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Computer-aided molecular design and selection of CO₂ capture solvents based on thermodynamics, reactivity and sustainability†

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The identification of improved carbon dioxide (CO₂) capture solvents remains a challenge due to the vast number of potentially-suitable molecules. We propose an optimization-based computer-aided molecular design (CAMD) method to identify and select, from hundreds of thousands of possibilities, a few solvents of optimum performance for CO₂ chemisorption processes, as measured by a comprehensive set of criteria. The first stage of the approach involves a fast screening stage where solvent structures are evaluated based on the simultaneous consideration of important pure component properties reflecting thermodynamic, kinetic, and sustainability behaviour. The impact of model uncertainty is considered through a systematic method that employs multiple models for the prediction of performance indices. In the second stage, high-performance solvents are further selected and evaluated using a more detailed thermodynamic model, *i.e.* the group-contribution statistical associating fluid theory for square well potentials (SAFT- γ SW), to predict accurately the highly non-ideal chemical and phase equilibrium of the solvent–water–CO₂ mixtures. The proposed CAMD method is applied to the design of novel molecular structures and to the screening of a data set of commercially available amines. New molecular structures and commercially-available compounds that have received little attention as CO₂ capture solvents are successfully identified and assessed using the proposed approach. We recommend that these solvents should be given priority in experimental studies to identify new compounds.

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Design, System, Application

We propose a computer aided molecular design (CAMD) method which employs optimization to support the synthesis and selection of high performance molecules for use in process systems and to guide experimental efforts. The method can be used to address challenging applications where a) the desired molecules exhibit phase and chemical equilibria, b) numerous combinations of molecules need to be evaluated, and c) multiple criteria must be considered to capture the effects of molecular chemistry on the process system performance. The method is applied to the design of solvents in chemical absorption processes for the separation of carbon dioxide (CO₂) from gas streams. The molecular design problem is first approached *via* a fast screening stage where molecules are evaluated based on the simultaneous consideration of multiple performance indices pertaining to thermodynamics, reactivity and sustainability. A few high-performance solvents are further evaluated using an advanced group contribution equation of state to predict reliably the highly non-ideal equilibrium behavior of solvent–water–CO₂ mixtures. Several promising novel solvents for CO₂ capture are proposed and can now be assessed experimentally. The proposed method can readily be applied to other chemical absorption processes to accelerate the identification of novel solvents.

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1. Introduction

In view of the pressing need to curtail carbon dioxide (CO_2) emissions to the atmosphere in a world that remains highly dependent on carbon-based fuels for its energy provision, a large number of technological solutions for CO_2 capture are currently being investigated.¹ Chemical absorption processes^{2,3} represent a well-established industrial technology for CO_2 capture compared to many of the alternatives that are being developed: it can be retrofitted onto existing plants and the conditions for both absorption and solvent regeneration (desorption) are relatively easy to meet. However, some major downsides must be overcome to enable the widespread adoption of this technology. These include the high energy input required for solvent regeneration and negative environmental impacts associated with the solvents, to name but a few.⁴

Many of these issues can be linked to the solvents most commonly used in such processes, namely, amine-based organic compounds. In view of the shortcomings of these solvents, significant efforts are being devoted to identify solvents that can significantly improve the economic and sustainability performance of chemisorption processes, compared to existing options. The identification of improved solvents, however, is very challenging due to a) the highly non-ideal solvent– CO_2 –water chemical interactions, b) the countless combinations of potential capture solvents and blend candidates and c) the complex interactions between the solvent and the process that require the simultaneous consideration of multiple criteria⁵ in the selection of solvents with optimum capture features. To address this last aspect, one must avoid focusing on a narrow property target (e.g. Oexmann and Kather⁶ argue convincingly against searching for low heat of absorption solvents) and instead consider a comprehensive set of properties related to thermodynamics, kinetics and sustainability.

A large number of experimental studies have been undertaken to identify solvents and solvent blends that perform better than the current benchmark solvent, aqueous solu-

tions of monoethanolamine (MEA). Based on the collective experience of a large community of researchers, several rules of thumb have been formulated to help generate molecular structures that are likely to perform well as CO_2 chemisorption solvents. For example, Singh *et al.*^{7–9} and Singh and Versteeg¹⁰ performed a large set of experiments to derive useful insights into the effects of amine structure on important parameters such as absorption rate and solvent capacity. Other researchers have developed qualitative design rules which can be used for the heuristic screening of solvents, and a selection of these heuristics is listed in Table 1, with more details provided in section A in the ESI.† While qualitative relationships that link structure and properties offer a very useful guide to search the vast space of possibilities, they also reduce the diversity of the options considered, thereby decreasing the potential for novel designs. Additionally, they do not reduce the significant cost of obtaining a measure of the performance of the postulated solvents, which requires the synthesis and characterization of each new solvent. For instance, the laboratory-based investigation of DEAB has required extensive effort as reflected in publications related to compound identification^{11,12} and investigation.^{13–16} Thus, in addition to acquiring high-quality data for different solvents, there is a need to accelerate the search using computational methods.¹⁷

Systematic computer-aided molecular design (CAMD) methods offer a promising alternative route to the identification of solvents that should be investigated experimentally, by allowing the fast, cost-effective, and automated evaluation of a larger and more diverse set of solvent properties compared to what is possible through purely experimental studies.²³ CAMD methods have been particularly successful in addressing some of the challenges in the design and selection of solvents for a range of separation systems and other applications; they have been used to explore a very wide range of solvent structures, leading to the identification of either novel molecular structures or conventional, but previously overlooked, optimum molecules. The reader is referred to a few general works^{24–27} and references therein to gain a historical perspective.

Table 1 Examples of qualitative structure–property relationships for CO_2 capture

Label	Evidence	Compound type(s)	Structure–property relationship
(1)	Puxty <i>et al.</i> ¹⁸ Yamada <i>et al.</i> ¹⁹ Tontiwachwuthikul <i>et al.</i> ¹²	Hydroxylamines	2–4 carbons between hydroxyl and amine functional groups increase the absorption capacity.
(2)	Singh and Versteeg ¹⁰ Aronu <i>et al.</i> ²⁰	Diamines	Longer chains between amine groups, up to 6 carbons, increase basicity and improve desorption.
(3)	Singh and Versteeg ¹⁰ Singh <i>et al.</i> ^{8,9}	Hydroxylamines Diamines	At least 2 carbon atoms between amine and hydroxyl or first amine and amine branch improve desorption.
(4)	Singh and Versteeg ¹⁰	Linear hydroxylamines	Up to 4 carbon atoms between hydroxyl and amines improve desorption.
(5)	Zhang <i>et al.</i> ²¹	Branched alkylamines	An alkyl branch at the α carbon improves the kinetics; at the β carbon, it leads to precipitation.
(6)	Sartori <i>et al.</i> ²²	Sterically hindered amines	<ul style="list-style-type: none"> • A primary amine is hindered when the amino group is attached to a tertiary carbon; • A secondary amine is hindered when the amino group is attached to at least one secondary or tertiary carbon.

Because many of the predictive models used are relatively simple and yet cover a very broad set of molecular structures, uncertainty has emerged as an important issue in CAMD. Approaches to mitigate the impact of uncertainty have been previously proposed within systematic CAMD methods for the design of solvents as separation^{28–30} and reaction³¹ media, of polymers,³² and of heat exchange fluid mixtures.³³ An uncertainty quantification method for property predictions through GC was also recently proposed.^{34,35}

While research on CAMD methods has led to the development of many sophisticated and successful CAMD techniques, the deployment of a systematic approach in the context of chemisorption is not without difficulty. The models typically used in chemisorption process design, while of high accuracy, are specific to a given solvent and require extensive experimental data on each solvent to be studied; this is the case of models of the thermodynamics and kinetics of aqueous alkanolamine and CO₂ mixtures (*e.g.* eNRTL models^{36–38}) and of the kinetics of degradation reactions.^{39–41} A few predictive models that relate solvent molecular structure or solvent blend composition to properties, and hence performance, are available to support CAMD activities. As a result, recent research efforts to screen CO₂ capture solvents *quantitatively* have mostly been based on the use of simple approximation models or statistical correlations.^{42,43} While such approaches led to some promising results, the narrow range of performance criteria considered and the relatively low accuracy of the predictive models have not allowed the full benefits of *in silico* solvent design to be realized.

Encouragingly, three CAMD-based approaches have been reported for the design of CO₂ capture solvents for chemisorption processes. Eden and co-workers^{44,45} have proposed solvents to replace MDEA in an absorption/desorption process, using a range of physical properties to define the optimum molecular design space⁴⁴ and developing a new CAMD algorithm.⁴⁵ Salazar *et al.*⁴⁶ used different physical properties as performance criteria to identify a few promising solvents. These solvents were then evaluated based on their stripping energy requirement, calculated using ASPEN Plus®⁴⁷ process models and with the reaction and thermodynamic models derived in part from similarity with MEA and DEA (diethanolamine) and in part by using undisclosed NRTL⁴⁸ parameters derived based on UNIFAC⁴⁹ groups to model the liquid phase non-ideality.

Among these CAMD-based works, only Salazar *et al.*⁴⁶ considered the multicomponent chemical and phase equilibria that are central to solvent performance as an explicit part of the design. However, to the best of our knowledge, the physical model used has not been validated against experimental data and its predictive capabilities are unknown. In this context, the increasing availability of reliable predictive models of relevance to chemisorption provides opportunities to enhance CAMD approaches to CO₂ capture solvent design by broadening the range of performance metrics and increasing their reliability. Chemical reactivity, for instance, has been predicted using continuum solvation models, among other computational chemistry methods, for the calculation of the

amine base strength as a measure of molecular reactivity.^{50,51} Although such models are computationally expensive, they could, in the future, be included in CAMD approaches that embed quantum mechanical models.^{52,53}

Another interesting route is the use of a predictive equation of state, such as the statistical associating fluid theory equation for potentials of variable range, SAFT-VR,^{54,55} which has been applied within a CAMD methodology to the design of solvents for the separation of CO₂ from a natural gas stream through physical absorption using a single family of compounds⁵⁶ or within a group contribution version⁵⁷ for a broader range of compounds.⁵⁸ The use of the SAFT platform to design CO₂ capture solvents for physical absorption was also proposed by Bardow *et al.*,⁵⁹ Oyarzún *et al.*,⁶⁰ Stavrou *et al.*⁶¹ and Lampe *et al.*⁶² using the PC-SAFT EoS, the perturbed-chain version of SAFT⁶³ and the PCP-SAFT EoS, its extension to polar fluids.^{64–66} In the context of chemisorption, the SAFT thermodynamic platform has been used to predict the phase and chemical equilibria of CO₂ capture fluids through a parameterization of a group contribution version of the statistical associating fluid theory for potentials of variable range equation of state, SAFT- γ SW.^{67,68} This approach has been applied successfully to model primary alkanolamines and their mixtures with water and CO₂.^{69–71} With such a model, it becomes possible to treat aqueous solutions of CO₂ and amines for which no data are available and to investigate the effect of decision variables such as composition and temperature, as well as the performance of mixtures containing several amine components.

