Methodological selection of demixing liquid-liquid solvents used in the absorption-regeneration carbon capture process

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Abstract

Since the 19th century, the carbon dioxide concentration in the atmosphere has never been so high due to anthropogenic emissions. This increase of the greenhouse gases concentrations in the atmosphere has been identified as the main cause of global warming. The absorption-regeneration post-combustion carbon capture technology has the highest Technology Readiness Level to limit the CO_2 emissions. Nevertheless, the type of process is a high consumer of thermal energy to regenerate the liquid solvent used to absorb carbon dioxide. A solution to reduce this high energy demand is the use of liquid-liquid biphasic (or demixing) solvents that have the capacity to split into two phases under certain conditions of temperature and CO_2 loading. The present work aims to classify the aqueous liquid-liquid biphasic solvents after a literature review of the existing solvents to determine the most promising ones for further investigations. This methodology is composed of two successive steps. The first step is based on six techno-economic indicators: the regeneration energy, the CO_2 absorption capacity, the CO_2 absorption rate, the volume ratio between the two phases, the volatility of organic compounds and the solvent cost. The contribution of each key indicator is weighted using the analytical hierarchy process method. The result of this first step is the ranking of the 30 solvents identified in the literature. The second step is a Health, Safety and Environment analysis. It excludes 17 solvents containing at least one molecule that presents a serious hazard for human life or the environment. After the application of this methodological evaluation, the final results show that the three most promising aqueous biphasic solvents are respectively composed of triethylenetetramine (30 wt.%) and propan-1-ol (50 wt.%), N,N-dimethylcyclohexylamine (35 wt.%) and triethylenetetramine (15 wt.%), and diethylethanolamine (64 wt.%) and methylaminopropylamine (19 wt.%).

1 Introduction

Since the second-half of the 19th century, the average global surface temperature has increased by 1.45 °C in 2023[1]. This average temperature increase causes extreme weather conditions in various regions around the world affecting people and nature, such as more powerful hurricanes, more intense heatwaves, or longer droughts. Therefore, the efforts to reduce, stop, and try to even inverse this trend of rising global temperature are crucial to maintain acceptable living conditions for large part of humanity, as well as for the Earth's global ecosystem. In its 6th assessment report, the International Panel on Climate Change (IPCC) links one more time the global temperature increase with the rise of the greenhouse gases (GHG) concentrations in the atmosphere[2]. Among them, anthropogenic carbon dioxide (CO_2) is responsible for a major factor of this increase of GHG concentrations leading to 422.38 ppm in October 2024 measured from Mauna Loa Observatory (Hawaii, USA)[3].

The anthropogenic CO_2 emissions come from various sectors. While some of them (such as the electricity and heat production at low or intermediate level of temperature) have a clear pathway to reduce their emissions by using renewable energy[4], other industrial processes emit intrinsic carbon dioxide such as mainly the cement or limestone production. Indeed, the main part of the CO_2 emissions comes from the process itself (decarbonation of limestone) and is therefore unavoidable. For such industries, it will be impossible to totally abate CO_2 emissions using new technologies and for the other sectors, the transition to zero-emission technologies will be very difficult at short term. Therefore, the development of carbon capture, utilization, and storage (CCUS) solutions is today one of the keyways to achieve net-zero CO_2 emissions by 2050. This goal is the application of the Paris Agreement on climate change to limit the average temperature increase to 1.5 °C compared to pre-industrial level[5]. Together with other measures such as improving energy efficiency or reducing energy consumption, the implementation of CCUS has been presented again, in the final statement of the COP28 at the end of 2023, as one of the pathways to reduce the greenhouse gases emissions, "(…) particularly in hard-to-abate sectors (…)"[6].

The first step of the CCUS chain consists of capturing the produced carbon dioxide. In industrial sectors, the three main technologies are the pre-combustion, the oxy-combustion and the post-combustion carbon capture depending on the location of the carbon capture unit in the industrial process chain as well as the CO_2 concentration of the flue gas[7]. In addition to the CO_2 produced by a combustion process, carbon dioxide can also be related to the industrial process itself, such as the decarbonation reaction in the cement or limestone production process. In this configuration, as the carbon dioxide is captured after the industrial process, this can be compared to the post-combustion emissions with a similar CO_2 concentration in the flue gases (between around 5 and 30 vol.%)[8].

Four main unit operations are currently used and/or under development in the carbon capture field: absorption, adsorption, membrane separation and cryogenic separation[9]. Among them, the chemical absorption-regeneration process using amine-based solvents is currently the most mature separation technology with a development of the process at industrial level (TRL 9)[10]. Nevertheless, the operative costs of this technique are quite expensive mostly due to the steam used in the reboiler for the solvent regeneration. The reference case commonly considered for this technology uses the aqueous monoethanolamine (MEA 30 wt.%) and requires a regeneration energy at the reboiler generally included between 3 and 4 GJ/tCO_2[11]. Several process improvements can be implemented to reduce these operative costs. For example, an intercooling stage in the absorption column enhances the absorption performance and therefore, decreases the relative solvent mass flow needed for the CO_2 capture[12]. When the solvent is regenerated under pressure (e.g., at 2 bar), another possibility to reduce the regeneration energy demand is the addition of a rich or/and lean vapor compression before the CO_2-rich solvent is carried to the stripper[13]. Other configurations such as a vapor recompression at the bottom of the reboiler have also been studied to reduce the heat demand[14].

However, another key element of the process to reduce the thermal energy consumption remains the solvent itself. Physical or chemical solvents as well as hybrid solvents are available for the CO_2 capture by absorption[15], each type having different characteristics. The carbon capture by physical solvents is based on the Henry's law principle linking proportionally the partial pressure of carbon dioxide to the CO_2 concentration in the liquid solvent. For example, methanol, propylene carbonate or dimethyl ethers of polyethylene glycol can be used as physical solvents[16]. Without any chemical reaction between the carbon dioxide and the solvent, the solubilization of CO_2 is only driven by its limit of solubility at CO_2 partial pressure given and is only improved by low absorption temperature. On the other hand, carbon dioxide absorption using chemical solvents improves the absorption at lower CO_2 concentration in the gas phase. Indeed, the CO_2 absorption is here mainly driven by the reaction between the dissolved carbon dioxide and reactive components of the solvent. However, this type of absorption is structurally limited by the reactions and achieved the saturation when the reactional equilibria are reached (see Figure S1). Physical-chemical (hybrid) solvents can also be used such as ionic liquids. This type of solvents is generally costly due to the complexity of its production methods[15]. Among the hybrid solvents, the deep eutectic solvents are recently more and more studied because of its lower cost and ecological footprint compared to classical ionic liquids[17].

