvent properties, the reduced thermal properties of hybrid solvents offered an opportunity to reduce the overall regeneration energy, yet on the expense of increased solvent viscosity. For standards

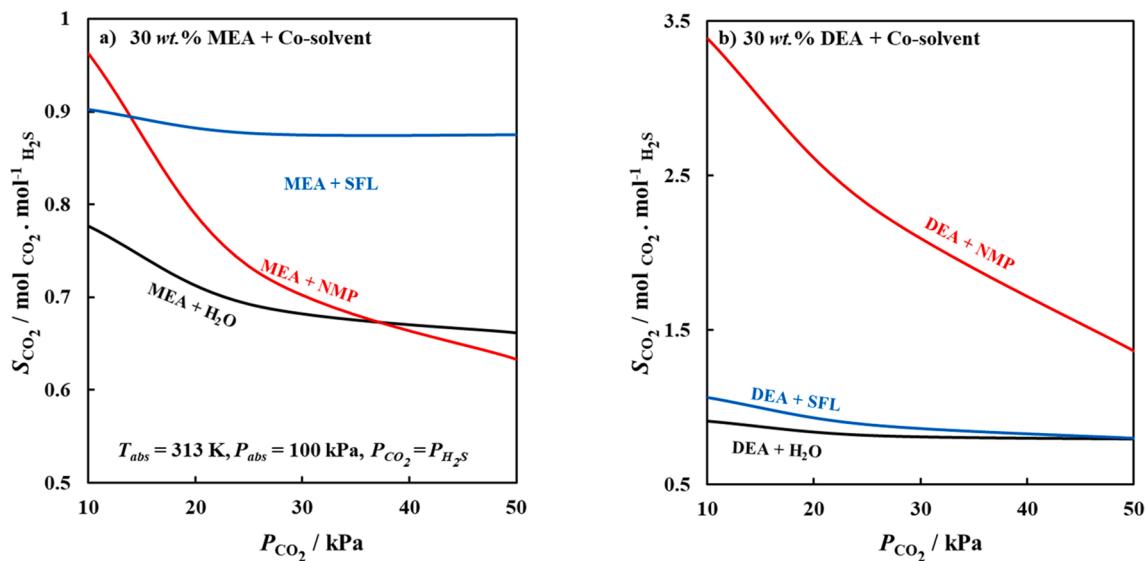


Fig. 11. Predicted CO₂ ideal selectivity in a) MEA-based solvents, and b) DEA-based solvents, at the examined absorption conditions.