Drawing on these advances, we aim in our work to identify a set of promising solvents that offer a simultaneously high performance in many criteria associated with effective chemical absorption of CO₂ and solvent regeneration. For the first time in CO₂ capture research, we take an approach that combines thermodynamic behaviour, reactivity and sustainability as performance criteria in solvent design or selection and that includes predictive models of the phase and chemical equilibria of the solvents identified. Furthermore, we recognise the inherent uncertainty in many of the methods we use and propose a strategy to address this issue and reduce the risk of premature elimination of solvent candidates. The proposed approach can easily be extended to include other aspects not considered here provided that appropriate structure–property models are available (*e.g.* the selectivity of the solvent towards CO₂ can be predicted using thermodynamic models similar to those used to predict CO₂ loading). Other considerations not accounted for here, such as propensity to oxidative degradation, can be investigated for the solvents in the final set obtained. The proposed computer-based solvent design framework is applied in two ways: (i) a database of commercially available molecules is screened systematically for high-performance capture options (solvent *selection*) and (ii) novel molecules that are found to be optimum capture solvents are identified (solvent *design*).

The article is organised as follows. In section 2, an overview of the proposed systematic CAMD methodology is given.

The approach is generic and can be applied to different molecular design applications depending on the properties and property models selected. In section 3, the specific choices required for the application of the method to CO₂ capture are discussed. The solvents identified are presented in section 4; the approach is assessed based on the predicted performance of the solvents generated relative to MEA, their novelty, and any indication from the literature that they are viable options.

2. Overview of generic design and selection framework

An overview of the proposed generic framework for solvent design and selection is presented in this section, together with a description of each step. Our aim is to enable the identification of efficient CO₂ capture solvents by investigating the following two cases:

- The *selection* of solvents from a database of pre-existing chemical compounds (selection problem).
- The *design* of novel solvents using an optimization-based CAMD method (design problem).

Both cases are addressed within a single framework whose major characteristics include the use of a wide range of properties as criteria for solvent selection and design, the use of simple models to develop an initial list of candidate solvents, the explicit consideration of uncertainty in decision-making and the pruning of the list of candidate solvents using a more advanced predictive model (here, we use the SAFT- γ SW EoS). Uncertainty is accounted for by generating a distribution of solvent ranks that results from the use of different prediction models for the same properties. The distribution of ranks is widely used in non-parametric statistics⁷² to detect patterns in data without requiring information on error distributions or other assumptions on the data under consideration. These ideas are implemented within a systematic, two-stage approach, as illustrated in Fig. 1. Each step is introduced in the remainder of this section.

2.1 Stage 1 of the methodology

The aim of stage 1 is to quickly identify and eliminate solvents of inferior performance, producing a “long list” of candidates. In the design problem, the algorithm used⁷³ can rapidly evaluate around 200 000 molecular structures to generate a few tens of solvents comprising the “long list”. Solvents are designed and/or evaluated using GC and non-GC-based models for the prediction of properties that are specifically selected to reflect the major driving forces for CO₂ capture. The selected properties provide a set of solvent performance measures that link the chemical structure of the solvent to thermodynamic, reactivity and sustainability characteristics of importance in the capture/regeneration process (see section 3 for details).

2.1.1 Step 1.1 – generation of an initial solvent list. Step 1.1 applies to the design problem, but not to the selection problem, in which the database constitutes the initial solvent

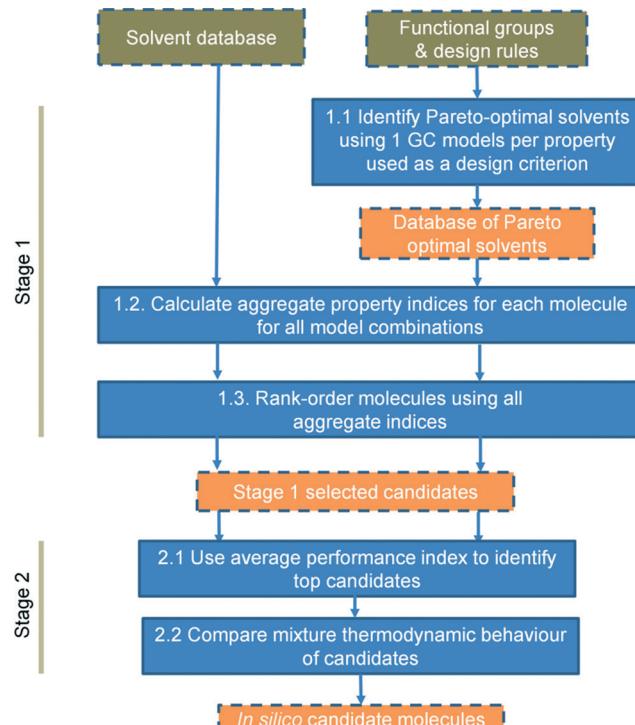


Fig. 1 Unified computer-aided molecular design framework for selection (left) or design (right).

list. In this step, candidate solvents are generated from the design space defined by the set of functional groups and the design rules that determine which molecules should be considered. The long list is generated by using a CAMD approach based on multiple property criteria to identify a set of high performance options.⁷³ It combines GC models with a multi-objective optimization approach to synthesize optimum novel or existing solvents. This approach enables the simultaneous evaluation of several properties as performance criteria, and hence, it is particularly suitable for the generation of a rich pool of optimum solvent candidates reflecting important property trade-offs. In optimization terms, this pool represents the non-dominated (Pareto) front of optimum solutions.⁷³ Every solvent in this front is such that it is not possible to improve the value of one of its properties without deterioration in at least one of its other properties. Additional details regarding the method may be found in Papadopoulos and Linke⁷³ and Papadopoulos *et al.*³³ The resulting non-dominated list of solvents includes high performance candidates but is sufficiently small so that every solvent can be further evaluated in subsequent steps.

2.1.2 Step 1.2 – calculation of aggregate property indices. In step 1.2, several aggregate property indices are generated for each molecule in the long list or database. GC models and non-GC models are used in order to calculate all properties of interest. Whenever possible, each property is evaluated with different property models. Each combination of property models is used to compute an aggregate index, and the collection of aggregate indices forms the basis for a balanced solvent selection that avoids biases towards specific properties.

To explain how the aggregate indices are computed, let us consider a set of properties $P_r = \{1, \dots, N_p\}$ that are linked to performance. Let each property $j \in P_r$ be calculated from a set of available models $l_j = \{1, \dots, N_j^{\text{md}}\}$ consisting of a total of N_j^{md} models per property. The number of all possible model combinations is given by

$$N_c = \prod_{j \in P_r} N_j^{\text{md}} \quad (1)$$

Furthermore consider a solvent i in the set $G = \{1, \dots, N_s\}$ of N_s candidate molecules. One can then define an aggregate property index $J_{i,k}$ for solvent i based on the k th model combination, $k \in \{1, \dots, N_c\}$, corresponding to some choice l_j of model ($l_j \in \{1, \dots, N_j^{\text{md}}\}$) for a property j :

$$J_{i,k} = \sum_{j \in P_r} a_j x_{i,l_j,j}^*, \quad (2)$$

where a_j represents a unit coefficient that is positive if property j needs to be minimized and negative if it needs to be maximized. $x_{i,l_j,j}^*$ represents a scaled value of property j for solvent i obtained using model l_j . Details on the scaling approach are reported in section B.1 in the ESI.[†]

The set of indices $J_{i,k}$, $i \in \{1, \dots, N_s\}$, $k \in \{1, \dots, N_c\}$, may be represented as a matrix \mathbf{J} of dimensions $(N_s \times N_c)$ with each model combination k (column of \mathbf{J}) indicating the performance of each solvent i (row of \mathbf{J}). As an example of matrix \mathbf{J} , assume a set G of $N_s = 4$ solvents is used and a set P_r of $N_p = 2$ properties with $N_1^{\text{md}} = 2$ and $N_2^{\text{md}} = 3$ models (hence, $N_c = 6$) is available for the calculation of properties 1 and 2, respectively. The elements of matrix \mathbf{J} are calculated as shown in Table 2.

2.1.3 Step 1.3 – identification of candidate molecules. In step 1.3, a rank-based approach is used to identify the top candidate solvents from the initial list (*i.e.* from the database in the selection problem or the Pareto set in the design problem) rather than focusing on the numerical value of the $J_{i,k}$ indices. If only one model were used for each property, making \mathbf{J} a one-dimensional vector, the solvents could be ranked from best to worst in order of increasing value of $J_{i,k}$. When several models are used for one property, the differences between the multiple columns in \mathbf{J} provide a measure of the underlying model uncertainty and make it possible to identify solvents with potentially high performance in spite of model uncertainty.

To this end, the elements in each column of \mathbf{J} are sorted in ascending order independently for every column (model combination) k , yielding a matrix \mathbf{J}' of independently rank-ordered columns. The transformations needed to go from \mathbf{J}

to \mathbf{J}' can be used to construct a matrix of ranked lists, \mathbf{L} , in which an entry $L_{r,k}$ is an integer that denotes the identity of the r th ranked solvent according to model combination k . Consider an example with the same dimensionality as that in Table 2: the elements of matrix \mathbf{L} will be of the form presented in Fig. 2a. The solvents may follow a different order for different k values (*i.e.* different combinations of models). For example, solvent 3 ranks first for $k = 2$, second for $k = 1, 3, 5, 6$, and third for $k = 4$. In addition, notice that all four solvents appear in the top 2 positions (ranks 1 and 2). For this small solvent set, the number of appearances of each solvent in the top 2 positions can be used to select solvents to be taken forward for further analysis, as shown in Fig. 2b: solvents 1 and 3 show the strongest predicted performance, closely followed by solvent 2, while solvent 4 appears to be an under-performer.

The frequent appearance of specific solvents at the top implies an agreement in the predictions made by multiple different models. On the other hand, even solvents that appear with lower frequency at the top are also considered due to the use of the distribution of ranks to select candidate molecules. This allows a reduction of the original solvent list without bias due to uncertainty in the predictions. This is important because there is often little or no prior knowledge on the predictive accuracy of the models employed. As a result, agreement in the predictions obtained from different models does not necessarily imply a higher accuracy than in the case where fewer models result in similar or different predictions. With the proposed approach, assumptions related to accuracy are avoided. Further details are provided in section B.2 in the ESI.[†]

The multi-criterion approach adopted for stage 1, which combines a range of properties and multiple property models, provides a robust evaluation of the solvents in the initial candidate list, in spite of the use of relatively simple models. As a result, a few effective solvents emerge as the best performers: this reduced solvent list is progressed to stage 2.

2.2 Stage 2 of the methodology

In stage 2, the most promising candidates from stage 1 are further evaluated using a combination of ranking, structure–property relationships and, where feasible, more detailed predictive models to assess mixture behaviour. This allows the solvent list to be narrowed down further and priorities to be set for further research and experimental investigation.