The chemical solvents include a large variety of mixtures that can be classified through their chemical composition. Among them, the wider category contains the mixtures based on amines and alkanolamines[18]. Other solvents are based on amino acid salts containing an amino-acid and an inorganic (K^+, Li^+, …) or organic counterion ($MAPAH^+$, $MEAH^+$)[19]. The salts solutions can also be formed by carbonates (such as sodium or potassium carbonate[20]) or hydroxides (such as calcium or potassium hydroxide[21]). These systems, especially the amino acid salts and the hydroxides, can be implemented in a precipitating way[22]. Such solvents used in the CO_2 capture lead to the formation of chemical products over the solubility concentration and the emergence of a solid phase during the CO_2 absorption process. Another chemical reactant for which the similar distinction can be made is ammonia. The conventional ammonia process is developed above or at ambient temperature in the absorption section[23]. On the contrary, the chilled-ammonia system is designed to capture carbon dioxide between 2 and 10 °C[24]. In such a process, the cold temperatures can also lead to precipitation at high CO_2 concentrations in the solvent.

The formation of a precipitate is one of the main categories of the biphasic solvents. This category (liquid – solid) can be used in certain cases[25]. However, this system needs a different process approach as the carbon dioxide is mainly contained in the solid phase. The separation and, above all, the transportation as well as the regeneration step of the solid phase is a specific challenge, especially at industrial scale, leading to a different process design. For the liquid – liquid biphasic process category, the precipitation should therefore be avoided. A schematic flowsheet of this process is represented in **Figure 1** (a schematic flowsheet of the standard process with monophasic liquid is presented in Figure S2 for eventual comparison). The addition of a phase separator (decanter) is the core difference from the conventional solvent process. This unit operation allows to split the liquid flow coming from the absorption column and loaded in carbon dioxide into two liquid flows: one stream with low CO_2 content (CO_2-lean phase) and one stream with high CO_2 content (CO_2-rich phase). The CO_2-lean phase, together with the regenerated solvent, is directly recirculated to the top of the absorption column while the CO_2-rich phase is transported to the stripping (regeneration) column. Therefore, the first advantage of the use of a demixing solvent is the reduction of the flow going to the regeneration part of the process to decrease the energy needed in the reboiler at the bottom of the stripping column. Moreover, this CO_2-rich stream has a higher concentration in carbon dioxide than the solvent in a conventional process leading to facilitate regeneration and reduce energy needed for the same produced CO_2 flow.

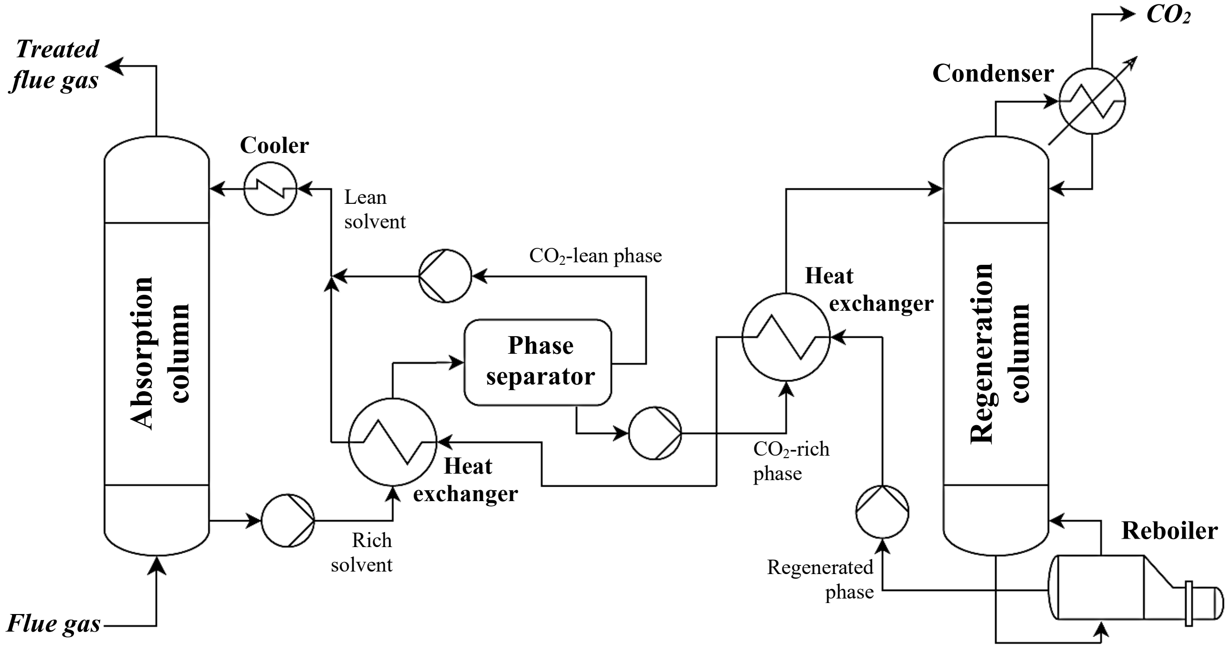

Figure 1. Typical flowsheet of an absorption-regeneration process using liquid-liquid biphasic solvent.

In this configuration, the liquid-liquid separation is a key factor. Both its conditions of occurrence and the composition and properties of the liquid phases are primordial to characterize the demixing phenomenon. This demixing behaviour is led by three main properties: the composition of the fresh solvent, the CO_2 concentration in the liquid and the temperature of the solvent. The pressure effect is generally negligible and neglected for equilibrium in condensed phases.

For binary chemical systems, the relationship between the temperature, the chemical composition and the presence of two liquid phases can be represented by diagrams (Temperature, composition)[26]. The composition is generally the fraction of one chemical component. Four main types of equilibria are represented in **Figure 2**. Depending on the case, one or two values of temperature are commonly used. The lower critical solution temperature (LCST) is the temperature below which the 2-component solution remains monophasic, whatever the proportion of the 2 components. Similarly, the upper critical solution temperature (UCST) is the temperature above which the 2-component solution remains monophasic, whatever the proportion of the 2 components. Where applicable, demixing behaviour occurs between LCST and UCST for variable compositions of the binary solution.