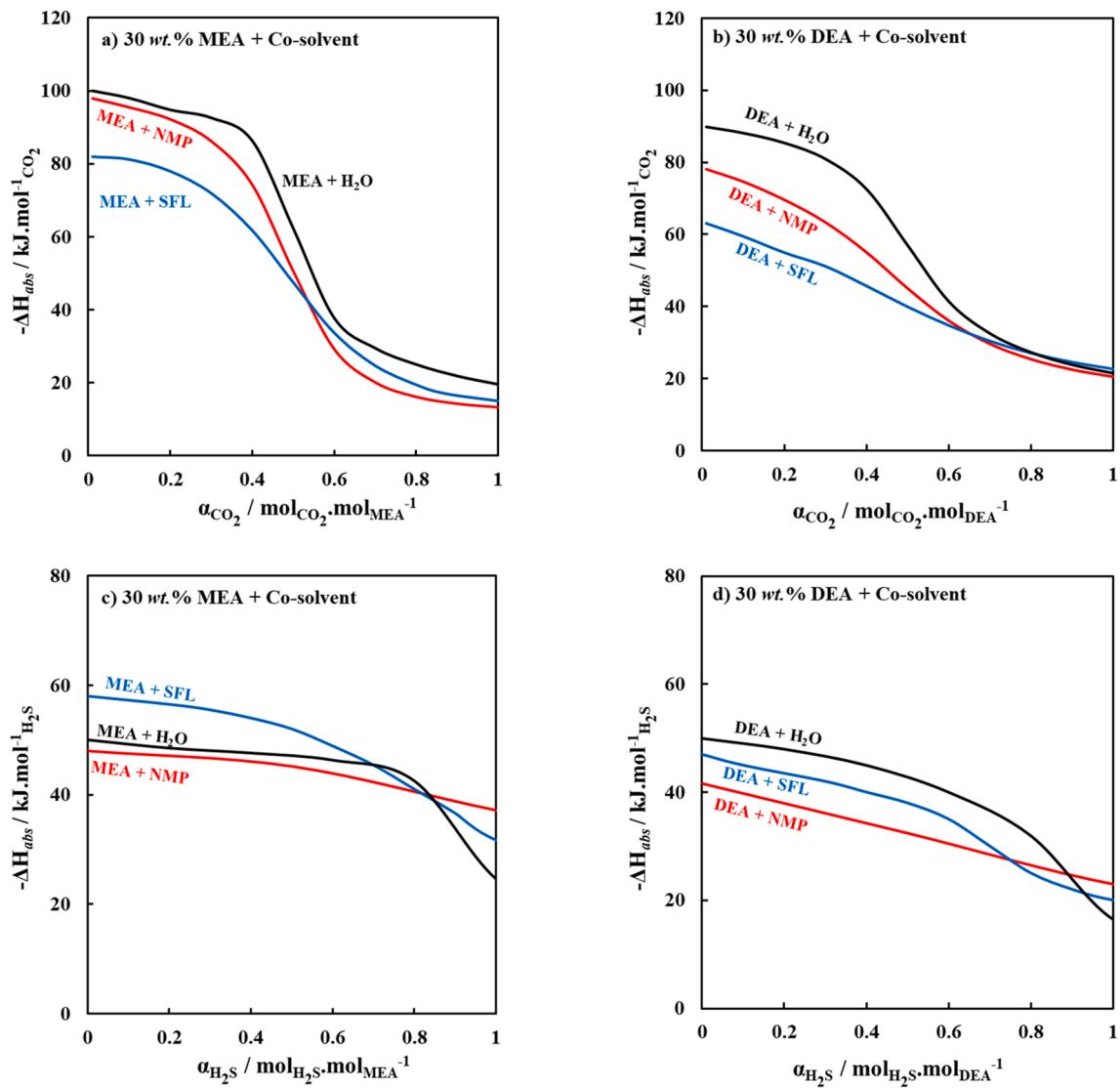


Fig. 12. Predicted acid gas absorption enthalpy as a function of acid gas loading for a) CO₂ absorption in MEA-based solvents, b) CO₂ absorption in DEA-based solvents, c) H₂S absorption in MEA-based solvents, and d) H₂S absorption in DEA-based solvents, as predicted from polar soft-SAFT and Eq. (6) (solid lines).

