

Efficient Screening and Selection of Post-Combustion CO₂ Capture Solvents

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We develop an approach for the screening and selection of post combustion CO₂ capture solvents using as the performance criteria the molecular and mixture properties associated with thermodynamics, reactivity and sustainability. The proposed approach involves a fast screening stage in which numerous solvents are evaluated based on the simultaneous consideration of pure component properties. Several properties are specifically selected to represent the effects of molecular chemistry on the capture process. A few high-performing solvents are further evaluated using predictive models accounting for the very non-ideal mixture behaviour. The prediction of pure component properties is supported by standard group contribution models. The solvent-water-CO₂ interactions are represented within the SAFT-VR and SAFT-γ equations of state to predict accurately the mixture vapour-liquid equilibrium behaviour. The proposed developments are tested successfully on a dataset consisting of 126 potential solvent candidates.

1. Introduction

The identification and selection of efficient post-combustion CO₂ capture solvents using chemical absorption is very challenging due to the non-ideal solvent-CO₂-water chemical interactions. It requires the combined consideration of several thermodynamic, kinetic and sustainability properties as performance criteria in order to select the optimum capture solvents. Most existing works focus on developing rigorous models, which are indispensable for the accurate prediction of solvent properties prior to the selection of very few, realistically useful options. For example, the Statistical Associating Fluid Theory for potentials of variable range (SAFT-VR) has been used as an equation of state (EoS) to model accurately the fluid-phase behaviour of multifunctional aqueous alkanolamines and CO₂ (Rodriguez et al., 2012) based on the transfer of parameters from mixtures containing monoethanolamine (Mac Dowell et al., 2010) and alkylamines (Mac Dowell et al., 2011). A more predictive approach is the development of group parameters for these mixtures (Chremos et al., 2013) for use with the group contribution (GC) SAFT-γ SW (square well) approach. By the same token, continuum-solvation models have been used among other computational chemistry methods for the calculation of the amine basicity to measure molecular reactivity (Sumon et al., 2012). Detailed reaction models have also been proposed for important properties such as degradation (Lepaumier et al., 2010), associated with sustainability. Despite the usefulness of rigorous modelling, significant complexity results from the multitude of models that need to be combined to arrive at a realistic assessment, due to the large number of relevant properties and underlying physical and chemical phenomena. Increased computational cost is also incurred in some models. This prohibits the simultaneous consideration of multiple performance criteria, leading to solvents of reasonable performance only for the properties considered, limiting the selection to a few choices compared to the very large

number of molecules and mixtures that may be considered as potential solvents. On the other hand, attempts to develop simpler models or statistical correlations that match structural molecular characteristics with pure component, mixture and/or kinetic properties associated with CO₂ capture are gradually appearing in published literature. Retief (2012) considered the Hansen solubility parameter as the sole index for screening of a large number of amine-based solutions using chemical absorption. Porcheron et al. (2011) developed a statistical, neural network, model for the fast prediction of the pseudo-acidity constant and the absorption isotherms for amines used in CO₂ capture. The results of such efforts provide significant evidence that prior to utilizing rigorous models or lab-scale experiments, simpler models may facilitate a quick and reliable screening of CO₂ capture solvents.

2. Proposed approach

The aim of our current work is to develop an approach to select solvents from a large pool of candidates that offer high performance simultaneously in many property criteria associated with effective chemical absorption of CO₂ and solvent regeneration. We use a systematic screening method, where accuracy is initially traded-off (although maintained at reasonable levels) for computational efficiency by using simple property models that have been specifically selected to identify useful capture candidates. Solvents with an inferior performance are easily eliminated while a few promising candidates are further evaluated using predictive models that account for non-ideal mixture behaviour. The simultaneous consideration of several properties that represent the effects of the molecular chemistry on the capture/regeneration process compensates for the initial use of simpler models and ensures the selection of fewer but more effective solvents. Selected candidates from the available pool are considered as discrete options in computations using the SAFT- γ SW EoS to restore accuracy in the prediction of important properties.

2.1 Property criteria for preliminary solvent screening

Numerous pure component solvent properties may be considered as preliminary screening criteria. Several are analysed in this section based on their potential to capture important thermophysical, equilibrium, kinetic and sustainability characteristics.