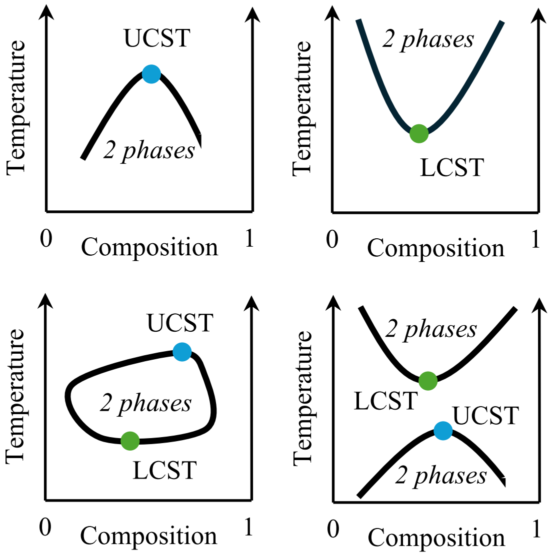

Figure 2. Diagrams representing the four types of biphasic liquid-liquid equilibria.

When the chemical mixture is composed of more than two components (which is usually the case for liquid solvents absorbing carbon dioxide), LCST and UCST can still be used but classically refer to a specific composition of the solvent. The other main parameter of the biphasic phenomenon is the minimal CO_2 concentration in the absorption solvent from which demixing behaviour occurs. For defined temperature and fresh solvent composition, this concentration, generally called critical concentration, is more often reported as it is quite easily measurable using a simple CO_2-absorption device. From a process point of view, this critical concentration also has an importance for the regeneration efficiency to assure that the lean solvent entering the absorption column is monophasic.

Different biphasic liquid-liquid solvents can be used in the absorption-regeneration CO_2 capture process. Numerous chemical mixtures have been studied and can present interesting characteristics in order to be used on an industrial scale. Several parameters have been more widely experimented to characterize these mixtures as they have major influence on the absorption – regeneration process. Some of these main parameters have been used as indicators to classify monophasic amine solvents such as the CO_2 absorption capacity, the CO_2 – amine absorption kinetics and the vapor pressure of the solvent[27].

The absorption capacity is a thermodynamic equilibrium variable representing the maximum concentration of carbon dioxide that can be transferred by the solvent in specific conditions of temperature and CO_2 partial pressure. The absorption kinetics is a measure of the speed of the carbon dioxide reactive transfer from the gas into the liquid solvent. The vapor pressure of the mixture is directly related to the gas emissions in the treated gas and linked to the environmental assessment of the chemical mixture. However, the advantages of various solvents can be related to multiple fundamental or process parameters. The energy requirement at the reboiler remains by far the most important feature as it represents the most important part of the operative costs in the industrial plant (more than two thirds[28]).

Multi-criteria selection methods have already been presented to improve the selection of solvents to a broader scope[29]. Some of them are based on indicators classified into two main families: techno-economical on one hand and health, safety and environmental properties on the other hand[28]. As far as today, it seems that no study has been published regarding specifically the selection of demixing solvents. After a literature review of the existing biphasic liquid-liquid solvents reporting qualitatively the main advantages of these mixtures, the purpose of the present work is therefore to propose a methodological selection of the most promising demixing solvents based on multiple criteria. This methodology is divided into two successive steps. The first part ends with a ranking of the solvents from a techno-economic evaluation. This evaluation is based on six key indicators: the regeneration energy, the CO_2 absorption capacity, the CO_2 absorption rate, the volume ratio between the two phases, the volatility of organic compounds and the solvent cost. The second step is a Health, Safety and Environment (HSE) analysis to exclude hazardous mixtures. Literature data used for this methodological selection (especially, for the techno-economic classification) are reported in Supporting Information.

2 State-of-the-art

For a few decades, biphasic liquid-liquid solvents have been studied to mainly reduce the regeneration energy (and so, the operative costs) of the absorption-regeneration carbon capture process. This section summarizes the demixing mixtures for carbon dioxide absorption reported in the literature. This review includes the chemical solvents presenting a liquid-liquid biphasic behaviour. Liquid-solid solvents, also called precipitating solvents are not in the scope of the present review. In the liquid-liquid biphasic systems, non-aqueous solvents are in recent years more and more studied at laboratory scale. For example, the total replacement of water in amine mixtures solvents has been explored using 1-propanol such as in Liu J. et al.[30] or dimethyl sulfoxide such as in Zhou X. et al.[31]. The ionic liquids (physical-chemical solvents) can also be used without water, where it is also replaced by an alcohol[32]. Nevertheless, the flue gases coming from industrial plants commonly already contain vapor water and are generally cooled through a direct contact cooler to improve CO_2 absorption capacities in solvents and cause water condensation or saturation depending on the inlet gas humidity level. The water tolerance of the solvent is therefore crucial and was projected for some mixtures. Even if this estimated tolerance was high, the steady-state water load remains unknown in most cases and was not experimented in pilot scale[33]. Moreover, this simulated value requires the condensation of water prior to the absorber and the increase of the reboiler temperature[33]. With such requirements on the process and uncertainties in the solvents water tolerance, the water-lean solvents require a particular and specific attention for further studies and comparison. The present work only focuses on biphasic liquid-liquid aqueous solvents.

Currently, the first pilot at industrial scale for testing liquid-liquid biphasic solvents (TRL 7) is implemented using the DMX™ process through the 3D and DINAMX projects at the ArcelorMittal plant in Dunkirk, France[34]. The DMX™ solvent is developed by IFPEN since over 15 years from laboratory scale and is composed of an aqueous blend of two amines regenerated up to 7 bar with steam at 160 °C[35,36]. The objective of this process is to reduce the regeneration energy consumption by around 30% compared to the MEA 30 wt.% reference case to achieve 2.3 GJ/tCO_2 [36]. The process includes a single internal heat exchanger after the phase separator device. Nevertheless, few information regarding the two amines composing the solvent and its performances is available for confidentiality reasons, leading to difficulties for the comparison to other solvents.

