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Systematic Selection of Mixtures as Post-Combustion CO_2 Capture Solvent Candidates

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We propose a systematic approach for the preliminary screening of binary amine mixtures as CO_2 capture candidates considering several important properties as selection criteria. The proposed approach consists of several decision making stages, which account for solvent-solvent and solvent-solvent-CO_2 interactions using standard group contribution models as well as equations of state and activity coefficient models to address the vapour and liquid phase non-idealities in several properties considered as selection criteria. The aim of the proposed approach is to be fast and sufficiently efficient to identify few useful amine combinations, which may then be evaluated using rigorous prediction models or experiments. A multi-criteria mixture selection methodology is employed to unveil important trade-offs among several important properties and to propose the mixtures that appear to be promising as CO_2 capture candidates. The proposed method is applied in mixtures resulting from numerous binary combinations of amines, which have been previously investigated in their pure aqueous form as CO_2 capture solvents.

1. Introduction

Binary amine mixtures are increasingly considered as CO_2 capture solvents due to their simultaneously high performance in several important properties (e.g. reaction rate, CO_2 capacity etc.). This is necessary to address shortcomings of single amines, which present favourable behaviour in few properties at the expense of strongly undesired effects in numerous others. The selection of the optimum mixture composition and concentration is a very challenging problem due to a) the highly non-ideal mixture-water-CO_2 interactions, b) the availability of countless combinations of molecules as potential mixture components and c) the need for combined consideration of several properties as CO_2 capture selection criteria. In current practice the amine components of the mixtures are first selected out of few options, mainly based on prior empirical knowledge regarding their suitability as CO_2 capture solvents in their pure aqueous form. The few selected binaries are then tested experimentally in lab or pilot-scale units to determine the most efficient concentration for the separation of CO_2. To this end, Monoethanolamine/ Methyldiethanolamine (MEA/MDEA) has received increased attention as a mixture (Singh, 2011) with pilot plant studies (Aroonwillas et al., 2007) indicating a large heat duty reduction by using MEA/MDEA instead of single MEA. 2-amino-2-methyl-1-propanol (AMP) has also been tested widely in mixtures with MEA indicating a more satisfactory removal of CO_2 than MEA/MDEA (Mondal et al., 2012). Combinations of AMP have also been considered with Diethanolamine (DEA) (Adeosun and Abu-Zahra, 2013) with favourable results in terms of energy requirements in regeneration and with Ethylenediamine (EDA) indicating higher overall absorption rate and loadings compared to MEA (Kemper et al., 2011), to name but a few.

Whereas experimental testing is clearly indispensable it cannot address the previously noted challenges. Model-assisted technology stands promising to exploit experimental know-how and guide the search for CO_2 capture mixture candidates as it is capable to cope with the investigation of an enormous range of options. However, the availability of models able to predict the non-ideal mixture-CO_2-water interactions for very few amine combinations limits the existing simulation or optimization-based studies in mixtures for

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which experimental results already exist (Adeosun and Abu-Zahra, 2013). Experiences in the selection of pure aqueous solvents for CO_2 capture applications (Papadopoulos et al., 2013) show that similar challenges may be successfully overcome using a rational selection approach. Simple predictive property models are combined with empirical knowledge to screen a wide set of molecules and identify few with favourable capture characteristics which can then be analysed using rigorous models or experiments. The same rationale is exploited here for the fast identification of binary amine mixtures with favourable CO_2 capture features, however the considerably more complex decision making requires efficient organization and coordination of the selection procedure.

2. Proposed approach

In this work we propose a systematic approach to select solvent mixtures from a large pool of candidates that offer high performance simultaneously in many property criteria associated with effective chemical absorption of CO_2 and solvent regeneration. The problem is approached in several decision making stages, where solvent mixtures are evaluated based on the simultaneous consideration of important mixture properties selected to capture the molecular physical and chemical effects on the absorption/desorption process. Mixtures meeting specific performance criteria are considered in successive stages, hence a set of mixtures gradually emerges which consists of fewer but more effective CO_2 capture candidates. The desired property criteria are calculated using predictive models, which are applicable in a large amount of molecular structures and range from standard group contribution methods to equations of state and activity coefficient models to account for vapour and liquid phase non-idealities of solvent-solvent and solvent-solvent-CO_2 interactions.

2.1 Property criteria for mixture selection

Prior to discussing the decision making stages of the proposed approach, this section presents the properties that may be used as criteria for the selection of suitable CO_2 capture mixtures. Several properties are analysed based a) on their potential to reflect on important capture characteristics, b) on the availability of appropriate models for their calculation and c) on the availability of sufficient data so that these models may be applied in a wide range of molecular structures, which may be subsequently combined into mixtures.