2.1.1 Thermodynamics and reactivity

- 1) The Hansen solubility parameter (δ_i) represents the cohesive energy density, i.e., the energy required to overcome the solvent-solvent interactions. It may be used as an indicator of the solubility of CO₂ in different solvents through the *RED* index (Stefanis and Panayiotou, 2008), expressed as a function of the solvent and solute dispersion, polar and hydrogen-bonding Hansen solubility parameters. Solvents with *RED* < 1 are generally considered to be favorable for the dissolution of the particular solute (e.g., CO₂).
- 2) The vapour pressure (P_{vp}) is an important parameter for absorption/desorption CO₂ capture systems because high P_{vp} is an indicator of high volatility and potential solvent losses.
- 3) Higher basicity (pK_a) is associated with higher solvent reactivity.
- 4) The liquid heat capacity (C_p) of the CO₂ rich stream after absorption is directly proportional to the sensible heat required in desorption (Oexman and Cather, 2010). Although the stream contains a solvent-CO₂ reaction product, it may be assumed that a solvent of low C_p facilitates the reduction of sensible heat.
- 5) The density (ρ), surface tension (σ), and viscosity (η) are solvent properties closely associated with the design and operating features of the separation columns. The density should be high to facilitate separation with reduced solvent flowrate and equipment size. Surface tension and viscosity should be low to improve the mass transfer in the packing material.
- 6) The melting point (T_m) should be lower than the lowest process temperature to avoid solidification. The boiling point (T_{bp}) should be higher than the highest process temperature to avoid vaporization.

2.1.2 Sustainability

The solvent sustainability characteristics are evaluated using two index categories. A cradle-to-gate Life Cycle Assessment (LCA) shows the environmental impacts of solvent production including the extraction, manufacture and disposal of raw and auxiliary materials. Safety, health and environmental hazard assessment (EHS) enables the estimation of harm potential in accidental scenarios within a CO₂ capture plant in the presence of the tested solvents.

- 7) In LCA the metrics used are the Cumulative Energy Demand (CED) in MJ-equivalent, a resource-oriented indicator which reflects the economic and the environmental impacts, the Global Warming Potential (GWP) in kg CO₂ equivalent, which is a damage-oriented indicator reflecting the effect of greenhouse gas emissions, and the Eco-Indicator-99 - EI-99 (Goedkoop and Spriensma, 2000), providing an aggregated score for the end-point impact categories of human health, ecosystem-quality and resource consumption.

8) The EHS method (Sugiyama et al., 2008) represents an intermediate between hazards and exposure and it uses a comprehensive set of characteristic dangerous properties for each hazard category estimated from a prioritized list of physical and chemical substance properties. Substance properties are collected from material safety data sheets whenever possible and Quantitative Structure Activity Relationships (QSARs) are used to fill some of the data gaps.

2.2 Rigorous evaluation using SAFT

The SAFT-VR equation of state (Gil-Villegas et al., 1997) is a molecular-based EoS in which molecules are modelled as chains of homonuclear segments interacting via a variable range potential (here, a square-well potential), with association sites where appropriate. It provides an accurate description of the thermodynamic fluid-phase behaviour of a wide variety of compounds and their mixtures, including mixtures of CO₂, water and amines (Mac Dowell et al., 2010) as well as ammonia and members of the n-alkyl-1-amines homologous series (Mac Dowell et al., 2011). To increase the predictive capability of the thermodynamic description its formulation within a GC approach is required. In SAFT-γ SW (Lymeriadis et al., 2007), molecules are formed from fused heteronuclear segments representing distinct functional groups. The underlying assumption (as in any GC approach) is that once the parameters for a particular functional group have been determined from regression to experimental data for specific molecules, they can be transferred to other molecules including that functional group without any further parameter adjustment, to predict the fluid-phase behaviour of compounds that have not yet been probed experimentally. A first step towards the description of multifunctional amines with the SAFT-γ SW EoS was presented in Lymeriadis et al. (2008) and extended in Chremos et al. (2013) to capture additional groups. This approach and the SAFT-VR models of multifunctional amines (Rodriguez et al., 2012) are used in our current work.