The main studied biphasic liquids remain amine blends. The reactional characteristics of the amino molecules depend largely on the types of the amino groups present. Primary and secondary amino groups are generally classified as absorption activators (or kinetic promoters)[37] and tertiary amino groups as regeneration promoters[38]. The absorption activators are characterized by a faster reaction rate but a higher reaction enthalpy. This higher value is related to the reaction products formed by the absorption of carbon dioxide in amine solvents[39]. The formation of a stable carbamate anion as described in Eq. 1 involves a higher requirement of energy for the desorption of CO_2.

$$CO_2 + 2\,R_1R_2NH \rightleftarrows R_1R_2NCOO^- + R_1R_2NH_2^+ \qquad (1)$$

On the contrary, the tertiary amine reacts with the carbon dioxide according to a different mechanism (Eq. 2) resulting in different products: protonated amine and hydrogen carbonate ion[40]. This reaction has a lower reaction enthalpy. Moreover, the reactional mechanism of tertiary amines provides a higher absorption capacity leading to more concentrated CO_2-rich solvent going to the regeneration column. Therefore, the tertiary amines are so classified among the regeneration promoters as they need less energy to be regenerated together with reducing the solvent flow needing to be regenerated.

$$CO_2 + H_2O + R_1R_2R_3N \rightleftarrows R_1R_2R_3NH^+ + HCO_3^- \qquad (2)$$

Sterically hindered amines show a specific behavior regarding their reaction with carbon dioxide. They are defined as a primary amine attached to a tertiary carbon atom or a secondary amine linked to a tertiary or secondary carbon. As primary or secondary amine, the reactional mechanism leads to the formation of a carbamate. However, this anion is particularly unstable due to steric hindrance. This low stability lowers the energy required to desorb the carbon dioxide. Sterically hindered amines can so be used in some solvents used in carbon capture as they combine the three main effects of a faster absorption rate (in comparison with tertiary amines), a high absorption capacity[41] and easier regeneration[42] (in comparison with primary/secondary amines).

Therefore, a significant number of aqueous amines blends (including for biphasic solvents) is composed of an aqueous mixture of an absorption activator and a regeneration promoter. Even if diethylethanolamine (DEEA) is quite volatile as other amine molecules[43], several studies have been conducted using it as tertiary amine in combination with a primary and/or secondary amine as activator. The molecular structure and the amine type (if applicable) of compounds present in the different aqueous mixtures reviewed in this section are alphabetically listed in Supporting Information (Table S1), as well as their full name, chemical formula and CAS number.

2.1 Two-amine aqueous blends

The mixture diethylethanolamine (DEEA) – methylaminopropylamine (MAPA) has been investigated in some concentrations. The two most studied are DEEA (64 wt.%) – MAPA (19 wt.%) and DEEA (62 wt.%) – MAPA (9 wt.%). Both have shown higher CO_2 absorption capacities (around 25% more) and also faster initial absorption rate (between 2 and 9 times more) compared to the MEA reference[44,45]. Moreover, the first blend owns a lower estimated regeneration energy by around 30% from the reference case[46]. The mixture DEEA (50 wt.%) with 2-((2-aminoehtyl)amino)ethanol (AEEA – 25 wt.%) has roughly the same characteristics of absorption capacity and kinetics as well as regeneration energy as the mixtures DEEA – MAPA[47,48]. The same study also presents the blend including the reference MEA (25 wt.%) and the tertiary amine DEEA (50 wt.%) as a potential biphasic solvent, its CO_2 absorption capacity being even higher than for the blend DEEA – AEEA[47]. Among a screening of multiple DEEA blends with diethylenetriamine (DETA) and N,N,N',N'-tetramethyl-1,3-propanediamine (TMPDA)[49], the mixture DEEA (30 wt.%) – DETA (32 wt.%) gives the best results on CO_2 absorption capacity (around 2 times the value for MEA 30 wt.%) but also in terms of component partition between the two liquid phases (up to 250 for CO_2 partition factor). N,N-dimethylbutylamine (DMBA) was also studied in a blend containing DEEA in the solvent[50]. The composition DMBA (47 wt.%) – DEEA (27 wt.%) shows the highest absorption rate and good reaction stability. At carbon dioxide saturation, this solvent (reported as the best among 12 tested solvents) exhibits a CO_2 concentration ratio of 25 between the CO_2-rich phase and the CO_2-lean phase (for a global absorption similar to MEA 30 wt.%)[51]. Finally, DEEA (47 wt.%) with triethylenetetramine (TETA – 15 wt.%) has also a quite good potential for carbon capture as it has a higher absorption capacity than MEA (30 wt.%) with an estimated lower regeneration energy[52,53]. In a screening study of around 50 amines blends on absorption equilibrium tests, it is finally presented as the most desirable mixture[54].

Numerous mixtures with N,N-dimethylcyclohexylamine (DMCA) have been also evaluated. This tertiary amine molecule is associated with several primary or secondary amine as well. The combination DMCA (35 wt.%) – TETA (15 wt.%) was experimented and modelized, leading to good results, both in terms of absorption capacity (3.32 $molCO_2/L$) and of regeneration energy consumption (around 50% of the MEA 30 wt.% reference)[55]. The association of DMCA with N-methylcyclohexylamine (MCA) is the most studied of the DMCA blends. Two main compositions of this blend were tested in the literature depending on the molar ratio between DMCA and MCA. The composition DMCA (13 wt.%) – MCA (35 wt.%) presents better characteristics on absorption capacity (around 60% more), kinetics (20% faster) and regeneration energy (around 40% less) than the reference MEA case. The mixture with DMCA (39 wt.%) and MCA (12 wt.%) owns similar characteristics except for the CO_2 absorption kinetics (25% slower than MEA 30 wt.%). This difference can be explained by the lower concentration of MCA which is a secondary amine[56]. These mixtures are part of the lipophilic amine blends also called thermomorphic biphasic solvents[57]. The lipophilic amines are composed of two parts: a hydrophilic part (amino group) and a lipophilic part (alkyl chain).

Other ternary mixtures (including water and two organic compounds) have also been studied. TETA with 1-dimethylamino-2-propanol (1DMA2P) was tested as a combination of tertiary and primary/secondary amine. The optimal concentration of each amine molecule is 2 M (respectively corresponding to 31 wt.% and 22 wt.%) for CO_2 absorption capacity as well as for CO_2 concentration and proportion of each phase according to absorption bubbling tests[58]. Regeneration tests were also conducted and show better performance (around 2 times for the regeneration efficiency) than the MEA (30 wt.%) reference case. N,N,N,N,N-pentamethyldiethylenetriamine (PMDETA – 75 wt.%) – DETA (11 wt.%) is an aqueous amine blend which has also a high absorption capacity especially due to the number of amine groups in these molecules (more than 3 molCO_2/L). The CO_2 concentration ratio between the CO_2-rich and CO_2-lean phases is very high (more than 100). This mixture is also remarkable by the high dynamic viscosity of the CO_2-rich phase (more than 250 mPa.s at 50 °C at saturation)[59]. This high viscosity can be correlated by the branched and long structure of the amine molecules and the number of amino groups for each molecule.