1) Solubility (δ): The selection of mixtures for CO_2 capture requires the consideration of solvent-solvent interactions to ensure that the investigated molecules are miscible under the capture conditions as well as the solvent-solvent-CO_2 interactions to ensure that they may dissolve CO_2. The Hansen solubility parameter (δ_t) represents the cohesive energy density, i.e. the energy required to overcome the solvent-solvent or solvent-solute interactions hence it may be used as an indicator of the miscibility of different solvents and of the CO_2 solubility in different solvents. The relative energy difference (*RED*) index (Stefanis and Panayiotou, 2008) may be used in both cases with values of $RED<1$ generally indicating desirable interactions. In the case of solvent-solvent miscibility, the Hansen solubility parameter may be replaced by the method of Conte et al. (2011) which employs the Gibbs free energy of mixing hence accounting for liquid phase non-idealities at different concentrations.

2) Vapour pressure (P_{vp}): It is an important parameter for absorption/desorption CO_2 capture systems because high P_{vp} is an indicator of high volatility and potential solvent losses through the process stages. In the case of amine mixtures, it requires a vapour-liquid equilibrium (VLE) calculation to determine the bubble point pressure at a range of concentration.

3) Bubble point temperature (T_{bp}): It acts as a constraint to avoid vaporization resulting in increased solvent losses at the absorption/desorption operating conditions. Bubble point calculations require the consideration of the VLE between the amine solvents, which may be calculated by the combination of an equation of state (EoS) with activity coefficient models.

4) Density (ρ), viscosity (n) and surface tension (σ): These properties are 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 and it may be calculated by an EoS for mixtures. Surface tension and viscosity should be low to improve the mass transfer in the packing material and may be calculated using appropriate activity coefficient models (Hukkerikar et al., 2012).

5) Melting point temperature (T_m): The calculation of this temperature is important to avoid solidification of the mixed solvent at absorption conditions. For the case of mixtures it is sufficient to simply ensure that the highest melting point temperature of the two components remains below the absorption temperature.

2.2 Mixture selection methodology

The above criteria are evaluated through a methodology consisting of 6 stages so that numerous mixture candidates may be quickly screened, prior to identifying the ones that satisfy all criteria. It is assumed that an initial pool of amine molecules with favourable CO_2 capture features exists, which will be exhaustively combined into pairs to form the mixtures that will be evaluated:

1) In Stage 1 the initial pool of amines is separated into a group of primary or secondary amines and a group of tertiary amines. Binary combinations of amines between the two groups are only allowed. This is based on the general rule of thumb that tertiary amines exhibit a high capacity for CO_2, whereas primary or secondary amines exhibit fast kinetics (Singh, 2011). This stage serves to ensure that the developed mixtures are balanced in terms of absorption capacity and reaction rates.

2) In Stage 2 the pairs that result from stage 1 are evaluated in terms of bubble and melting point temperatures to ensure that mixture evaporation and solidification is avoided at the desired absorption and desorption process temperatures.

3) In stage 3 mixtures that satisfy the bubble and melting point temperature constraints are evaluated in terms of solvent-solvent miscibility, which is determined through the Gibbs free energy approach. Mixtures that are immiscible are removed from the set.

4) Stage 4 involves the evaluation of solvent-solvent-CO_2 solubility through the *RED* index to determine the ability of mixtures to dissolve CO_2. Mixtures that exhibit very low CO_2 solubility compared to others are removed from the set.

5) In stage 5 we calculate the remaining properties for the co-solvent mixtures; namely vapour pressure (P_{vp}), density (ρ), viscosity (n) and surface tension (σ).

6) In stage 6 the mixtures are evaluated using a multi-criteria selection approach (Papadopoulos et al., 2013). The ones that are part of the generated Pareto fronts are then rank-ordered through a scaled index in order to select the ones with the highest performance in all the criteria simultaneously. In all cases the Pareto optimal mixtures form a clear front which represents the mixture performance that needs to be sacrificed in one criterion in order to increase or reduce the mixture performance in another criterion. The dominated mixtures represent inferior solutions simultaneously in all the considered performance criteria. The investigation of different criteria is exploited to identify important trade-offs, which are transformed into handy conditions for the selection of few optimum mixtures. Note that stage 4 may be employed either as a constraint to remove solvents exhibiting low CO_2 miscibility from the considered set or as a performance criterion (through the *RED* index) together with the properties of stage 5.