2.2.1 Step 2.1 – prioritisation using average indices and heuristics. The solvent candidates are prioritised by using average values of the property indices. A single average index, $J_{i,\text{ave}}$, is calculated for each solvent i , using average values of

Table 2 Example of matrix \mathbf{J} for 4 solvents and 6 property model combinations

Solvent	$k = 1, j = \{1, 2\}$ and $l_1 = 1, l_2 = 1$	$k = 2, j = \{1, 2\}$ and $l_1 = 1, l_2 = 2$...	$k = 6, j = \{1, 2\}$ and $l_1 = 2, l_2 = 3$
1	$J_{1,1} = a_1 x_{1,1,1}^* + a_2 x_{1,2,1}^*$	$J_{1,2} = a_1 x_{1,1,1}^* + a_2 x_{1,2,2}^*$...	$J_{1,6} = a_1 x_{1,1,2}^* + a_2 x_{1,2,3}^*$
2	$J_{2,1} = a_1 x_{2,1,1}^* + a_2 x_{2,2,1}^*$	$J_{2,2} = a_1 x_{2,1,1}^* + a_2 x_{2,2,2}^*$...	$J_{2,6} = a_1 x_{2,1,2}^* + a_2 x_{2,2,3}^*$
3	$J_{3,1} = a_1 x_{3,1,1}^* + a_2 x_{3,2,1}^*$	$J_{3,2} = a_1 x_{3,1,1}^* + a_2 x_{3,2,2}^*$...	$J_{3,6} = a_1 x_{3,1,2}^* + a_2 x_{3,2,3}^*$
4	$J_{4,1} = a_1 x_{4,1,1}^* + a_2 x_{4,2,1}^*$	$J_{4,2} = a_1 x_{4,1,1}^* + a_2 x_{4,2,2}^*$...	$J_{4,6} = a_1 x_{4,1,2}^* + a_2 x_{4,2,3}^*$

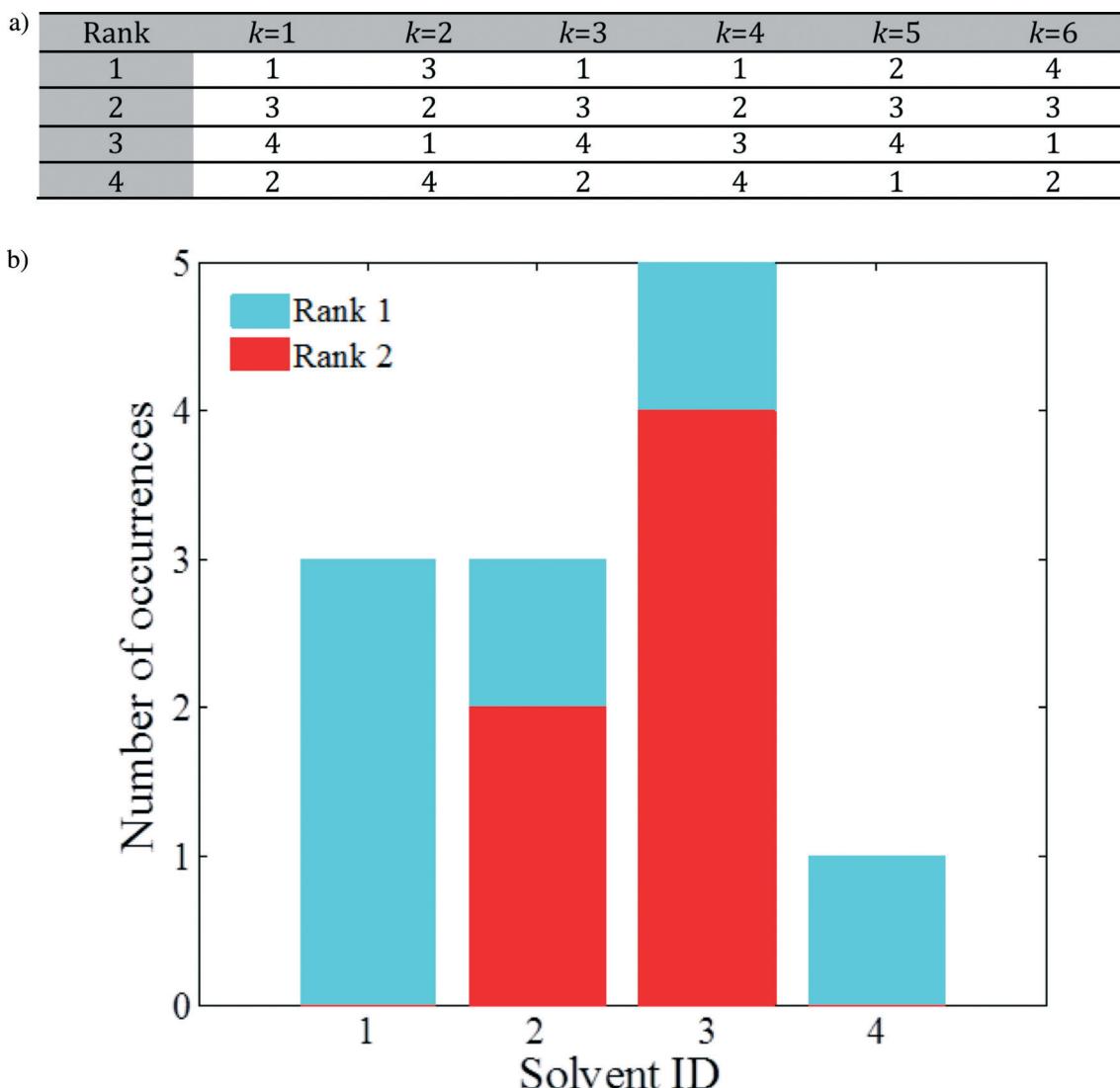


Fig. 2 a) Example of rank-ordered solvents in matrix L where each entry represents the identity of a solvent. b) Number of occurrences of each molecule in the top 2 solvents, based on (a).

the properties for which multiple models are available, as follows:

$$J_{i,\text{ave}} = \sum_{j \in F_i} a_j \cdot x_{i,j}^{\text{ave}}, \quad (3)$$

where $x_{i,j}^{\text{ave}}$ is the average value of property j for solvent i (calculation details are available in section B.2 in the ESI†). The resulting ranked list can be used to prioritise further investigation, with the number of solvents to be pursued depending on the resources available. The list of candidate solvents can also be further refined by comparing the molecular structures identified to existing solvents and by gathering evidence from the literature on the effectiveness or lack thereof of similar molecules. This information is especially useful in the context of solvent design, where the structures designed in stage 1 may represent multiple isomers due to the lack of full connectivity information in most group contribution models. Molecular structures of interest can be fully specified based

on prior knowledge and heuristics, such as those shown in Table 1.

2.2.2 Step 2.2 – evaluation of mixture properties with advanced property models. As a final stage before experimental investigation, advanced property models can be applied to the top-ranked solvents arising from step 2.1 to assess more accurately their likely behaviour within the application of interest. This may require the calculation of mixture properties (*e.g.* absorption of CO₂) over a range of pressures and temperatures, of reactivity or other relevant properties. This stage may lead to a revision of the rank-ordered list of solvents to help prioritise experimental effort.

3. Application of proposed framework to CO₂ chemisorption

In this section, we discuss the specific application of the generic framework presented in section 2 to the selection and

design of CO₂ capture solvents. At the heart of the framework is the identification of relevant property criteria spanning thermodynamics, reactivity and sustainability, as well as appropriate models to relate these to the solvent molecules; the models and criteria relevant to stage 1 are introduced in section 3.1, while those for stage 2 are discussed in section 3.2. In section 3.3, we define the “molecular search space”, *i.e.* the rules that define the new and existing molecules that are considered as potential capture solvents.

3.1 Selection of relevant properties and property models for stage 1

Numerous solvent properties can be considered as screening criteria to select optimum CO₂ capture solvents; Hoff *et al.*⁷⁴ recommended a large set of relevant properties, independently of the effort required for their calculation. Several authors^{7–10,12,42,43} have provided significant evidence that, prior to using rigorous models or lab-scale experimentation, simpler models, indices or guidelines facilitate a quick yet reliable screening of CO₂ capture solvents. Several properties are selected for stage 1 based a) on their potential to reflect important thermodynamic, reactivity and sustainability characteristics relevant to this application, b) on the availability of models that enable their fast calculation, and c) on the availability of sufficient data so that these models may be applied for a wide range of molecular structures. These properties are summarized in Table 3, together with stage 2 properties

and their connections with broader criteria for design⁵ are highlighted. The property models used are presented in Tables B1 and B2 in the ESI.[†] The rationale for the property choices made and the relevant criteria are described in the remainder of this section.

3.1.1 Thermodynamic property criteria at stage 1. The relative energy difference (RED) is derived from the solubility parameter (δ) and is used as a measure of miscibility. Two compounds with similar values of δ are likely to be miscible. The solubility parameter can be related to the cohesive energy density,^{75,76} *i.e.* to the energy required to overcome the solvent–solvent interactions.⁴² Solvents with RED < 1 are generally considered to be favourable for the dissolution of a particular solute.^{77,78} Clearly, this concept is very useful for the identification of CO₂ capture solvents. Calculation details are reported in section B.4 in the ESI.[†]

The vapour pressure (P_{vp}) is an indicator of solvent losses and should be as low as possible. Several amine-based solutions used as solvents present a high P_{vp} ; hence, water sprinklers are often used in the absorption column to reduce losses.

The liquid heat capacity (C_p) plays an important role in determining the heat required to regenerate the amine-based solution during desorption. This heat can be divided into three components:⁷⁹ the sensible heat, the heat of vaporization (mostly that of water, which is the main component evaporated in the reboiler), and the heat of absorption necessary to desorb one mole of CO₂. The sensible heat represents the heat required to raise the temperature of the solution

Table 3 Properties considered as criteria for solvent design and selection in stage 1 and their impact on absorption/desorption process characteristics and the key performance indicators (KPIs) highlighted by Kim and Svendsen:⁵ energy consumption, environmental impact and cost (CAPEX – capital expenditure and OPEX – operating expenditure)

Criterion	Impact on absorption/desorption process
Thermodynamics	
-CO ₂ solubility	Ability and capacity to dissolve CO ₂ /all design and operating parameters are affected (CAPEX and OPEX, energy consumption)
• Solubility parameter (δ) (stage 1)	
• Chemical and phase equilibria (stage 2)	
-Vapour pressure	Solvent losses (OPEX and environmental impact)
• Amine pressure (P_{vp}) (stage 1)	
• Phase equilibrium (stage 2)	
-Liquid heat capacity (C_p) (stage 1)	Sensible heat/reboiler duty/heat exchanger size (CAPEX and OPEX, energy consumption)
-Density	Equipment size-capacity (directly CAPEX)
• Amine density (ρ) (stage 1)	
• Phase equilibrium (stage 2)	
-Surface tension (σ) (stage 1)	Mass transfer coefficient-packing material characteristics (directly CAPEX)
-Viscosity (η) (stage 1)	Mass transfer coefficient-packing material characteristics (directly CAPEX)
-Boiling point temp. (T_{bp}) (stage 1)	Solvent evaporation losses/reboiler duty (OPEX, energy consumption, environmental impact)
-Melting point temp. (T_m) (stage 1)	Solvent solidification (directly OPEX)
Reactivity	Solvent ability to react and solvent kinetics/all design and operating parameters are affected (CAPEX and OPEX, energy consumption)
-Amine basicity (pK_a) (stage 1)	
-Chemical equilibrium (stage 2)	
Sustainability	Inherent hazards of solvent in the capture processes/cradle-to-gate environmental impact of solvent (per kg of solvent used)/environmental impact of the reclamer waste (<i>e.g.</i> characterization as hazardous waste according toxicity and corrosion indices) if landfilled
-Environmental health and safety hazards (EHS) (stage 1)	
-Cumulative energy demand (CED) (stage 1)	
-Global warming potential (GWP) (stage 1)	
-Eco-indicator 99 (EI-99) (stage 1)	

from the absorption to the desorption temperature. This is directly proportional to the heat capacity, C_p , of this solution. Hence, a solution containing an amine with a low C_p may be assumed to contribute towards reducing the sensible heat requirements. C_p is predicted *via* a GC method⁸⁰ developed specifically for amine-based solvents used in CO₂ capture.