2.2 Presence of a phase-splitting agent in the blend

The demixing behavior of aqueous mixtures in presence of carbon dioxide can also occur or be enhanced through the presence of a phase-splitting agent. It can also modify the conditions (temperature or CO_2 concentration) of the demixing phenomenon. This component can either be a chemical reactant with CO_2 (e.g., alkanolamine) or a non-reactant (e.g., an alcohol or an ether).

2.2.1 AMP used as a phase-splitting agent

Among the reactant phase-splitting agents, 2-amino-2-methyl-1-propanol (AMP) has been added to two ternary mixtures. The first one is DMCA (39 wt.%) – MCA (12 wt.%) with an addition of AMP (9 wt.%). This additive has the advantage of increasing by more than 20 °C the phase separation temperature (LCST) and therefore assure a homogeneous liquid solution in the absorption column[60]. Tests also show the good chemical stability of such mixtures in oxidative conditions. The same reactant (AMP) is also used with the mixture DETA – PMDETA in the composition DETA (6 wt.%) – PMDETA (56 wt.%) – AMP (14 wt.%). The high proportion of tertiary amine in the blend involves a low estimated regeneration energy (1.83 GJ/tCO_2) and high desorption rate (maximal value is 10 times more than without AMP). AMP brings relative low viscosity even for the CO_2-rich phase (around 140 mPa.s maximum at 40°C compared to 550 mPa.s without AMP)[61].

2.2.2 Alcohol used as a phase-splitting agent

Other proposed solvents include an alcohol as non-reactants phase-splitting agent. The solvent DEEA (47 wt.%) – TETA (15 wt.%) – water (21 wt.%) with propan-1-ol (PROP – 17 wt.%) exhibits a slightly lower cyclic capacity (less than 10 %) than the equivalent aqueous DEEA (47 wt.%) – TETA (15 wt.%) solvent[30]. However, the presence of PROP enhances the phase separation performance of the solvent after CO_2 absorption and is therefore relevant to be compared to other demixing solvents. In most cases, the presence of an alcohol molecule not only improves the biphasic behavior but induces by itself the demixing phenomenon. Therefore, alcohol is added in aqueous classical solvents such as MEA or MAE. The solvent MEA (30 wt.%) – butan-1-ol (BUT – 40 wt.%) has been tested and gives similar results as aqueous MEA (30 wt.%) for the CO_2 absorption capacity. The advantages of this solvent can mainly be found in the calculated regeneration energy (around 20% less) and in the desorption rate (around 40% more) thanks to the reduction of the volume flow (around only 55% of the total liquid flow) going to the stripper column and the higher CO_2 concentration in this phase compared to the classical MEA case[62]. With MAE (30 wt.%), 40 wt.% of BUT and 30 wt.% of water is the most promising ratio for carbon capture according to multiple absorption and desorption experiments and shows similar characteristics for desorption rate and calculated regeneration energy as the MEA – BUT – water[63].

PROP has also been reported to be a good phase-splitter agent, especially due to a low vaporization heat (47.45 kJ/mol at 25 °C[64]) and heat capacity (144.4 J/mol.K at 25 °C[65]). The association of this alcohol (40 wt.%) with the aqueous MEA (30 wt.%) presents an interesting possibility to reduce the regeneration energy by around 20 % with a higher initial mass transfer for CO_2 absorption[66]. Linear (primary and secondary) amine molecules are also combined with propan-1-ol in aqueous blends. The two amine molecules TETA and DETA (for 30 wt.%) with PROP (50 wt.%) give very interesting results with less than 50 % of the total volume for the CO_2-rich phase and favorable absorption kinetics due to the type of amine. Both solvents appear to achieve a reduction of more than 40 wt.% of the estimated regeneration energy (just above 2 GJ/tCO_2) compared to the MEA 30 wt.% case[67,68]. Cyclic multi-amine (namely, 1-(2-aminoethyl)piperazine – AEP 20 wt.% with PROP 40 wt.%) shows significantly higher absorption rate (around four times) and regeneration efficiency (around two times) than the classical reference case. These characteristics are accompanied by an estimated reboiler energy of 2.74 GJ/tCO_2 [69]. For this blend as well as for the other amine-alcohol-water blends, the alcohol is mainly present in the upper phase (low density phase) while the absorbed carbon dioxide is overwhelmingly in the lower phase (as reaction products such as carbonates and carbamates in high density phase).

2.2.3 Other phase-splitting agents

Sulfolane (SULF) and ethers have also recently been used as phase-splitting agents in aqueous mixtures. Sulfolane has been blended with one or two amine molecules in seven different solvent compositions. The sulfolane fraction in these solvents is generally relatively high (more than 40 wt.%). Ether molecules, namely diethyleneglycolmonoethylether (DGME) and diethyleneglycoldimethylether (DGM) are also combined with one or two amines to form the two blends presented in the literature. More details about these nine solvents are provided in Supporting Information.

2.3 Summary of the identified liquid-liquid biphasic solvents

Many biphasic liquid-liquid solvents can potentially be used in the absorption-regeneration carbon capture. Table 1 summarizes the 30 solvents described above with a corresponding number used in the following parts of this work to represent the different blends. The mass fractions of the different aqueous blends come from literature. Several solvents in the literature are described through the molar concentrations of their constituents. The corresponding mass fractions were calculated and used in this work to uniformize the notations. Thermodynamic model NRTL-RK[70] was used to convert molar concentration (expressed in mol/L) to mass fraction (expressed in wt.%). For the selection of the most promising ones, the development of an evaluation methodology is important. The robustness of this methodology is mostly based on the relevancy of the considered criteria.