3. Implementation

An initial pool of 10 aliphatic, acyclic amines is used to develop binary mixtures considering Stage 1 of the proposed methodology. The 10 amines have been previously identified as good candidates for CO_2 capture (Papadopoulos et al., 2014) considering thermodynamic and reactivity properties and include: N,N,N',N'-Tetramethyl-1,2-Ethanediamine (S1), N,N,N',N'-2-Pentamethyl-1,2-Propanediamine (S2), N,N-Dimethyl-1,3-Propanediamine (S3), Di-N-Propylethylamine (S4), 1-Hexanamine (S5), 2-Methyl-N-(2-Methylpropyl)-1-Propanamine (S6), 1-Ethyl-N,N-Dimethyl-Butylamine (S7), N-Butyl- 1-Butanamine (S8), N-(1-methylpropyl)- 2-Butanamine (S9), N-(1-methylethyl)-1-Butanamine (S10). The initial pool includes 6 primary or secondary amines and 5 tertiary amines. S3 includes both a primary and tertiary amine hence it is considered in both groups. The implementation of Stage 1 results in 29 binary amine mixtures (i.e. M1-M29), which are further evaluated considering the remaining stages of the proposed method. The binary mixtures are formed by combining S1 with S3 (mixture M1), S1 with S5 (mixture M2) and so forth, provided that a primary or secondary amine is allowed to be combined only with a tertiary amine (this is why a mixture between S1 and S2 is excluded).

After stage 6 of the proposed methodology a scaled index is used to identify the mixtures with the highest performance in all the properties considered as screening criteria. Assuming a set of mixtures G={1,…,N_s} and a set of properties P_r={1,…,N_p}, the selection problem may be formulated mathematically as follows:

$$\begin{aligned} &\text{Max } \rho \\ &\text{Min } P_{vp}, \sigma, \mu, RED \\ &\text{s.t.} \quad T_m < T_{abs} \\ &\qquad\;\; T_{bp} > T_{Des} \end{aligned} \tag{1}$$

$$\min_{i \in G} J_i = \sum_{j \in P_r} a_{i,j} \cdot x_{i,j} \tag{2}$$

In Eq(2) $x_{i,j}$ represents the considered scaled property (e.g., ρ, *RED* and so forth) for each mixture i, and $a_{i,j}$ represents a unity coefficient that is positive for properties that need to be minimized and negative for those to be maximized. The considered mixture evaluation index J_i is exploited in diagrams that indicate performance trade-offs between the index and each property simultaneously, in the context of a multi-criteria assessment methodology (Mavrou et al., 2014). The aim is to highlight the impact of each property in the overall performance of the mixtures. Formally, the resulting diagrams include the Pareto optimal or non-dominated solutions of a multi-objective assessment problem (Papadopoulos et al, 2013). Note that all diagrams indicate mixtures at different concentrations between 10 % and 90 % with a 10 % interval of increment. The term “mixture concentration” used in the elaboration of the results represents the amount of the first component in the binary mixture. Custom-developed models are used for the predictions in each stage. Mixtures are first selected and then introduced in each stage to perform calculations.

4. Results and Discussion

After implementation of stages 1, 2 and 3 we observe that all mixtures satisfy the melting and bubble point constraints while they are also miscible with each other. Figure 1 illustrates an optimum set of mixtures (Pareto front) resulting after implementation of stages 4, 5 and 6 of the proposed approach and highlighting the trade-offs between density, viscosity and J_i. The grey dashes represent all the dominated (suboptimal) mixtures. Note that mixtures that share the first component are shown with the same colour. M13, M18 and M19 are included in the Pareto front in the case of density. Note that mixtures M13, M18 and M19 share the component N,N-Dimethyl-1,3-Propanediamine (S3).