The density (ρ), surface tension (σ) and viscosity (n) of the liquid are three properties tightly associated with the design and operating features of the absorption column. In particular, the solvent liquid density, ρ , should be high because this leads to reduced solvent flow rate, equipment size and pumping power requirements. Furthermore, ρ , σ , and n have an effect on the mass transfer coefficient, which increases with increasing values of the density and decreasing values of the surface tension and viscosity, as shown, for instance, in Dvorak *et al.*⁸¹

The melting point temperature (T_m) should be lower than the lowest absorption/desorption temperature to avoid solvent solidification under processing conditions.

The boiling point temperature (T_{bp}) should be higher than the highest absorption/desorption temperature to avoid excessive vaporization of the pure solvent under processing conditions.

T_m and T_{bp} are considered in the calculations as an average from Marrero and Gani⁸² and Hukkerikar *et al.*³⁴

3.1.2 Reactivity property criterion. The basicity (pK_a) is an important solvent property as it provides information on the reactivity of amines³ and the prevailing reactions.⁸³ Reaction rates increase with increasing amine basicity;⁸⁴ hence, amines with higher basicity are desirable. Quantum chemistry continuum-solvation models^{50,51} provide a robust prediction of pK_a , but the screening of large solvent sets requires less computationally-demanding approaches. There are two empirical methods⁸⁵ which utilize simple rules for the calculation of pK_a , namely, the Perrin–Dempsey–Serjeant (PDS) method and the Taft equation method. PDS has been shown to result in pK_a values for several amine solvents which are as accurate as predictions using quantum chemistry calculations.⁵⁰ The Taft method also provides sufficiently accurate predictions for many well-known amine solvents. Both methods are based on an analysis of the effects of substituents in molecules and employ rules for determining the pK_a when a particular substituent is attached to a given position within a molecular structure. In our work, pK_a is obtained from the publicly available version of the Marvin 6.0.5 (ref. 86) software which combines calculations of molecular partial charge distributions⁸⁷ with PDS and Taft method principles.⁸⁸

3.1.3 Sustainability property criteria. The sustainability characteristics of the investigated solvents are evaluated and compared using two categories of indices: a cradle-to-process gate life cycle assessment (LCA) showing the cumulative environmental impacts of the solvent production process chain and a safety, health and environmental hazard assessment (EHS) that enables the estimation of harm potential in accidental scenarios within a CO₂ capture plant in the presence of the tested solvents. Details on the employed calculation methods and values for all metrics are reported in section C in the ESI.† The LCA metrics used for a functional unit of 1

kg of solvent produced are the cumulative energy demand, the global warming potential and the Eco-indicator 99.

The cumulative energy demand (CED), measured in MJ equivalent, is a resource-oriented indicator which reflects the total primary energy demand during the production cycle and therefore also reflects to some extent the economic impacts.⁸⁹

The global warming potential (GWP),⁹⁰ measured in kg CO₂ equivalent, is a damage-oriented indicator reflecting the effect of greenhouse gas emissions, considered here for a period of 100 years.

The Eco-indicator 99 (EI-99)⁹¹ provides an aggregated score (*i.e.* EI-99 points) for the end-point impact categories of human health, ecosystem quality and resource consumption.

The required cradle-to-process gate data for the environmental impact of the production of solvents are either obtained from the Ecoinvent database⁹² or estimated using the state-of-the-art FineChem tool⁹³ from molecular descriptors. The FineChem tool provides estimations with an average error of 30–40% but is very useful in the case of data gaps, especially for the design of new molecules.

The EHS hazard categories represent the safety hazards regarding accidental release of energy or material, the health aspects associated with the long term effects on workers due to workplace exposure and the environmental hazards referring to the damage to flora and fauna. Koller *et al.*⁹⁴ used a prioritized list of physical and chemical substance properties to estimate a comprehensive set of characteristic dangerous properties for each hazard category. In the safety category, the properties include mobility, fire and explosion and acute toxicity effects. In the health category, properties include irritation and chronic toxicity effects. In the environmental category, properties include air and water mediated effects as well as persistency and the potential for accumulation in the food chain.

Note that the environmental index of the solvent also refers to a part of the environmental impact of the reclamer waste, if landfilled (*e.g.* sludge including the part of the solvent that is not recycled by the reclamer). The toxicity and corrosion indices used in the EHS characterize indirectly the reclamer waste as hazardous or not (and thus requiring special treatment). The LCA indices (*i.e.* CED, GWP and EI-99) refer to the environmental impact of the make-up solvent, *i.e.* per kg of solvent. The LCA relevant reclamer impact is partly described by the solvent physical and hazard properties, but also from the amount of purge stream, which depends on the amount and type of degradation products not included in this study. Furthermore, energy related gate-to-gate sustainability aspects are represented by many of the indicators used for solvent design and selection (*e.g.* boiling point and vapour pressure of the solvent affect not only the reboiler duty but also the reclamer energy demands).

A comprehensive sustainability assessment should also include the degradation potential of the solvent under the capture process conditions, as well as the type of degradation products. These issues are directly associated with the amount of solvent make-up (*i.e.* the complementary factor of the “per-kg of solvent” LCA indices) and indirectly with the

environmental burden of the reclamer (*i.e.* because of the purged amount treated by the reclamer in order to avoid accumulation of the degradation products in the main capture system). Moreover, certain degradation products (*e.g.* nitrosamines) are associated with additional health hazards to those described by the solvent inherent health indices. However, there is severe lack of mechanistic studies relating degradation potential to the molecular structure of the solvent. Some rules have been proposed for instance, requiring the presence of secondary amines for the formation of stable nitrosamines or supporting the use of tertiary amines (typically in blends because of their slower absorption kinetics) because they have much lower nitrosation rates. However, they are too broad and qualitative to play a useful role in a CAMD approach.

3.1.4 Summary of property criteria at stage 1. Based on the criteria identified in sections 3.1.1 to 3.1.3, an optimal solvent at the end of stage 1 can be interpreted as a solution to the following multi-objective optimization problem:

$$\begin{aligned} \max \quad & \rho, pK_a \\ \min \quad & C_p, P_{vp}, \sigma, n, \text{EHS, CED, GWP, EI99, RED} \\ \text{s.t.} \quad & T_m < T_{\text{Abs}} \\ & T_{\text{bp}} > T_{\text{Des}} \end{aligned} \quad (4)$$

where T_{Abs} and T_{Des} are the average temperatures of the absorption and desorption columns (313 K and 393 K). The inequalities for the two temperatures represent minimum requirements to avoid solvent solidification or significant vaporization under processing conditions. Based on eqn (1) and the property models listed in Tables B1 and B2 in the ESI,[†] the total number of $J_{i,k}$ values that can be obtained for each solvent is 252.

3.1.5 Formulation of step 1.1. In the case of the design of new solvents (Fig. 1), the first task (step 1.1) is to derive a set of Pareto-optimal solvents from the molecular search space. The solvent performance criteria used during this CAMD step are calculated exclusively from GC models; hence, this step accounts only for properties which may be calculated using such models. Uncertainty is not considered in this step and the following models are used from Tables B1 and B2 in the ESI:[†] 1.2, 2.1, 3.1, 4.2, 5.1, 6.1, 7.1 and 8.1. Group-contribution models are not available for pK_a , EHS, CED, GWP and EI-99 so these are not taken into account in this step of the methodology. These properties are calculated and considered for further evaluations of the Pareto optimal solvents in step 1.2. Given the property models chosen for stage 1, the multi-objective optimization problem is thus reduced to:

$$\begin{aligned} \max \quad & \rho \\ \min \quad & C_p, P_{vp}, \sigma, n \\ \text{s.t.} \quad & T_m < T_{\text{Abs}} \\ & T_{\text{bp}} > T_{\text{Des}} \\ & \text{RED} \leq \text{RED}^{\text{up}} \end{aligned} \quad (5)$$

Note that RED is used as a constraint during CAMD, with RED^{up} being an upper limit which may be set to 1 as noted

previously or to a higher value, for example using MEA as a reference point. The RED of MEA is 3.94 using model 1.2 of Table B1 in the ESI.[†] The multi-objective formulation in problem (5) is solved to identify the set of non-dominated optimum solvents using the approach of Papadopoulos and Linke.⁷³

3.2 Selection of relevant models for stage 2

At stage 2 (step 2.2), more detailed models are required to estimate mixture behaviour and, in particular, the absorption capacity of the candidate solvents. Most models of the thermodynamic behaviour of reactive mixtures of aqueous solvents and CO_2 require extensive experimental data on the specific solvent of interest. However, more predictive models have recently been derived from the SAFT^{95,96} equation of state. A systematic approach to the modelling of the thermodynamics of CO_2 chemisorption solvents based on limited data has been developed for monoethanolamine (MEA)⁹⁷ and *n*-alkylamines⁹⁸ and further extended by Rodriguez *et al.*⁹⁹ using the SAFT-VR EoS applied to various aqueous mixtures of alkanolamines and carbon dioxide. To enhance the predictive capabilities of this approach, models to predict the phase behaviour and thermophysical properties of aqueous alkanolamine mixtures with CO_2 using the GC formalism embedded within the SAFT- γ SW framework^{67,68} have been proposed.^{69–71} This provides a much firmer basis for the design of novel solvents, enabling the design of molecular structure and mixture composition to be varied. Thus, in step 2.1, the fluid-phase behaviour of mixtures of the candidate solvents with carbon dioxide and water is evaluated using the SAFT- γ SW EoS, provided that the relevant building blocks are available in the corresponding group contribution table (*cf.* section D in the ESI[†]). Both phase and chemical equilibria are taken into account simultaneously *via* this model, enabling a more detailed assessment of the selected solvents. Partial pressure profiles are used to assess the relative performance of the solvents in terms of absorption potential. Saturated vapour pressures and densities can also be evaluated with the approach.

3.3 The molecular search space

The final specification required to enable the application of our approach to CO_2 capture solvents is the definition of the search space. The search space for solvent design is defined by a set of 13 functional groups, namely, CH_3- , $-\text{CH}_2-$, $>\text{CH}-$, $>\text{C}<$, $-\text{OH}$, $-\text{CH}_2-\text{NH}_2$, $-\text{CH}_2-\text{NH}-$, $-\text{CH}_2-\text{N}<$, $>\text{CH}-\text{NH}_2$, $>\text{CH}-\text{NH}-$, $\text{CH}_3-\text{NH}-$, $\text{CH}_3-\text{N}<$, and $\geq\text{C}-\text{NH}_2$. These groups are chosen due to the availability of the input data required for the calculation of pure-component molecular properties through GC methods and their frequent occurrence in existing CO_2 capture solvents.

Using these 13 groups as building blocks, a database of existing molecules is also developed by conducting a broad search for acyclic, aliphatic and hydroxylamines available in an in-house data repository at ETH Zurich, in publicly available databases^{100,101} and in the commercial catalogue of Sigma-

Aldrich.¹⁰² The search results in a database of 126 amines and hydroxylamines, each with a unique CAS registry number.

The database is partitioned into two classes: firstly, the reference class (R), containing 25 solvents previously considered extensively in CO₂ capture in the open literature (Table E1 in the ESI†), serves as a benchmark to assess the viability of the new capture solvents proposed in our work and to assess the potential performance improvements; secondly, the commercial class (C) containing 101 acyclic, aliphatic amines for which we had limited or no knowledge regarding their suitability as CO₂ capture solvents, prior to this work (Tables E2, E3 and E4 in the ESI†). The C-class solvents are assumed to be commercially available because they were retrieved from public and commercial databases. The database is not exhaustive but provides a varied set of amines with different structural characteristics (*e.g.* primary, secondary, tertiary, branching at different positions).