3. Implementation

3.1 Solvent database and reference set

The molecules considered as candidate CO₂ capture solvents consist of 126 acyclic, aliphatic amines and hydroxyl-amines. They are obtained from an in-house database available from ETH Zurich, publicly available databases (NIST, 2014; EPA, 2014) and the commercial catalogue of Sigma-Aldrich (2014). The database is not exhaustive but provides an inclusive set of amines with different realizations of molecular structures assigned a CAS registry number. All the molecules are obtained from combinations of the following functional groups: CH₃-, -CH₂-, >CH-, >C<-, -OH, -CH₂-NH₂, -CH₂-NH-, -CH₂-N<, >CH-NH₂, >CH-NH-, CH₃-NH-, CH₃-N<, ≥C-NH₂. These are selected due the public availability of data required for property calculations through GC or other models. The available molecular set is separated in 3 classes:

- The reference class (R) contains 25 amines previously considered in the published literature as CO₂ capture solvents (e.g., through determination of vapour-liquid equilibrium or reactivity properties etc.);
 - The class of commercially available amines (C) contains the entire set of the 126 molecules;
 - The class of commercially available hydroxyl-amines (L) contains molecules with at least a -OH group.
- The proposed separation is useful to investigate the possibility of identifying new molecules that might be effective as capture solvents compared to the amines in the R set. The term “commercially available amines” indicates that the molecules considered are chemical substances that have been synthesized previously (although not necessarily previously used in CO₂ capture) as opposed to molecules proposed only theoretically (e.g., computationally). The reference set includes well-known solvents such as: 2-Amino-2-Methyl-1-Propanol (AMP); 2-(Methylamino)-Ethanol (MMEA); N-Methyl-1,3-Propanediamine (MAPA); 2-(Amino)-Propanol (AP); Ethylaminoethanol (EMEA); 1,2-Propanediamine (MEDA); N,N-Dimethylaminoethanol (DMMEA); 3-Amino-1-Propanol (MPA); Monoethanolamine (MEA); N,N-Diethyl-2-aminoethanol (DEEA); 2-Amino-2-methyl-1,3-propanediol (AMPD); Triisopropylamine (TIPA); 4-diethylamino-2-butanol (DEAB); Diethylenetriamine (DETA), N-(2-Aminoethyl)ethanolamine (AEEA).

3.2 Solvent selection and ranking

Considering the thermodynamic and reactivity properties presented in section 2.1 as performance measures, it is desired to select solvents based on the criteria set in Eq(1):

$$\begin{aligned} \max & \quad \rho, pK_a \\ \min & \quad C_p, P_{vp}, \sigma, n, RED \\ \text{s.t.} & \quad T_m < T_{Abs} \\ & \quad T_{bp} > T_{Des} \end{aligned} \quad (1) \quad \min J_i = \sum_{j=1}^{N_p} a_{i,j} \cdot x_{i,j} \quad (2)$$

T_{Abs} and T_{Des} are the temperatures of the absorption and desorption columns. Molecules that fail to satisfy the temperature constraints are removed from the set while the remaining molecules are rank-ordered

using J_i to merge the considered properties in a unified criterion based on Eq(2). Term x_{ij} represents a scaled value of property J (e.g., ρ , pK_a and so forth) for solvent i from the total of N_p properties, and a_{ij} represents a unity coefficient that is positive for properties that need to be minimized and negative for those to be maximized. Solvents are ranked by minimising J_i . The liquid molar density ρ is calculated as the inverse of liquid molar volume V_m (Constantinou et al. 1995), σ and n from Conte et al. (2008), T_m and T_{bp} from Marrero and Gani (2001), P_{vp} from the Riedel correlation (Poling et al., 2001), C_p from Rayer et al. (2012), and pK_a from Chemaxon Marvin (2014). After ranking the solvent set based on Eq(1) and Eq(2), the sustainability indices are calculated for each one of them. The FineChem tool (Wernet et al., 2009) is used to provide estimates (with an average relative error of 30-40 %) for LCA-based metrics using molecular descriptors as inputs. The functional unit is 1 kg of solvent produced. The Estimation Program Interface (EPI) Suite and the Toxicity Estimation Software Tool - TEST (EPA, 2014) are used for the calculation of EHS metrics. An average of the dangerous properties calculated by each variation of the EHS method based on Sugiyama et al. (2008) is used to avoid missing scores in case of data gaps. The EHS score is taken as the sum of the safety, health and environment scores.