Table 1. Aqueous solvents evaluated through this selection methodology

Number	Aqueous blend composition	Ref.
Solv. 1	DEEA (64 wt.%) – MAPA (19 wt.%)	44–46
Solv. 2	DEEA (62 wt.%) – MAPA (9 wt.%)	44,45
Solv. 3	DEEA (50 wt.%) – AEEA (25 wt.%)	47,48
Solv. 4	DEEA (50 wt.%) – MEA (25 wt.%)	47
Solv. 5	DEEA (30 wt.%) – DETA (32 wt.%)	49
Solv. 6	DMBA (47 wt.%) – DEEA (27 wt.%)	50,51

Solv. 7	DEEA (47 wt.%) – TETA (15 wt.%)	[52–54]
Solv. 8	TETA (15 wt.%) – DMCA (35 wt.%)	[55]
Solv. 9	DMCA (13 wt.%) – MCA (35 wt.%)	[56,57]
Solv. 10	DMCA (39 wt.%) – MCA (12 wt.%)	[56,57]
Solv. 11	TETA (31 wt.%) – 1DMA2P (22 wt.%)	[58]
Solv. 12	DETA (11 wt.%) – PMDETA (75 wt.%)	[59]
Solv. 13	DMCA (39 wt.%) – MCA (12 wt.%) – AMP (9 wt.%)	[60]
Solv. 14	PMDETA (56 wt.%) – DETA (6 wt.%) – AMP (14 wt.%)	[61]
Solv. 15	TEPA (30 wt.%) – DGME (30 wt.%)	[71]
Solv. 16	MAE (15 wt.%) – 3DMA1P (21 wt.%) – DGM (48 wt.%)	[72]
Solv. 17	DEEA (47 wt.%) – TETA (15 wt.%) – PROP (17 wt.%)	[30]
Solv. 18	MEA (30 wt.%) – BUT (40 wt.%)	[62]
Solv. 19	MAE (30 wt.%) – BUT (40 wt.%)	[63]
Solv. 20	MEA (30 wt.%) – PROP (40 wt.%)	[66]
Solv. 21	TETA (30 wt.%) – PROP (50 wt.%)	[68]
Solv. 22	DETA (30 wt.%) – PROP (50 wt.%)	[67]
Solv. 23	AEP (20 wt.%) – PROP (40 wt.%)	[69]
Solv. 24	DEEA (25 wt.%) – TETA (10 wt.%) – SULF (40 wt.%)	[73]
Solv. 25	DEEA (46 wt.%) – TETA (14 wt.%) – SULF (24 wt.%)	[53]
Solv. 26	MEA (15 wt.%) – EAE (15 wt.%) – SULF (50 wt.%)	[62,74]
Solv. 27	MAE (27 wt.%) – SULF (55 wt.%)	[75]
Solv. 28	MEA (21 wt.%) – SULF (51 wt.%)	[75,76]
Solv. 29	DETA (20 wt.%) – SULF (40 wt.%)	[77]
Solv. 30	DETA (24 wt.%) – SULF (44 wt.%)	[78]

3 Methodology

Multiple studies to select the most promising monophasic amine solvents have been performed. Some of them only use widely-experimented parameters as indicators to classify the solvents such as the CO_2 absorption capacity, the CO_2 – amine absorption kinetics and the vapor pressure of the solvent.[27]

However, multiple criteria must also be considered to improve the selection of solvents to a broader scope. A proposed selection method classifies 14 indicators into two main families: technical properties (thermodynamic, kinetic and mass transfer properties) on one hand and operability and HSE (for health, safety and environment) on the other hand[29]. The technical group includes 7 indicators. Among them are, for example, the heat of absorption, the reaction kinetics, the pKa of the studied amine molecules, the viscosity and the volatility. The operability criteria include the economic aspect (cost of the solvent) as well as some technical and environmental aspects (corrosivity, degradation…).

Another list of 10 criteria has been proposed, partly recovering the 14 indicators previously described[28]. The similar criteria include the heat of absorption, the vapor-liquid equilibrium (for the thermodynamic part), the CO_2 absorption kinetics, the mass transfer between the gas and liquid phases, the solvent corrosion and degradation. Additionally, the regeneration energy is directly presented as a selection indicator. The solvent reclaiming due to volatility and degradation, as well as the speciation of products and the reactional mechanism for the CO_2 absorption, are also considered as criteria to classify the different available solvents.

All these criteria concern classical solvents that do not present a demixing phenomenon. As far as today, a detailed methodological study regarding specifically the selection of biphasic amine solvents seems missing. Therefore, in this section presenting a new method for such solvents, it appears logical that at least one indicator will be related to the demixing phenomenon occurring during the carbon dioxide absorption.

The developed selection methodology for the biphasic solvents includes two steps which will be successively implemented. The first one is a classification based on techno-economic criteria. First the selected indicators are presented followed by a method for exploiting these different criteria. The second step includes safety, health, and environmental aspects based on the molecules contained in the different mixtures and rejecting the most dangerous ones as industrial applications are planned.

3.1 Techno-economic evaluation

3.1.1 Key techno-economic indicators

For the first step, technical and economic dimensions are intrinsically bound as the technical data of a solvent have direct consequences on the cost of the CO_2 capture plant, both for the investment and for the operating costs. For example, the CO_2 absorption capacity of a solvent has a direct impact on the solvent flow needed to capture a defined amount of carbon dioxide. This parameter therefore influences the size of the pipes carrying the solvent in the installation, and finally its costs. For this selection step, the chosen indicators (precisely defined later in this section) are the regeneration energy, the CO_2 absorption capacity, the CO_2 absorption rate, the demixing volume ratio, the volatility of the organic compounds and the solvent cost. In the present methodology, five of the six indicators are normalized to the reference value of MEA 30 wt.%, notably to allow a fair comparison between the data. These indicators are noted ‘RE’ (for the regeneration energy), ‘AC’ (for the CO_2 absorption capacity), ‘AR’ (for the CO_2 absorption rate), ‘OV’ (for the volatility of the organic compounds) and ‘SC’ (for the solvent cost). The only exception is the demixing ratio ('DR') as the reference solvent does not present a biphasic behavior.

Some parameters such as the CO_2 concentration ratio between the rich phase and the lean phase or the viscosity of the CO_2-loaded solvents have not been selected as indicators due to the non-significant impact linked to the weak range of indicator values for the studied solvents. For example, the CO_2 concentration ratio is, for all solvents, of at least several dozen between the rich and lean phases[51,67]. Other parameters are too dependent on the experimental device or method to be compared between the demixing solvents such as the demixing time. Moreover, some characteristics such as degradation were not considered due to the lack of data for most of the chemicals. The degradation can occur through multiple process (oxidative, thermal, reaction with other components like SOx or NOx…). The degradation products may have a negative impact on the performance of the solvent and require the continuous addition of fresh solvent to maintain the needed solvent composition. Unfortunately, very few specific studies regarding the degradation of demixing solvents have been published until now. Moreover, the degradation of very common solvents such as MEA (30 wt.%) or CESAR1 (AMP 27 wt.% + PZ 13 wt.%) is still recently under investigation[79,80]. A specific discussion on the degradation and solvent renewability topics is provided in Supporting Information.