4. Results and discussion

The proposed systematic approach is applied in selection mode, using classes R and C, and in design mode, using the set of 13 functional groups. In this section, we present the top solvents identified after stages 1 and 2 and analyse the results with the aim to address the following two questions:

1. How successful is the proposed approach at identifying realistic solvents for CO₂ capture?
2. Which molecules are most promising for further investigation as CO₂ capture solvents?

4.1 Selection of top candidate solvents from the reference and commercial classes

4.1.1 Stage 1 of solvent selection. In the selection problem, the matrix J' of property indices includes all solvents in the R and C classes and is therefore of size 126 × 252. The application of steps 1.2 and 1.3 results in a matrix of ranked lists, L; the molecules that occur most frequently in the top 15 solvents are selected from L. This yields a set of 29 candidates, including 9 from class R and 20 from class C. The 29 solvents are presented in Tables 4–6, arranged based on structural characteristics, to reflect the qualitative structure–property relationships in Table 1.

MEA, which was included in class R, is not found amongst the top solvents due to its low environmental health and safety performance (it exhibits a high EHS value). When sustainability indices are not considered, MEA appears in the top 15 solvents. Solvents in class R have been investigated to a wider extent in the published literature compared to C class solvents with respect to their CO₂ absorption capacity and/or reaction kinetics as well as other properties (Table 7). Additional details are provided in sections E and F in the ESI†.

An examination of the solvents in class C shows that:

- Nine of the twenty class C solvents are potentially novel capture options: very limited or no evidence that these molecules have been considered for application to CO₂ capture could

be found in the open literature. The performance of these solvents for each property is shown in Fig. 3, relative to MEA.

- Solvents 2A1B, 2A1PN and 2A1H have been considered in mixtures with methyldiethanolamine (MDEA) where they were tested experimentally in terms of stability and corrosiveness with respect to carbon steel.¹¹⁶ The tests were motivated by the discovery that an aqueous mixture comprising a tertiary alkanolamine and a primary alkanolamine with a secondary carbon atom attached to the amino group (such as 2A1B, 2A1PN and 2A1H) is not only effective in removing acid gases, but it also exhibits unexpectedly low degradation, corrosiveness and metal solubility properties. However, very few details are disclosed on these compounds; hence, they may be worthy of further investigation in mixtures with MDEA and other amines of similar structure.

- Solvents DIBA, DsBA, DBA and HEXA are phase-change solvents^{21,117,118} associated with significant reductions in the desorption energy requirements because they can be partly separated in a non-thermal process after absorption and before entering the desorption column. This class of solvents contains also several other options,¹¹⁸ which are very promising for use either in their pure aqueous form or in mixtures. A review of other types of phase-change solvents is available in Wang and Li.¹¹⁹

- Solvents PAE, IPAE,¹²⁰ TMEDA¹²¹ and 5AP^{7–9} have been investigated considerably less than the other solvents and mainly with respect to their CO₂ absorption capacity; hence, they may be worthy of further investigation.

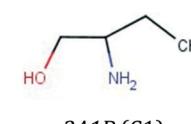
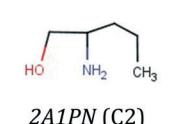
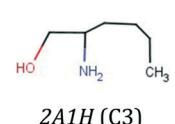
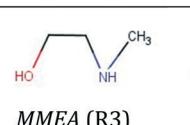
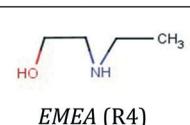
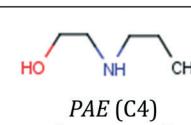
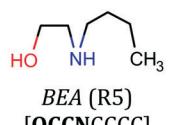
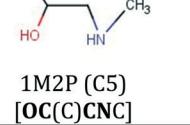
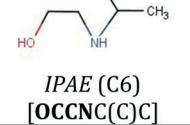
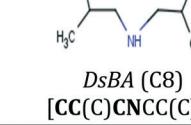
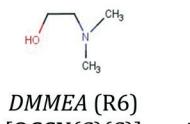
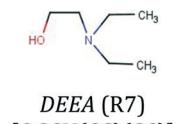
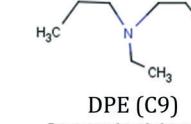
Note that the solubility parameter values of solvents 4A2B, 3DAP, ND1B, 1EDB and 2P12P are within 14–17 (J cm⁻³)^{1/2} which is the range of solubility parameter values exhibited by the biphasic solvents HEXA, DsBA and DBA.^{7–9,21} These solvents are therefore expected to exhibit low solubility in water and may also be biphasic candidates. Finally, the EHS index shows clearer, more favourable trends than the LCA metrics (Tables C1a and C1b in the ESI†) for these solvents. In this regard, 1EDB exhibits much lower acute and chronic toxicity values than the rest of the solvents in this set, and while DPE, 4A2B and 4D1B have higher acute toxicity indices, they are still less than half the MEA index value. DPE, 4A2B 2P12P and 4D1B, however, all have flash points lower than 35 °C.

4.1.2 Stage 2 of solvent selection. In step 2.1, average performance indices are computed for all 29 solvents and the top 10 solvents are selected for further exploration. Two rankings are derived: one based on all properties, as shown in Fig. 4a, and one excluding the sustainability indices, as shown in Fig. 4b. The results are reported using MEA as the reference solvent. These figures highlight some interesting trade-offs between different properties:

- V_m, C_p, EI-99: the performance of almost all solvents deteriorates compared to MEA. V_m reflects density; hence, all solvents exhibit lower density than MEA.

- P_{vp} and CED: the performance of all solvents is slightly better or slightly worse than MEA in Fig. 4a, while it deteriorates when sustainability indices are not considered (Fig. 4b).

Table 4 Amines with [OCCN] or [CCCN] patterns. The square brackets give a hydrogen-free representation of the molecular formula, with atoms in parentheses indicating branching that starts from the previous atom. Each molecule is further labelled by an acronym (e.g. AMP) and a label that indicates its class and number within the class (e.g. R2, for the second solvent in class R). Where an acronym is shown in italics, this indicates that the compound has been previously considered as a potential CO₂ capture solvent in at least one publication or patent. The rows indicate different types of amines (primary, secondary or tertiary). In each row, molecular size increases from left to right. Further details are provided in Tables E1–E4 and section F in the ESI together with a discussion of the compounds in terms of their structural characteristics and likely CO₂ capture potential based on the literature

NH ₂	-				
NH	-				
NH	-				
N	-			-	

- σ , RED, n , pK_a: the performance of almost all solvents improves compared to MEA. When sustainability is not considered (Fig. 4b), σ and n of the selected solvents appear to be better than for the solvents in Fig. 4a, while pK_a appears to be slightly worse.

- EHS and GWP: the performance is worse when sustainability indices are not considered, but better performance than MEA is observed in most cases.

As seen in Fig. 4, 2AP, MMEA, EMEA and MPA are repeated in both cases, indicating that they are not affected by the variation in the employed performance indices. DBA is the only solvent from the C class that is shared between the two sets in Fig. 4. The consideration of sustainability indices has a significant effect on the selection of solvents from the C class. The evaluation of the selected solvents based on mixture behaviour (step 2.2) will be considered in section 4.3, where solvents that have been found *via* selection or design are compared.

4.1.3 Performance of selected solvents. The solvents listed in Fig. 4 are first assessed using literature sources for prior evidence of their potential as CO₂ capture options. This is useful as part of the prioritisation process but also in the

context of assessing the efficacy of the proposed approach to solvent selection and design. Where we have been unable to identify prior use of a solvent as a CO₂ capture option, the qualitative structure–property relationships listed in Table 1 are used. Further analysis for all 29 solvents identified at the end of stage 1 is provided in section F in the ESI.[†] A summary of the main performance characteristics of the solvents and relevant literature sources is presented in Table 8. From the top 10 solvents, those that have been previously investigated in the literature present very favourable characteristics compared to MEA. This indicates that the selection procedure points toward useful CO₂ capture options, despite the use of simple property prediction models.

Focusing on sustainability performance, the EHS index generally shows clearer trends than the LCA metrics (Tables C2a and C2b in the ESI[†]) for the top 10 solvents. DMMEA, DEEA, DBA and HEXA are flammable with flash points lower than 50 °C. DEEA is a recognized skin sensitizer. HEXA also exhibits aquatic toxicity that is an order of magnitude higher than MEA. 2A1PN, 2A1B, IPAE, 4AP, and DEAB are predicted to have lower acute toxicity than MEA due to their relatively high oral lethal dosage (LD₅₀oral) values. On the other hand,

Table 5 Amines with [OCCCN] and [CCCCN] patterns. The nomenclature is the same as for Table 4. Further details are provided in Tables E1–E4 in the ESI

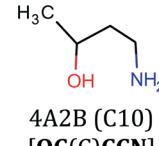
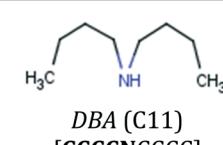
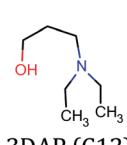
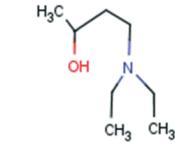
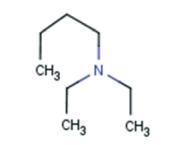
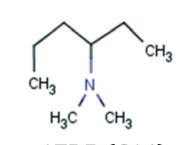
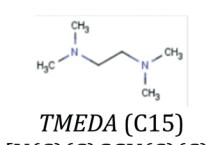
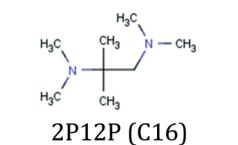
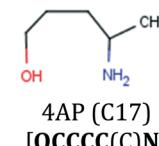
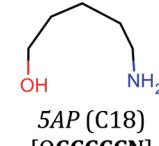
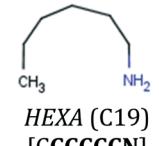
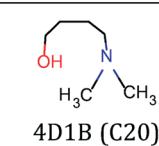
NH ₂			—	—
MPA (R8) [OCCCN]		4A2B (C10) [OC(C)CCN]		
NH	—	—		—
			DBA (C11) [CCCCNCCCC]	
N				
	3DAP (C12) [OCCCN(CC)(CC)]	DEAB (R9) [OC(C)CCN(CC)(CC)]	ND1B (C13) [CCCCN(CC)(CC)]	1EDB (C14) [CCCC(CC)N(C)(C)]
				
			TMEDA (C15) [N(C)(C)CCN(C)(C)]	2P12P (C16) [N(C)(C)C(C)(C)CN(C)(C)]

Table 6 Amines with longer carbon chains. The nomenclature is the same as for Table 4. Further details are provided in Tables E1–E4 in the ESI

NH ₂			
	4AP (C17) [OCCCC(C)N]	5AP (C18) [OCCCCCCN]	HEXA (C19) [CCCCCN]
N			
	4D1B (C20) [OCCCCN(C)(C)]		

MEA is characterized by higher toxicity indices due to its low immediately dangerous to life and health (IDLH) threshold value generated by the National Institute for Occupational Safety and Health (NIOSH). This indicator, however, is not available for the rest of the molecules in the data set.