3.3 Results and discussion

The average values of the index J for the top 10 molecules in each class are shown in Figure 1 (left). It is apparent that the molecules in class C perform considerably better overall than those in the other classes. All classes contain molecules that may perform much better than MEA (dash marker) based on the properties considered as performance criteria. From a comparison of the C and L classes it appears that -OH has a detrimental effect on the overall performance. The close performance of the L and R classes indicates that most molecules in R are alkanolamines. The pK_a and RED values are shown in Figure 1 (right) for the top 15 molecules selected based on J from the C and L classes. These are compared to the pK_a and RED values of all 126 molecules. Most selected molecules indicate a simultaneously higher pK_a (i.e., reaction rate) and RED (i.e., CO_2 absorption capacity) than MEA. Note that the performance (J value) of MEA is 67 % lower than the top molecule of class C. Some molecules have lower RED or pK_a than molecules not selected in the top 15, but their performance is much better in the remaining properties.

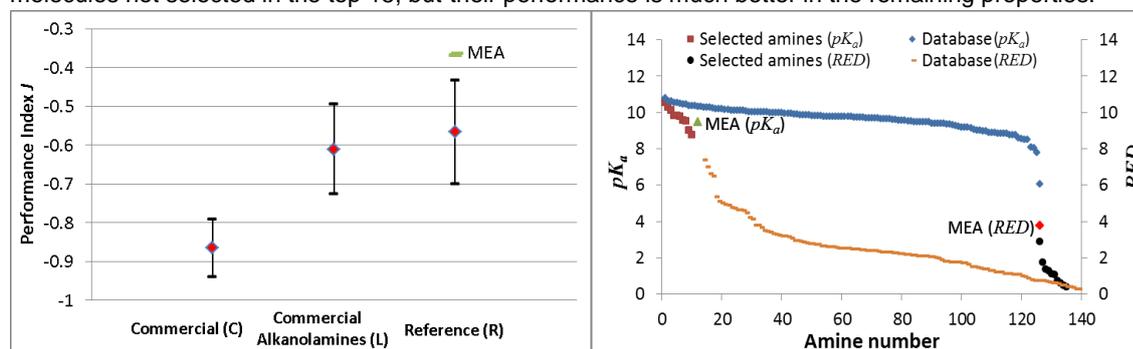


Figure 1: Average performance index values with 95 % confidence intervals for the 3 classes (left); pK_a and RED values for database and selected solvents compared to MEA (right)

The top 5 molecules contained in class R are shown in Table 1, in addition to *n*-hexylamine (HEXA), selected from class C. MAPA exhibits a high pK_a and low RED but ranks in the middle due to its high P_{vp} . The 20 molecules of class R mentioned in section 3.1 are ordered based on their J values, and the top 5 are reported in Table 1. Some of these molecules are outranked by those of Table 1 despite their high performance in a few property criteria. The proposed evaluation approach allows the consideration of such trade-offs. The data reported in Table 1 for several of the properties are either experimental or based on Antoine coefficients in the case of P_{vp} . However, the molecules were rank-ordered using the GC methods reported in section 3.2. The average absolute deviation error (AADE) (from use of GC methods) is generally very low for the molecules of Table 1 compared to the standard deviation of the experimental or the Antoine correlations. For example the standard deviation in the P_{vp} obtained from accurate Antoine models is approximately 1,100 Pa while the AADE from GC models is 340 Pa. This is an indication that the proposed approach is relatively robust to model uncertainty. Similar trends were observed for all properties. Molecules such as AMP and MAPA were considered in experimental published literature as good CO_2 capture options and this is reflected in the results. HEXA is selected as an indicative example from class C. Its surface tension, viscosity, RED index, and pK_a indicate it may be a good capture solvent.