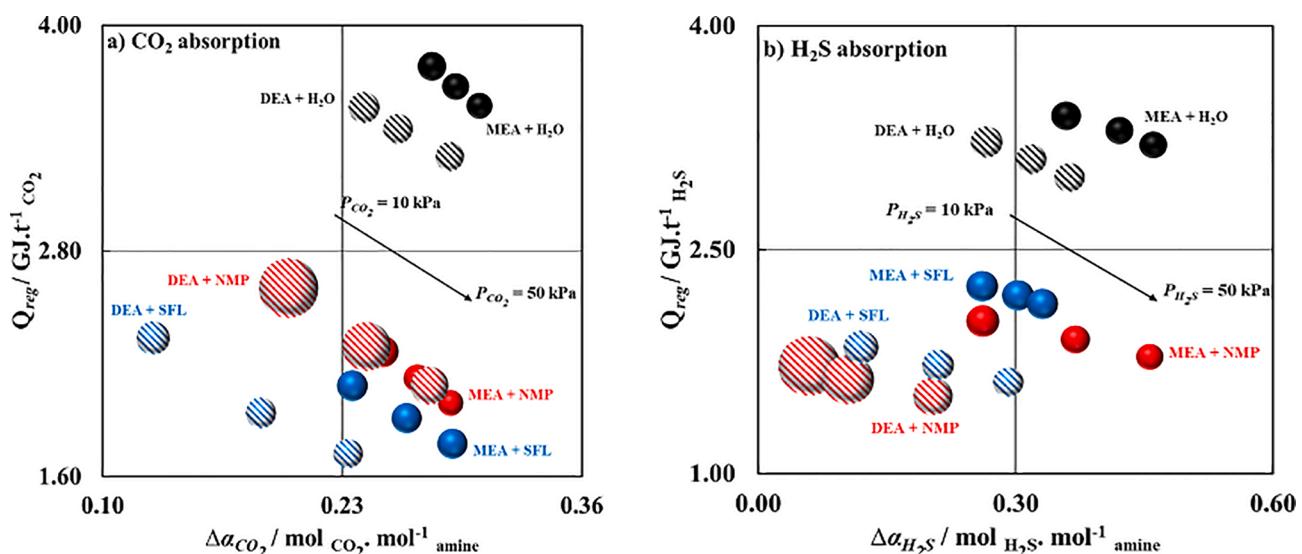


Fig. 13. Standard KPIs (cyclic capacity (x-axis), regeneration energy (y-axis), and CO₂ ideal selectivity (size of sphere)) comparative assessment of aqueous and hybrid solvents for a) CO₂ absorption and b) H₂S absorption, with MEA-based solvents (solid spheres), DEA-based solvents (striped spheres), H₂O co-solvent (black), NMP-co solvent (red), and SFL co-solvent (blue). All calculations were obtained from polar soft-SAFT at T = 313 K, P_{abs} = 100 kPa, and P_{AG} = 10 – 50 kPa (from left to right). See text for details.

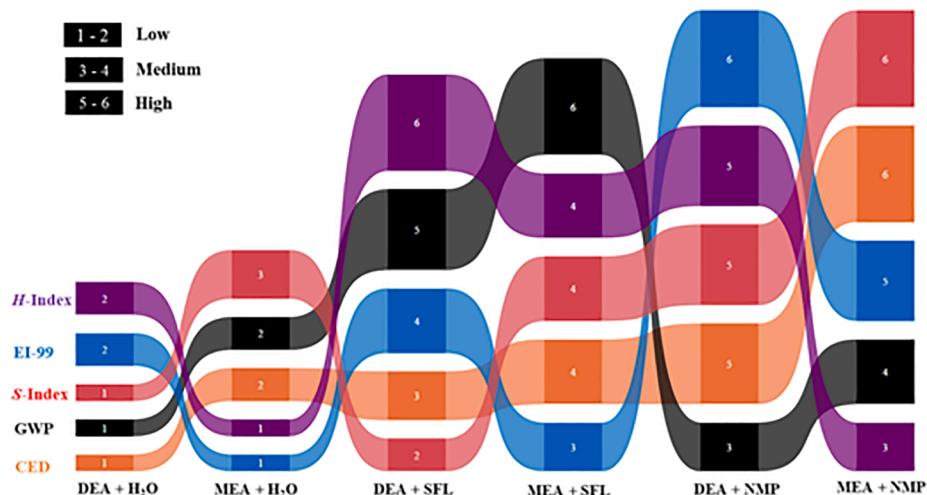


Fig. 14. Ranking of solvents based on their environmental impact using sustainability metrics, with ranking 1 – 6, denoting low to high impact.