4.2 Design of top candidate solvents from functional groups

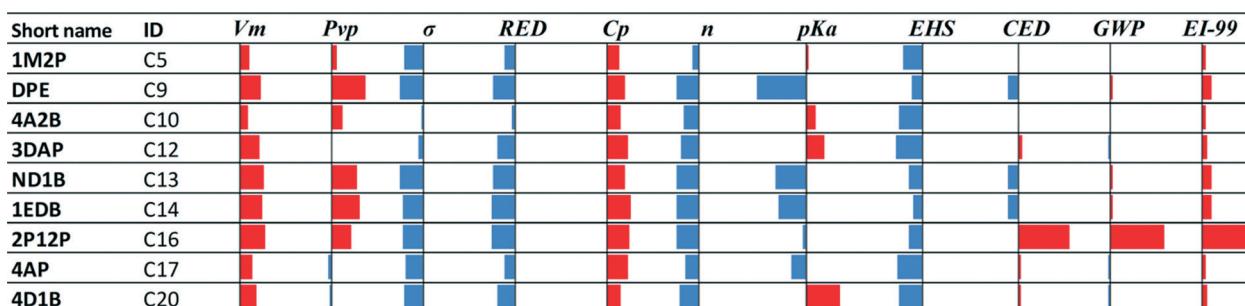
4.2.1 Stage 1 of solvent design. Using the molecular design space given by the chosen functional groups, the solution to problem (5) leads to the identification of 157 molecular structures on the Pareto front. The molecular structures are de-

fined by the number of groups of each type in the molecule, without full connectivity information, so that each molecular structure may correspond to several isomers. In this case, 2492 isomers can be constructed from the 157 structures identified.

The resulting database of designed structures (class D) is analyzed using the same strategy as classes C and R. The matrices J' and L are thus of size 157×252 . The calculation of the thermodynamic properties is carried out using first-order functional groups except for the pK_a that can only be calculated using a specific structure as input in the Marvin 6.0.5

Table 7 Indicative literature sources and properties investigated for selected class R amines

Solvent	Source	Investigated properties
2AP (R1)	Da Silva ¹⁰³	Carbamate stability
AMP (R2)	Fernandes <i>et al.</i> ¹⁰⁴ Sartori <i>et al.</i> ²² Harbou <i>et al.</i> ¹⁰⁵ Zheng <i>et al.</i> ¹⁰⁶	Protonation constant, standard molar enthalpy and entropy Chemical behaviour due to steric hindrance Process behaviour (e.g. reboiler duty, plant operation)
MMEA (R3)	Ma'mun <i>et al.</i> ¹⁰⁷ Suda <i>et al.</i> ¹⁰⁸ Ali <i>et al.</i> ¹⁰⁹	Reaction kinetics Absorption rate Absorption rate, mass transfer coefficient
EMEA (R4)	Kumar ¹¹⁰	Reaction kinetics Equilibrium solubility
BEA (R5)	Yamada <i>et al.</i> ¹⁹ Ma'mun <i>et al.</i> ¹⁰⁷ Yamada <i>et al.</i> ¹⁹ Ali <i>et al.</i> ¹⁰⁹	Absorption capacity Absorption rate Absorption capacity Reaction kinetics
DMMEA (R6)	Tong ¹¹¹ Versteeg <i>et al.</i> ³	Equilibrium solubility Reaction kinetics
DEEA (R7)	Sutar <i>et al.</i> ¹¹² Xu <i>et al.</i> ¹¹³	Equilibrium solubility and reaction kinetics Equilibrium solubility and heat of absorption
MPA (R8)	Henni <i>et al.</i> ¹¹⁴ Dong <i>et al.</i> ¹¹⁵	Reaction kinetics
DEAB (R9)	Sema <i>et al.</i> ^{11,13} Maneeintr <i>et al.</i> ¹⁴ Naami <i>et al.</i> ¹⁵ Shi <i>et al.</i> ¹⁶	Equilibrium solubility Equilibrium solubility and reaction kinetics Equilibrium solubility and cyclic capacity Mass transfer coefficient in packing material Vapour liquid equilibrium model

**Fig. 3** Comparative performance with respect to MEA (solid vertical lines) of commercial molecules which have not been traced (or for which data may be rare) as CO_2 capture solvents. The blue bars to the left of the solid vertical lines indicate better performance than MEA. The red bars to the right of the solid vertical lines indicate worse performance than MEA.

(ref. 86) software. For this purpose, we use the isomers exhibiting the highest pK_a value as the representative for each solvent structure. As in the case of solvent selection, top structures are identified using the criteria set out in formulation (4): five structures are obtained with the use of the sustainability indices and five without.

The set of candidates identified in this way consists of the 10 molecular structures (listed in Table 9) appearing most frequently with top ranks and representing 114 isomers. The structures are reported in the form of functional group combinations with their frequency of appearance in the molecule because this is how they are designed using the CAMD method. The results in Table 9 provide a first indication of the group combinations which may favour CO_2 capture.

Structures D1–D5 are obtained using eqn (4) without considering the sustainability indices. Structures D2 and D7–D10 are obtained using the entire set of equations in eqn (4). Some of the structures obtained are multifunctional amines

containing up to 3 amine groups, while some contain only a single amine group. The fact that only D2 is common to both sets of structures shows that the consideration of sustainability plays an important role in assessing the performance of the designed solvents. Structure D6 is not in the top 5 structures of the case examined in Fig. 5a, due to undesirably high C_p . It is reported here because one of its isomers is a novel molecule which closely resembles bis-(3-dimethylaminopropyl) (TMBPA).²⁰ This is a solvent containing 3 amine groups and that has been found experimentally to exhibit very favourable CO_2 capture features in mixtures with piperazine, including 70% higher cyclic capacity and 41% higher CO_2 removal than a 5 M MEA solution.²⁰

The performance of structures D1–D10 relative to MEA is presented in Fig. 5. Except for EHS, all the sustainability indices point to lower performance than MEA. This is a reasonable outcome because the sustainability indices were not considered during CAMD in step 1.1 but as a subsequent

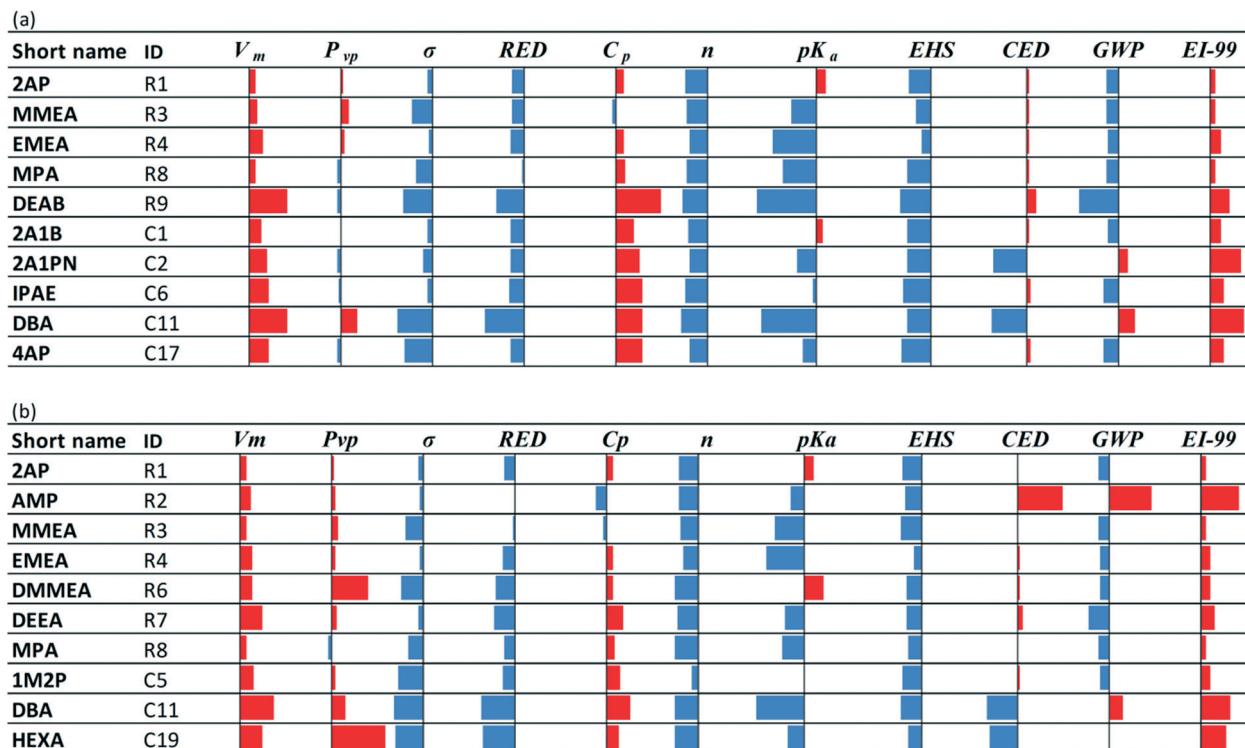


Fig. 4 Comparative results for the top 10 solvents selected based on (a) the set of equations in eqn (4) and (b) the set of equations in eqn (4) but without considering sustainability indices EHS, CED, GWP, and EI-99. The results are standardized with respect to MEA (shown by a solid vertical line). The blue bars to the left of the solid vertical lines indicate better performance than MEA. The red bars to the right of the solid vertical lines indicate worse performance than MEA. Solvents in the reference class (R) are reported first, followed by solvents in the commercial class (C), regardless of their ranking in the top 10.

Table 8 Main performance characteristics and literature sources for the top 10 solvents in Fig. 4a

Solvent	Main characteristics	Source
2AP (R1)	The closest similar structure is MIPA which presents very similar solubility to MDEA under the same conditions but has higher pK_a than MDEA.	Rebolledo-Morales <i>et al.</i> ¹²²
MMEA (R3)	Higher absorption rate and capacity than MEA.	Ma'mun ¹⁰⁷
EMEA (R4)	Higher CO_2 loading than MEA, DEA and MMEA (at 30% w/w) over a wide range of pressures.	Kumar ¹¹⁰
MPA (R8)	Higher reaction rate and absorption capacity than MEA. In mixtures with AMP, it exhibits considerably reduced corrosiveness, oxidative degradation and formation of nitrosamines than mixtures of MEA and AMP.	Henni <i>et al.</i> ¹¹⁴ Dong <i>et al.</i> ¹¹⁵ Hoff <i>et al.</i> ¹²³ Sema <i>et al.</i> ¹¹ Maneeintr <i>et al.</i> ¹⁴
DEAB (R9)	Designed specifically for high CO_2 capacity, reaction constant similar to AMP and DEA but higher than MDEA and much lower regeneration energy than MEA.	Rooney ¹¹⁶ Rooney ¹¹⁶
2A1B (C1)	Exhibiting high stability and low corrosiveness in mixtures with MDEA.	—
2A1PN (C2)	Similar to 2A1B.	Yamada <i>et al.</i> ^{19,120}
1M2P (C5)	Not traced as a CO_2 capture solvent. The structure is similar to MMEA.	Zhang <i>et al.</i> ²¹
IPAE (C6)	Slightly higher absorption capacity but lower reaction rate than the similar PAE which exhibits a high absorption capacity, similar to EMEA and BEA.	—
DBA (C11)	A biphasic solvent exhibiting phase change and regeneration at 90 °C, hence of much lower energy requirements than usual.	—
4AP (C17)	Not traced as a CO_2 capture solvent. The structure is similar to 2AP.	—

measure to identify the solvents with lower impacts among those obtained from CAMD. In this case (Fig. 5b), EHS and EI-99 improved, but CED and GWP slightly deteriorated, possibly due to the effect of the remaining property indices.