Table 1: Property values for top solvents

Solvent	CAS number	V_m^a (cm ³ /mol)	P_{vp}^b (Pa)	σ^a (dyn/cm)	C_p (J/molK)	n^c (cp)	RED	pK_a
AMP	124-68-5	98.7	315	47.9	176.0	0.66	2.27	9.7
MMEA	109-83-1	80.4	456	34.6	206.1	0.96 ^d	3.05	9.85
MAPA	6291-84-5	104.4	1,384	32.6	238.4	0.78 ^d	1.77	10.5
AP	6168-72-5	78.5	196	47.0	239.1	0.85 ^e	2.60	9.37
EMEA	110-73-6	98.1	255	47.6	237.5	0.69 ^f	2.91	10.1
HEXA	111-26-2	132.9	2,707	25.8	258.9	0.85	0.74	9.7

^aYaws (2010a), ^bYaws et al. (2009), ^cYaws (2010b), ^dat 309 K, ^eat 327 K, ^fat 322 K.

The CO₂ partial pressure (P_{CO_2}) in aqueous mixtures of HEXA (SAFT-VR), MEA (SAFT- γ SW) and AMP (SAFT-VR) is shown in Figure 2 as a function of CO₂ loading (Θ_{CO_2}) at T=313 K. A solvent composition of 30 wt % was used for MEA, 35 wt % for AMP, and 70 wt % for HEXA. MEA yields higher CO₂ loading at low P_{CO_2} , while AMP performs better at higher P_{CO_2} . HEXA, which is a promising solvent (Zhang et al., 2012), has the same level of performance as MEA and AMP at $P_{CO_2} \approx 3$ MPa.

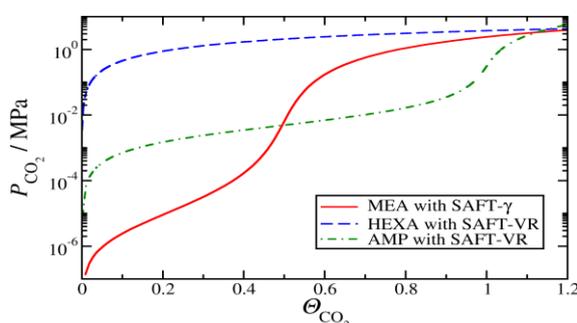


Figure 2: Predicted CO₂ partial pressure vs CO₂ loading at T = 313 K

Table 2: Sustainability metrics for top solvents

Solvent	EHS	CED (MJ _{eq} /kg)	GWP (kgCO _{2eq} /kg)	EI-99 (point/kg)
AMP	2.95	123.37	3.82	0.33
MMEA	3.16	105.76	3.39	0.20
MAPA	3.46	141.13	4.76	0.64
AP	2.68	105.76	3.39	0.20
EMEA	3.57	106.12	3.40	0.22
HEXA	3.88	94.22	3.48	0.28
MEA	3.95	105.49	3.48	0.18
TIPA	1.18	98.76	4.50	0.27

The sustainability metrics calculated for the top molecules are shown in Table 2, with MEA and TIPA values for comparison. The combined EHS scores range from 1.18 to 5.07 (average of 2.86) for the 126 molecules. TIPA is the least hazardous substance in the dataset. This is due to its relatively higher flash and boiling points. Of the top molecules AP seems to be the least hazardous substance followed by AMP. All top solvents show good potential from an EI-99 perspective with values higher than the set average of 0.45 points/kg and close to the minimum of 0.18 points/kg (MEA). AP has one of the smallest estimated environmental impact for production (CED, GWP) among the top molecules together with MMEA.

4. Conclusions

The evaluation of 126 commercially available amine-based molecules in terms of their suitability as CO₂ capture solvents has been presented. It is based on a systematic approach enabling a pre-screening stage using simple property models, followed by a SAFT EoS to enable a rigorous evaluation of important vapour-liquid equilibria properties. The pre-screening stage combines several important pure component properties associated with thermodynamics, reactivity and sustainability. The results indicate commercially available amines which are good candidates although they have yet to be evaluated. The results also highlight solvents that received significant attention in literature due to their favourable capture behaviour.

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