A. Regeneration energy

The regeneration energy is the thermal energy required at the bottom of the regeneration column (stripping) to regenerate the solvent and desorb the carbon dioxide. It is commonly given by the amount of CO_2 produced and remains the key parameter as it has a significant impact on the total CO_2 capture costs, both investment and operating costs. This value is a process parameter as it depends not only on the thermodynamic properties of the solvent but also on the design and the operating conditions of the plant (such as the regeneration pressure or the efficiency of the solvent regeneration). Nevertheless, several studies (e.g., in Wang et al.[68]) have performed an estimation of the regeneration energy (Q_{reg}) based on solvent thermodynamic properties using the contribution of three terms (see Eq. 3): the reaction heat of CO_2-desorption from the amine (Q_{rxn}), the sensible heat of the solvent to achieve the temperature of the reboiler (Q_{sen}) and the latent heat of the vaporized chemical components (Q_{lat}) in the regeneration column. This last contribution is notably related to the volatility of the solvent and is usually reduced to the vaporization of water.

$$Q_{reg} = Q_{rxn} + Q_{sen} + Q_{lat} \tag{3}$$

The reaction heat of CO_2 desorption (Q_{rxn}) is assumed to be equal to the absolute value of the reaction heat of CO_2 absorption. This term includes the solubilization of the carbon dioxide into the liquid solvent and the heat of reaction of solubilized CO_2 with amine. As the CO_2 reaction with an amine involves multiple steps, the global reaction heat can also be divided into several contributions[81]. However, the reaction heat Q_{rxn} commonly includes all the contributions.

Compared to the classical MEA-solvent, the main reductions for the demixing solvents can be realized in the sensible and latent heat contributions[82]. Indeed, the splitting of the CO_2-loaded solvent into two immiscible phases after the absorption column can considerably reduce the flow going to the regeneration column, and therefore, also reduces the sensible heat. Moreover, this demixing behavior concentrates the CO_2 in the phase going to the regeneration and reduces the water concentration in this stream. This leads to a reduced amount of vaporized water and reduces the latent heat contribution. For the selection methodology, the regeneration energy of each biphasic solvent is normalized by the value of the MEA (30 wt.%) case. 3.99 GJ/CO_2 has been considered as this reference value[68].

B. CO_2 absorption capacity

The CO_2 absorption capacity of the solvent is the CO_2 concentration in the liquid solvent at equilibrium for defined conditions of temperature and CO_2 partial pressure. For chemical solvents, even with a very low partial pressure, the CO_2 concentration in liquid phase rapidly gets close to the concentration achieved with much higher partial pressure and is close to the saturation conditions. It particularly impacts the solvent flow needed to capture a fixed CO_2 flow. This CO_2 loading of the liquid phase is often presented in the units of mole of carbon dioxide by mole of amine present in the same liquid phase: e.g., the theoretical CO_2 absorption capacity of the monoethanolamine is 0.5 mol CO_2/mol amine[83]. The theoretical value is related to the reaction mechanism of primary and secondary amine with carbon dioxide which uses two amine molecules for reacting with one molecule of CO_2. In practice, this stoichiometric capacity can be slightly exceeded by dissolving CO_2 in water, for example[84]. For the tertiary amines, the theoretical absorption capacity increases to 1 mol CO_2/mol amine due to another reactional mechanism[85] as presented in section 2.

However, the choice of these units (mol CO_2/mol amine) gives values dependent of the number of amine groups present in the molecule. This means that, by using these units, a polyamine has numerically a bigger absorption capacity per mole of amine than a monoamine such as MEA. For the present selection methodology, the absorption capacity (which is used for the design of the absorption column[86]) is expressed on a volume (mol CO_2/L) or mass (mol CO_2/kg) basis depending on the available data, and it corresponds to the CO_2 absorption capacity of the total solvent, even if it splits into two phases. These bases allow to compare more fairly the absorption capacity of biphasic solvent to the absorption capacity of MEA 30 wt.% which corresponds to a molar concentration of 5 M. For this concentration, the theoretical value of 0.5

mol CO_2/mol amine is equal to 2.5 mol CO_2/L and 2.46 mol CO_2/kg[87]. The indicator used in this methodology is therefore the value of the CO_2 absorption capacity normalized by the corresponding value for MEA 30 wt.%.

C. *CO_2 absorption rate*

The CO_2 absorption rate is also very important in the design of an industrial plant, especially in the calculation of the height of the absorption and regeneration columns. For this selection, the main challenge to compare various solvents according to absorption kinetics is to select a common parameter. Moreover, some kinetic parameters such as the overall mass transfer coefficient K_G (mol/(cm².s.Pa)) or the absorption flux (mol/(m².s)) are dependent on the experimental device design and the experimental conditions (e.g., temperature, gas flow, CO_2 partial pressure). Therefore, the parameter value for each solvent has to be normalized to the value for MEA solvent (30 wt.%) measured in the same conditions as the studied solvent. This step gives the absorption rate indicator which is comparable between the different solvents.

For all the different solvents through the dedicated literature, four parameters are globally present: the global mass transfer coefficient (K_G), the absorbed CO_2 flux, the absorption rate and a pseudo-first order constant (k_{obs}). The three first parameters consider not only the CO_2 absorption reaction with amine, but also the overall transfer of the carbon dioxide from the gas to be treated to the liquid absorbent.

The absorbed flux is the amount of CO_2 that goes from the gaseous phase to the liquid phase in a certain period of time. The flux is normalized by the value of the contact area between the gas and liquid phases, and it is generally expressed in mol/(s.cm²). The flux is dependent on gas flow, among several other parameters[50]. The overall mass transfer coefficient (K_G) is related to the absorbed flux and the CO_2 partial pressure in the gaseous phase (see Eq. 4)[56] where P_{CO2} is the CO_2 partial pressure and P^*_{CO2} is the CO_2 partial pressure at the equilibrium state.

$$K_G = \frac{\text{Flux}}{P_{CO_2} - P^*_{CO_2}} \tag{4}$$

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{E.k_L^0} \tag{5}$$

The overall mass transfer resistance ($1/K_G$) can be decomposed into a gas mass transfer resistance ($1/k_G$) and a liquid mass transfer resistance (see Eq. 5). This liquid resistance is calculated from the non-reactive liquid mass transfer coefficient (k_L^0), the CO_2 Henry constant in the liquid solvent (H) and the enhancement factor (E) involved by the CO_2-amines reaction(s). The sum of these gas and liquid resistances gives the overall transfer resistance[50] which is also dependent of the gas flow rate[56]. The absorption rate is commonly defined in terms of the flow of CO_2 transferred from the gas to the liquid phase. On the contrary to the flux, for the absorption rate, the CO_2 flow is normalized with volume or mass amount of the liquid phase[59] (or the molar amount of amine in the liquid[69]). Therefore, the absorption rate is expressed in mol/(s.L), mol/(s.kg) or $mol_{CO2}/(min.mol_{amine})$ and generally decreases over time when the CO_2 loading increases[59].