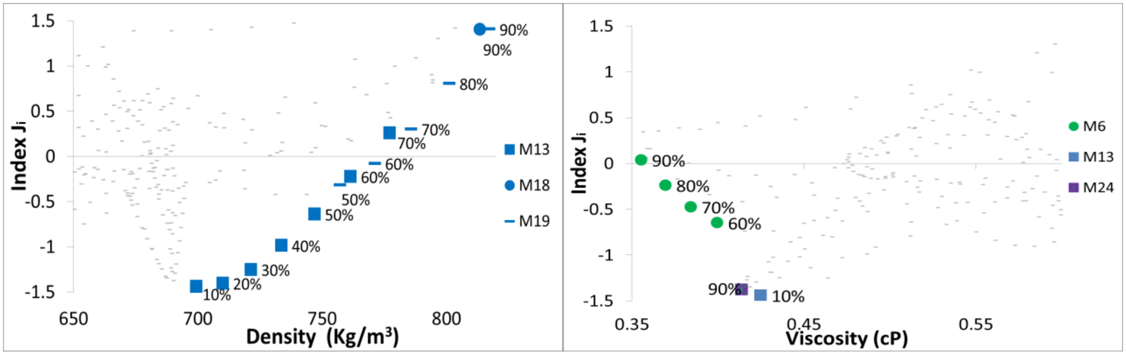

Figure 1: Trade-offs between Index and Density (left); Trade-offs between Index and Viscosity (right).

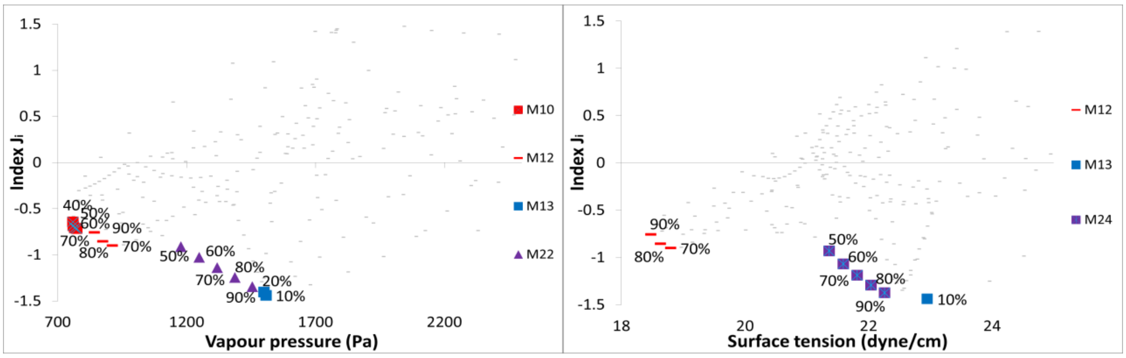

Figure 2: Trade-offs between Index and Vapour pressure (left); Trade-offs between Index and Surface tension (right).

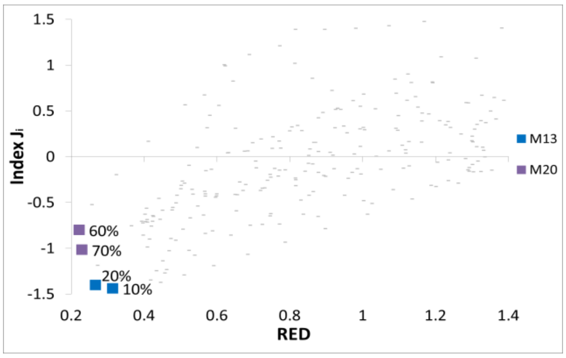

Figure 3: Trade-offs between Index and RED

In the case of viscosity M6, M13 and M24 are included in the Pareto front. Figure 2 illustrates the trade-offs between vapour pressure, surface tension and J_i. M12, M13, and M24 are included in the Pareto front in the case of surface tension. M10, M12, M13 and M22 are included in the Pareto front in the case of vapour pressure. Figure 3 illustrates the trade-offs between RED and J_i. We observe that M13 and M20 are part of the Pareto front.

The 9 unique mixtures included in all Pareto fronts (36 when different concentrations are considered for each mixture) are gathered and rank-ordered separately in each property and index value based on whether it needs to be maximized or minimized (see Eq.(1)). Table 1 presents the top 12 mixtures in each property obtained from the Pareto fronts. The property areas of high performance trade-offs are summarized in the area of 0.355-0.45 cP for viscosity, 18.48-21.3 dyne/cm for surface tension, 710-817 kg/m^3 for density, 758-1,395 Pa for vapour pressure and finally 0.22-0.42 for *RED*. Using MEA/MDEA as a reference mixture to compare the performance of the mixtures identified in the top 12 of Table 1, it is observed that MEA/MDEA ranks high in terms of density and vapour pressure (i.e. it would be part of the top 12 in these two properties) whereas it ranks low in the remaining properties (i.e. it wouldn't be part of the top 12 in the remaining three properties). Hence the selected mixtures perform either similarly or better with the experimentally investigated MEA/MDEA (Mondal et al., 2012).