KPIs, hybrid solvents exhibited significant reductions in regeneration energy on the expense of reduced acid gas absorption capability. Lastly, in terms of sustainability metrics, aqueous solvents were far less hazardous and environmentally friendly compared to their hybrid counterparts. Combining all examined criteria for each category established the promise held with hybrid solvents, mainly MEA + NMP, in terms of standard KPIs, and solvent properties. Unfortunately, the same solvent failed in terms of sustainability metrics, deeming the benchmark aqueous MEA as the solvent with the most acceptable trade-offs, given the environmental benefits of water versus NMP. It should be considered, though, that a simple linear combination of the three criteria was used for the ranking, the differences between the solvents from the perspective of the sustainability metrics can greatly differ depending on the specific weights given to each criterion. Nonetheless, the results clearly established the potentiality of hybrid solvents as a new generation solvent for removal of acid gases, guiding future efforts towards the inclusion of “greener” solvents.

The results of this contribution not only established the advantageous application of molecular-based EoSs (polar soft-SAFT in this case)

as reliable platforms for solvent screening and assessment, but also demonstrated the need for holistic assessment inclusive of multiple criteria needed to capture possible trade-offs offsetting solvent selection, in particular, the overlooked impacts on environment, health, and safety.

Authors Contribution

Ismail I. I. Alkhatib carried polar soft-SAFT calculations, data analyses and interpretation, and first writing of the manuscript. Omar Khalifa performed the sustainability analysis. Daniel Bahamon and Mohammad R. M. Abu-Zahra helped in the contextual analysis of the results and the figures. Lourdes F. Vega, together with Ismail I. I. Alkhatib, defined the strategy of the work, followed up on the results and interpretation and revised the overall work. All named authors have contributed to the drafting and the revision of the article.

CRediT authorship contribution statement

Ismail I. I. Alkhatib: Conceptualization, Data Curation, Formal analysis, Methodology, Visualization, Writing – original draft, Writing –

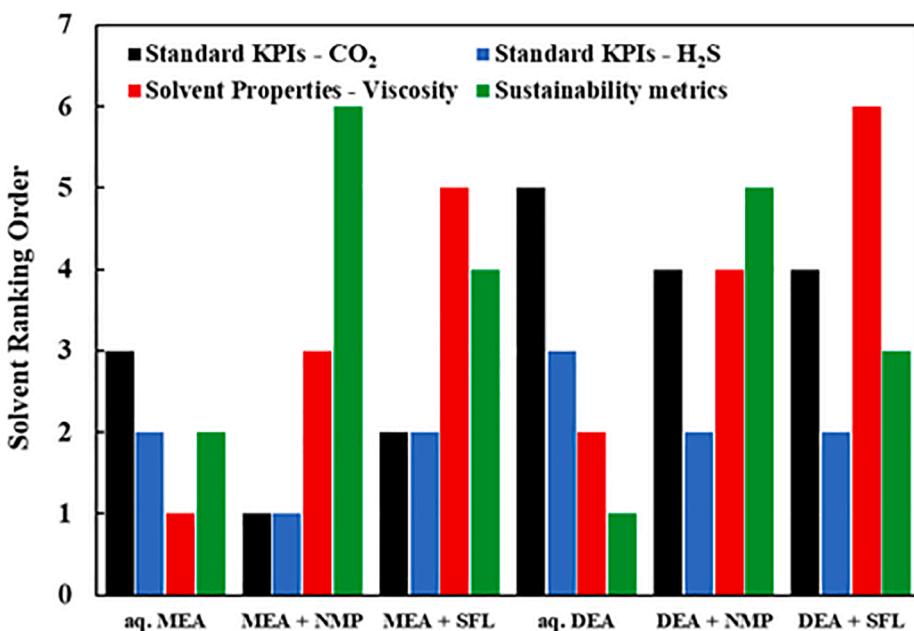


Fig. 15. Solvent ranking based on each assessment category ranked from 1 to 5, where 1 = best rank, and 5 = worst rank.

review & editing. **Omar Khalifa:** Investigation, Visualization. **Daniel Bahamon:** Formal analysis, Validation, Visualization. **Mohammad R. M. Abu-Zahra:** Formal analysis, Validation. **Lourdes F. Vega:** Conceptualization, Methodology, Project administration, Resources, Funding acquisition, Supervision, Writing – review & editing.

Declaration of Competing Interest

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

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2021.119516>.

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