Furthermore, the apparent trade-off between the EHS and LCA indices could be attributed to the fact that molecules

which are structurally larger and more complex than MEA would have longer production chains with higher environmental impacts, while they could be more stable with higher boiling points and thus lower mobility index values. The mobility index is also used as a correction factor for the toxicity and flammability indices to account for the relative ease of

Table 9 Top molecular structures obtained from the class of designed solvents (D)

ID	Groups in molecule	Frequency of groups
D1	[−CH ₃ , >CH ₂ , −>C−NH ₂ , −CH ₂ −NH−, −CH ₂ −N<]	[4 1 1 1 1]
D2	[−CH ₃ , >CH ₂ , >C<, −OH, −>C−NH ₂]	[4 1 1 1 1]
D3	[−CH ₃ , >CH ₂ , −>C−NH ₂ , −CH ₂ −NH−, CH ₃ −N<]	[3 1 1 1 1]
D4	[−CH ₃ , >CH ₂ , −>C−NH ₂ , −CH ₂ −NH−]	[3 2 1 2]
D5	[−CH ₃ , >CH ₂ , −>C−NH ₂ , CH ₃ −NH−, −CH ₂ −NH−]	[2 1 1 1 1]
D6	[−CH ₃ , >CH ₂ , >CH−, −CH ₂ −NH−, −CH ₂ −N<]	[5 1 1 1 2]
D7	[−CH ₃ , >CH ₂ , >CH−, −OH, −>C−NH ₂]	[3 2 1 1 1]
D8	[−CH ₃ , −OH, −>C−NH ₂ , −CH ₂ −NH−]	[2 1 1 1]
D9	[−CH ₃ , >CH ₂ , −OH, −CH ₂ −NH−]	[1 2 1 2]
D10	[−CH ₃ , >CH ₂ , −OH, −>C−NH ₂ , −CH ₂ −NH−]	[2 1 1 1 1]

vapour formation promoting the risk of inhalation or catching fire. All the molecules in Table 9 show improved toxicity indices and slightly better flammability indices due to the improved mobility indices. However, they suffer from worse environmental indices such as aquatic toxicity and persistence in the environment. This could be a result of the more complex structure that is less naturally occurring and thus less prone to degradation in the environment. Tables C3a and C3b in the ESI† present, respectively, the LCA metrics and the various hazard indices and the parameters used to calculate them for the molecular structures listed in Table 9.

4.2.2 Stage 2 of solvent design. The main task in step 2.1 is to identify specific molecules from the set of isomers presented in Table 9. To this end, we exploit the qualitative structure–property relationships (1) and (2) reported in Table 1 to identify isomers that are likely to exhibit favourable CO₂ capture performance. The structures are transformed into the generic, hydrogen free representations of [OCCN], [OCCCN] (structure–property relationship (1)) and [NC···CN] with up to 6 carbon atoms (structure–property rela-

tionship (2)) which can then be processed computationally. The proposed motifs are sought systematically in the structures of the isomers using the publicly available Small Molecules Subgraph Detector software¹²⁴ which employs a maximum common subgraph method¹²⁵ to identify similarities between molecular structures. Note that structure–property relationship (2) was considered by Aronu *et al.*²⁰ who started from a structure similar to TMEDA (C15) and heuristically identified TMBPA (E7) for further testing as a CO₂ capture solvent. We adopt a similar rational approach for the selection of isomer candidates, but we combine two structure–property relationships in our search. The results are shown in Table 10.

4.2.3 Analysis of designed solvents. Among the solvents in Table 10, isomer D6 is clearly very similar to TMBPA, indicating that the CAMD method has delivered a potentially highly performing molecule despite its complex structure. Isomers D1, D3, D4 and D5 present a side chain with a longer carbon backbone. Structure–property relationship (2) has been applied in the form of [NCCCN] for at least one pair of nitrogen

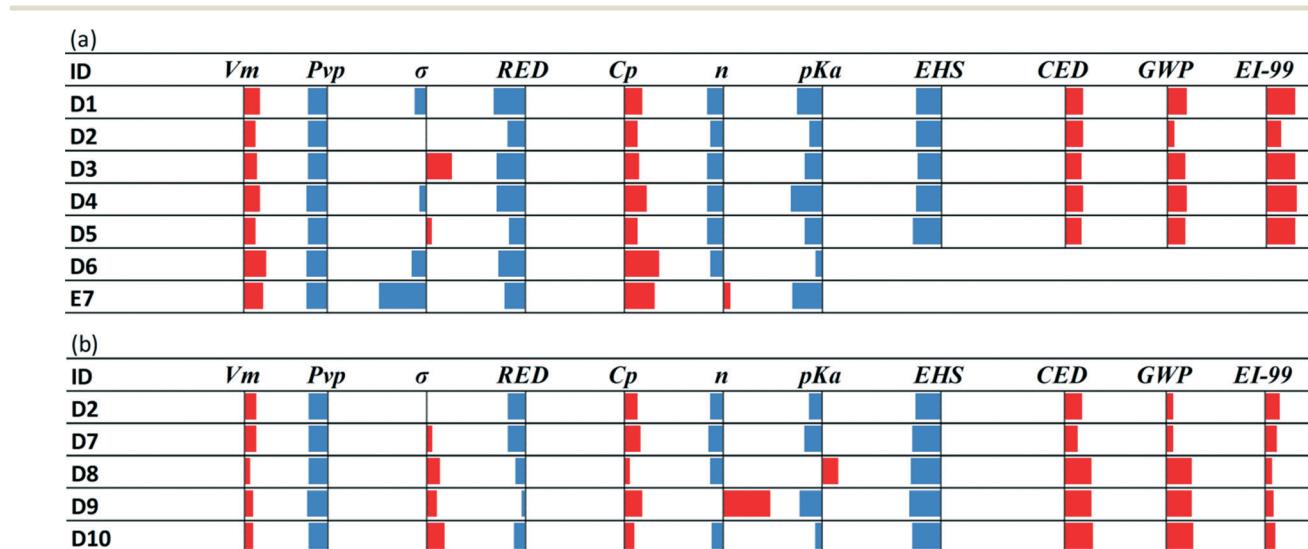


Fig. 5 Comparative performance of novel solvents designed using the proposed CAMD approach with respect to MEA: a) solvents D1–D5 were obtained using the set of equations in eqn (4) without considering the sustainability indices (although their values are reported here) and b) solvents D2 and D7–D10 were obtained using the entire set of equations in eqn (4). TMBPA (E7) is a commercial solvent previously tested as a CO₂ capture option.²⁰ D6 was not in the top choices, but it is reported here to compare its performance to that of E7 since the structure of a D6 isomer is very similar to E7. Fig. 5a compares solvents without considering sustainability; hence, these properties are not reported for E7 and D6.

Table 10 Isomers corresponding to structures in Table 9 based on structure–property relationships (1) and (2). IUPAC names have been assigned using Marvin 6.0.5 (ref. 86). The data for AEEA are available in Table E1 and for the other solvents in Tables E5 and E7 in the ESI

 D1: [3-amino-4-(dimethylamino)-3-methylbutyl] (methyl)amine	 D3: [3-amino-3-(dimethylamino) butyl] (methyl)amine
 D4: {3-[{2-amino-2-methylpropyl}amino] propyl}(methyl) amine	 D5: [3-amino-3-(methylamino) butyl](methyl)amine
 D6: (3-{[1-(dimethylamino)propan-2-yl] amino}propyl)dimethylamine	 E7: Bis-(3-dimethylaminopropanol) (TMBPA)
 D2: 4-amino-2,4-dimethylpentan-2-ol (CAS: 91875-44-4)	 D7: 3-amino-2,3-dimethylpentan-1-ol
 D8: 2-amino-1-(methylamino)propan-2-ol	 D10: 2-amino-4-(methylamino)butan-2-ol
 D9: 2-{[2-(methylamino)ethyl] amino} ethan-1-ol (CAS: 85771-07-9)	 R10: AEEA

atoms in each molecule. These molecules also contain a quaternary carbon atom bonded to a primary amine group, which introduces moderate steric hindrance to the molecule and resembles the structure of AMP. The existence of 3 amine groups with moderate steric hindrance is expected to increase the absorption capacity, while the appearance of at least one primary group and one secondary group is expected

to ensure reasonable kinetic performance, assuming that a carbamate will always be formed.

Isomers D2, D7, D8, D9 and D10 all contain a hydroxyl. D2 is a commercially available structure with a CAS registry number of 91875-44-4 and is the solvent shared between the two cases investigated in Fig. 5. It can be said to exhibit steric hindrance based on structure–property relationship (6) in

Table 1. These molecules all contain one or two primary or secondary amine groups. They are combined with a quaternary carbon atom; hence, they also resemble AMP, except for D9 which is a simpler hydroxyl-diamine. In isomers D2, D7, D8 and D10, structure–property relationship (1) appears as [NCCO] or [NCCCO], while structure–property relationship (2) also appears in D10. D9 is a commercially available amine with a CAS number of 85771-07-9. The structure is very similar to AEEA (shown next to D9 in Table 10) which exhibits absorption capacity, CO₂ reactivity, and energy efficiency higher than those of MEA, while it has also low vapour pressure.¹²⁶

4.3 SAFT-based evaluation of selected solvents (step 2.2)

The sets of selected and designed solvents are now considered jointly for further analysis. The SAFT- γ SW EoS is used to predict the phase behaviour of all solvents in these sets, which can be modelled with the approach using the current set of group interactions available (section D in the ESI†). These are MMEA, EMEA, MPA, 1M2P, DBA and D9. Comparisons with experimental data, where available, and with the performance of MEA are provided.

Several authors have measured the solubility of CO₂ in aqueous mixtures of MMEA^{127–129} and EMEA¹¹⁰ under conditions of chemical and vapour–liquid equilibria. In Fig. 6a and b, we compare SAFT- γ SW predictions for MMEA mixtures and EMEA mixtures, respectively, with experimental data. The agreement with experiments is good considering these calculations are purely predictive and that the group parameters have been characterised based on data for other alkanolamines at lower loadings.⁷¹ In particular, the relative solubility of CO₂ in the different solvents is found to be reliable. Furthermore, both models and experiments indicate

that CO₂ loading (*cf.* Figure D1 in the ESI†) decreases with solvent concentration at moderate to high pressures but increases with solvent concentration at low pressures. The qualitative agreement achieved provides a useful basis for solvent selection. We note that the accuracy of the model could be improved by developing group interaction parameters that account for the proximity effects between the groups of relevance to MMEA and EMEA, as has been done successfully for other groups.^{70,71}

A further comparison with experimental data can be seen in Fig. 7 for the solubility of CO₂ in aqueous solutions of MPA. The data for this mixture at two temperatures (*T* =

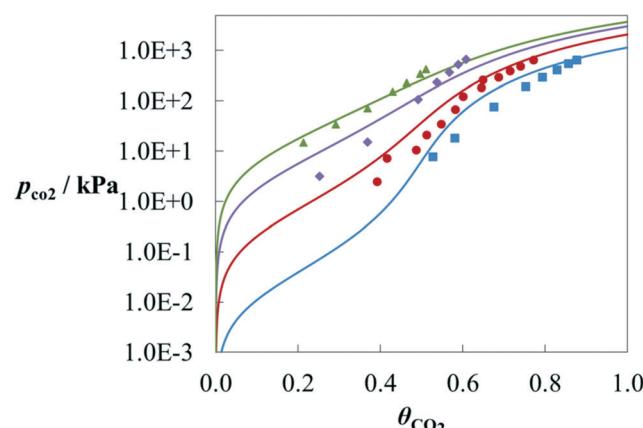


Fig. 7 Solubility of CO₂ in a 4 M (~30 wt% in mass) aqueous solution of MPA at *T* = 313.15 K (blue), 343.15 K (red), 373.15 K (purple) and 393.15 K (green) as a function of the partial pressure of CO₂ along the vapour–liquid equilibrium of the ternary mixture MPA + H₂O + CO₂. The solubility is represented as CO₂ loading θ_{CO_2} , defined as the moles of CO₂ absorbed in the liquid phase per mole of amine in the liquid. The symbols correspond to experimental data¹¹⁵ for the corresponding temperatures. The solid curves correspond to SAFT- γ SW calculations.