Table 1: Top 12 mixtures in each property

Viscosity (*n*)	Surface Tension (σ)	Density (ρ)	Vapour Pressure (P_{vp})	*RED*	Index (J_i)
90 % M6	90 % M12	90 % M19	40 % M10	60 % M20	10 % M13
80 % M6	80 %M12	90 % M18	50 % M10	70 % M20	20 % M13
70 % M6	70 % M12	80 % M19	60 % M10	20 % M13	90 % M24
60 % M6	70 % M10	70 % M19	70 % M10	30 % M13	90 % M22
90 % M24	60 % M10	70 % M13	90 % M13	10 % M13	80 % M24
90 % M22	50 % M10	60 % M19	80 % M13	80 % M12	30 % M13
80 % M24	60 % M6	60 % M13	70 % M13	60 % M10	80 % M22
10 % M13	70 % M6	50 % M19	50 % M22	50 % M10	70 % M24
70 % M24	80 % M6	50 % M13	60 % M22	40 % M13	70 % M22
80 % M22	90 % M6	40 % M13	70 % M22	70 % M10	60 % M24
60 % M24	40 % M10	30 % M13	80 % M22	70 % M12	60 % M22
20 % M13	50 % M24	20 % M13	50 % M19	90 % M22	70 % M20

Obviously, it is quite difficult to obtain mixtures which rank high in all the above property areas simultaneously. The point of performing a multi-criteria assessment analysis is to identify those mixtures that rank high in several of the identified property areas. The Pareto front obtained from the top 12 consists of 9 unique mixtures, whereas only 4 of them are common between the Index column and the remaining columns. Mixture M13 (N, N-Dimethyl-1,3-Propanediamine + Di-N-Propylethylamine), M22 (Di-N-Propylethylamine + N-Butyl-1-Butanamine) and M24 (Di-N-Propylethylamine + N-(1-methylethyl)-1-Butanamine) appear simultaneously in both the viscosity and Index columns. M13, M22 and M20 (Di-N-Propylethylamine+ 1-Hexanamine) appear in both the *RED* and Index columns. M13 and M22 appear simultaneously in viscosity, *RED* and Index columns indicating that mixtures dissolving CO_2 coincide with high performance in other properties. A thorough investigation of all the mixtures that participate in the Index column indicates a dominating molecule with concentration from 60 % to 90 % participating in all these mixtures, namely Di-N-Propylethylamine (S4). This molecule appears in all mixtures, which are common between the Index and the *RED* column as well as between the Index and viscosity column of Table 1, hence the *RED* and the viscosity affect the mixture performance through it. By considering S4 as part of the highly performing mixtures reported in Table 1 (e.g. with S3 in 10 % M13, with S8 in 90 % M22 and with S10 in 90 % M24) we observe that viscosity, *RED* and vapour pressure of these mixtures are improved compared to the corresponding properties of S4 as a pure component. This observation highlights the gains obtained from using S4 in mixtures. As a pure component, S4 was calculated to exhibit a high basicity for a tertiary amine (i.e. expected to have relatively fast kinetics compared to other tertiary amines). The calculated basicity is also close to the very similar Triethylamine, investigated experimentally and also found to exhibit a very high basicity (Hamborg, 2011). However, as a tertiary amine it is also expected to facilitate high CO_2 capacity (Singh, 2011). Considering the other amines forming mixtures with S4, it is worth noting that S3 (N, N-Dimethyl-1,3-Propanediamine) is very similar with the experimentally investigated 3-methylaminopropylamine which is of high basicity (Bruder et al., 2012). S8 (N-Butyl- 1-

Butanamine) has been reported by Zhang et al. (2012) as part of a solvent family called lipophilic biphasic solvents which have the potential to facilitate desorption at much lower temperatures than conventional amines hence requiring much lower heat for solvent regeneration. S10 (N-(1-methylethyl)-1-Butanamine) has a high basicity, possibly due to the observed branching at the alpha carbon (Zhang et al. 2012).

5. Conclusions

The present work assessed the performance of mixtures that appear to be promising as CO_2 capture solvents, considering both their composition and concentration. The proposed co-solvents were obtained in this work using mixture properties as performance criteria that enable a fast, efficient and eventually reliable screening of the available database. Mixtures 10 % M13 (N, N-Dimethyl-1,3-Propanediamine + Di-N-Propylethylamine), 90 % M22 (Di-N-Propylethylamine + N-Butyl-1-Butanamine) and 90 % M24(Di-N-Propylethylamine + N-(1-methylethyl)-1-Butanamine) present good performance indicating that they are worth of further investigation as CO_2 capture solvent candidates.

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