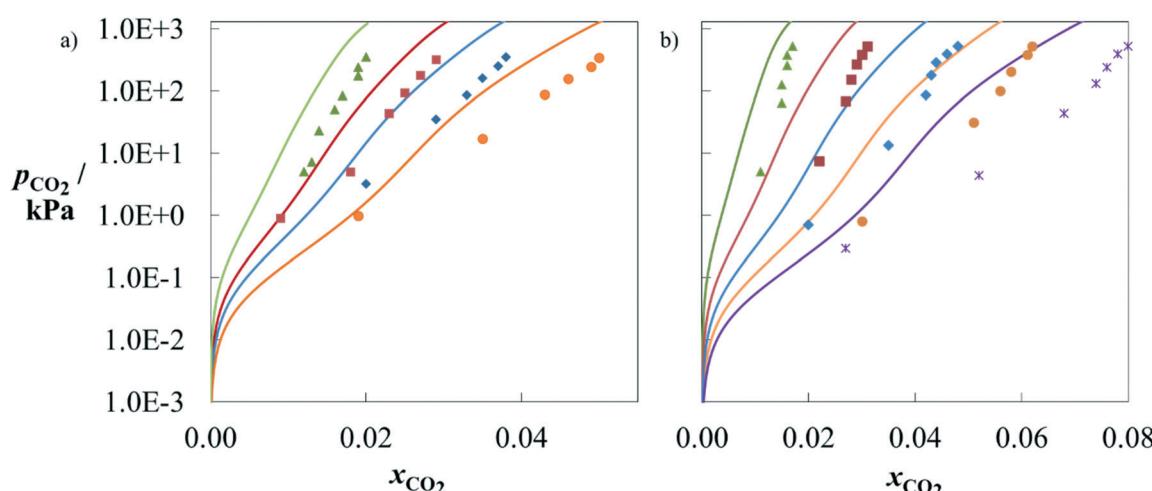


Fig. 6 Partial pressure of CO₂ as a function of mole fraction of CO₂ in aqueous solutions of alkanolamine + H₂O + CO₂. a) MMEA at 303.1 K. The symbols correspond to experimental data^{110,127} for aqueous solutions of MMEA of various weight percentages in mass: 6.8 wt% (green), 11 wt% (red), 14 wt% (blue) and 19 wt% (orange). b) EMEA at 303.1 K. The symbols correspond to experimental data¹¹⁷ for aqueous solutions of EMEA of various weight percentages in mass: 6 wt% (green), 12 wt% (red), 18 wt% (blue), 24 wt% (orange) and 30 wt% (purple). The solid curves correspond to SAFT- γ SW calculations for the same water : solvent ratios.

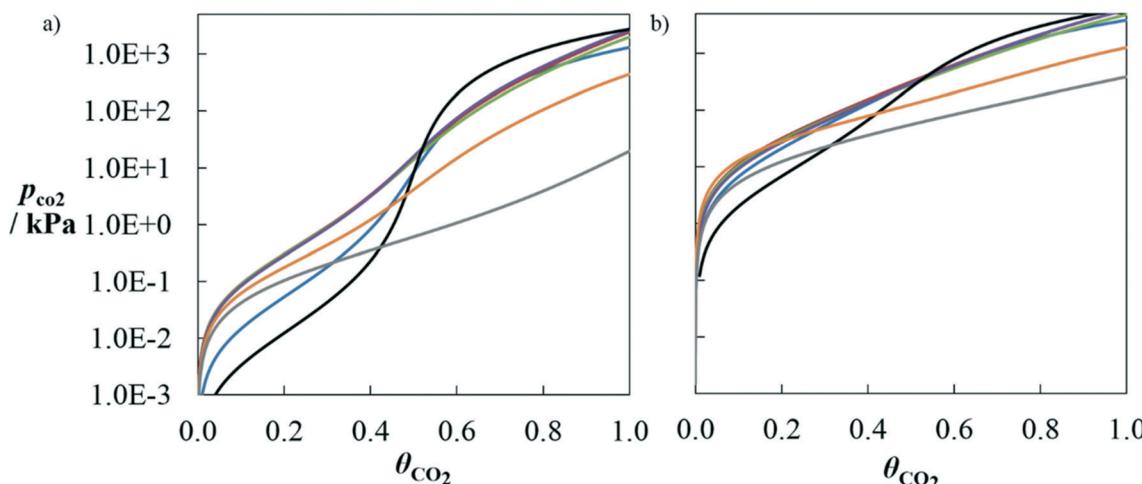


Fig. 8 Solubility of CO_2 in 30 wt% (in mass) aqueous solutions of MPA (blue), MMEA (red), EMEA (green), 1M2P (purple), MEA (black), DBA (orange) and D9 (grey) at a) $T = 313.15\text{ K}$ and b) 393.15 K as a function of the partial pressure of CO_2 along the vapour–liquid equilibrium of each ternary mixture alkanolamine + $\text{H}_2\text{O} + \text{CO}_2$. The solubility is represented as CO_2 loading θ_{CO_2} , defined as the moles of CO_2 absorbed in the liquid phase per mole of amine in the liquid. The solid curves correspond to SAFT- γ SW calculations.

313.15 K and 393.15 K) were used in the estimation of a number of group parameters;⁷⁰ and therefore, only the calculations at 343.15 K and 373.15 K can be seen as predictions. SAFT- γ is found to provide a very good description of the effect of temperature on the solubility of CO_2 in this case.

A comparison of the predicted performance of SAFT- γ for a number of high-performing solvents is presented in Fig. 8. These solvents are compared here based on the solubility of CO_2 in aqueous solutions of a given mass percentage. At a low temperature ($T = 313.15\text{ K}$) typical of an absorption process, there is a range of pressures at which all solvents are predicted to reach higher solubility loadings than MEA for a given partial pressure of carbon dioxide. The range of pressures at which this occurs is wider for DBA and D9. Solvents such as MMEA, EMEA and 1M2P present very similar solubility curves; this can be attributed to the similarities in their molecular structures (see Table 4). At a high temperature ($T = 393.15\text{ K}$) typical of a desorption process, and at solubility loadings lower than 0.5, most of the solvents appear to outperform the regeneration capacity of MEA, as they lead to partial pressures of CO_2 higher than those obtained with MEA. At high loadings, MEA leads to only slightly higher partial pressures than MMEA, EMEA, 1M2P and MPA.

The performance predictions obtained for the designed or selected solvents with SAFT- γ SW therefore confirm that these solvents should be investigated further for their CO_2 capture potential.

5. Conclusions

A systematic two-stage approach to molecular design has been proposed and applied to the discovery of CO_2 capture solvents. The approach is based on multiple criteria, is applicable to the identification of molecules from databases or functional groups, combines simple group contribution

models with the molecular-based SAFT framework, and takes model uncertainty into account. It has been used to generate a prioritised list of candidate molecules from hundreds of thousands of possible compounds.

The proposed methodology has clearly led to the identification of important candidate solvents for CO_2 capture, including novel compounds. Several of these have been tested experimentally in the published literature and recommended as highly performing alternatives to MEA, indicating that the proposed approach leads to the rapid identification of useful compounds. Others have received little attention or have yet to be considered as alternatives for CO_2 capture despite their commercial availability indicated by their CAS registry number, demonstrating that the proposed approach can help generate novel leads. For example in the cases of 2A1B, 2A1PN and 2A1H only a patent that mentions very good stability and reduced corrosiveness compared to MEA when they are used in mixtures with MDEA exists; however, no equilibrium or reaction kinetic data are reported. In several cases, the structural and property resemblance of these candidates with state-of-the-art solvents recently considered as CO_2 capture options provides significant motivation to undertake further experimental testing. Without prior intention or use of any specific constraints, the selection procedure also resulted in the identification of several thermomorphic biphasic solvents. Such solvents enable desorption at temperatures much lower than the 120 °C employed in the MEA case, hence requiring a significantly lower regeneration load.

The novel solvents designed using the proposed CAMD approach combine structural characteristics that are known empirically to promote both high CO_2 absorption capacity and increased reaction rates. D6 is a novel structure proposed by CAMD which is very similar to TMBPA, a multi-functional amine identified in the published literature as a solvent of high CO_2 absorption capacity and reaction rate in mixtures

with piperazine. The isomers corresponding to D2 and D9 are commercially available solvents. This is clear evidence that the systematic CAMD approach employed in this work points towards promising CO₂ capture options, despite the initial use of simple property prediction models. This is further confirmed by the phase and chemical equilibrium predictions obtained with the SAFT- γ SW equation of state. For example, D9 exhibits very high performance as it actually outperforms all the other amines in the commercial set for a wide range of pressures. The fact that such an assessment of absorption and desorption potential can be made without recourse to any experimental data on the candidate solvents, and indeed without ever synthesizing the proposed molecules, is a significant benefit of the use of a predictive model such as SAFT- γ SW, relative to approaches based on more qualitative rules for solvent selection.

Due to the use of sustainability metrics in different stages of the methodology, a clear opportunity has been identified to develop less hazardous solvents than MEA. However, the LCA metrics do not always point in the same direction as safety metrics, and the improvement potential with respect to MEA is limited to specific solvents and metrics. Of course, it has to be noted that these LCA metrics refer only to the life cycle impact of solvent production, and therefore, the extent of solvent fugitive losses and degradation has been neglected in this analysis, despite its known importance in the case of MEA. Additionally, other more significant life cycle impacts (*e.g.* the solvent regeneration life cycle impact) are indirectly covered by the thermodynamic properties considered in CAMD.

In our current work, we have shown that considering multiple and diverse criteria in the design of solvents using a CAMD method can lead to novel molecules. Building on this approach, the space of molecules to be explored and the range of criteria for the *in silico* assessment of candidate compounds could both be extended. For instance, the consideration of higher order groups in the group contribution models employed could increase the accuracy of the property predictions and allow the more reliable identification of the most suitable isomers as CO₂ capture options. Predictive group contribution property models that provide accurate caloric information⁵⁶ could also be used to achieve a more direct assessment of energy consumption and operating cost. Furthermore, the proposed uncertainty quantification method could be expanded to account for additional properties, especially those associated with sustainability. Sustainability metrics in the form of group contribution models combined with uncertainty quantification could also be considered during CAMD to enable a more focused search as well as to increase the robustness of the obtained results. Since the results obtained from CAMD also provide insights into the structural combinations that favour CO₂ capture, this could be used to prioritize the efforts to develop new group contribution parameters for the SAFT- γ SW equation, in the form of new functional groups, or of combinations of existing groups to form second-order groups and increase prediction accuracy. Such developments can provide further guidance for experimental studies and help to accelerate the search for better solvents.

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