Contrary to the three previously described parameters, considering not only the CO_2 absorption reaction with amine, but also the overall transfer of the carbon dioxide from the gas to be treated to the liquid absorbent, the pseudo-first order constant (k_{obs}) is only related to the speed of the CO_2-amine reaction itself and is expressed in s^{-1}. The reaction rate (r_{CO2}) is also proportional to the concentration of carbon dioxide in the liquid phase (c_{CO2}) (see Eq. 6)[88]. The pseudo-first order constant theoretically includes the kinetic constant of all the reactions involving carbon dioxide. However, the considered reactions can be restricted to the reactions having the most influence on the absorption rate.

$$r_{CO_2} = k_{obs} c_{CO_2} \tag{6}$$

Regardless of the parameter available in the literature, it is normalized by the value of the same parameter for the reference case of MEA 30 wt.%. In such a way, it is possible to compare the absorption rate of various demixing solvents even if the reported kinetic parameter is different.

Moreover, the absorption rate depends a lot on the CO_2 loading of the solvent prior to the experiments. As the initial absorption rate for unloaded solvent is the most frequent value given in the literature, it has been selected as the parameter for this techno-economic evaluation even if there may be divergence when CO_2 loadings increase.

D. Demixing volume ratio

The demixing volume ratio is the only parameter which is related to the biphasic behavior of the studied solvents. This demixing volume ratio (for a batch process, equivalent to a volumetric flow rate ratio for a continuous process), as a parameter measured at equilibrium, depends on temperature, pressure, and the chemical composition (especially, the CO_2 loading in liquid phase). For this selection methodology, the used values are the demixing volume ratios between the CO_2-rich phase (generally, the heavy phase) and the CO_2-lean phase (generally, the light phase) for the highest CO_2-loading available. This indicator is defined as presented in Eq. 7.

$$DR = \frac{V_{rich}}{V_{lean}} \tag{7}$$

Therefore, the indicator should be as low as possible to reduce the solvent flow going to the solvent regeneration process. For the same conditions, a lower volume ratio also leads to a more concentrated rich phase in carbon dioxide and, so, to a solvent regeneration in the stripper consuming less thermal energy.

E. Volatility of the organic compounds

The volatility of the organic compounds of the solvent is also an important indicator as it characterizes the tendency for organic molecules to be transferred in the gaseous phase during the absorption process. This transfer will require to add a washing step of the treated flue gas after the CO_2 absorption column to limit any release of organic compounds into the atmosphere. The volatility of organic compounds is also important during the regeneration process as the reboiler can vaporize organic substances. However, in this process part, the condenser at the top of the stripper is already present to condensate the solvent vapors and to purify the produced CO_2 flow. Therefore, a higher volatility of the organic compounds leads to a more significant additional cost due to the addition of a water-wash section. The volatility is the ratio between the molar fractions in the vapor phase (y) and in the liquid phase (x). For this methodology, this volatility ($K_{solvent}$) is evaluated through the overall volatility of all organic components at boiling temperature and atmospheric pressure (see Eq. 8). In the studied blends, the organic molar fractions ($y_{organic}$ or $x_{organic}$) are the complement of the water molar fraction (y_{H_2O} or x_{H_2O}).

$$K_{solvent} = \frac{y_{organic}}{x_{organic}} = \frac{1-y_{H_2O}}{1-x_{H_2O}} \tag{8}$$

This parameter is calculated in the Aspen Plus™ software using the thermodynamic model NRTL-RK (Non-Random Two liquid – Redlich Kwong). To compare all the possible demixing solvents, this volatility is normalized to the value for the reference solvent (MEA 30 wt.%), calculated through the same method, which is equal to 0.035 (K_{MEA}).

F. Solvent cost

The solvent cost is an economic indicator, but it can have an important impact on the operating costs of the capture plant. Indeed, due to several phenomena such as degradation or volatility, the solvent needs to be regularly replaced through the life of the plant to assure constant absorption efficiency. For this selection, the water has been considered priceless and the price of pure chemicals come from the commercialized price of VWR™ for the largest available volume. From these prices, the mass-based or volume-based prices of each solvent are calculated. These costs are then normalized to the respective price for the reference solvent (MEA 30 wt.%) to get the solvent cost indicator. The absolute cost corresponds for MEA 30 wt.% to 4.48 €/kg and 4.47 €/L. It should be noted that industrial-scale prices are certainly lower. Nevertheless, the cost ranking of solvents can be considered fairly similar.

3.1.2 Weighing of the key indicators

After the selection of the indicators for the further interest of a biphasic solvent, the relative weight for each of them representing their relative importance in the selection methodology must be evaluated. To achieve this goal, the analytical hierarchy process (AHP) method has already been implemented to selection methodology in the CCUS field, especially to compare the different ways of capture[89,90] or conversion[91,92] of carbon dioxide. The AHP method generally presents multilevel analysis structure to decompose the selection process into different criteria. In this case, each criterion is quantified by several indicators and each indicator is independent from the other criteria. However, as presented above, some of the six selected indicators are intrinsically related to both technical and economic fields. For example, regeneration energy can above all be related to both a technical and economic criterion. Indeed, it is related to multiple physical and chemical characteristics of the solvents but have also a major importance for the sizing (and so, the cost) of multiple unit operations of the process as well as for the operative costs to run it (e.g., for the thermal energy).

Therefore, for this first step of the selection method, only one level of analysis was chosen. In other words, there is one aggregate techno-economic criterion with the six indicators. The analytical hierarchy process is here used for the relative weighing of each indicator. This method requires to give a relative importance (from 1 for equal importance to 9 for absolute importance in this work) between each pair of indicators as described in Chauvy et al.[92], while each indicator has a specific scale from 1 (the best score) to 5 (the worst score). The advantage of this weighing method is to assure an evaluation of consistency of all the different relative importances set between all pairs of indicators and avoid to setting random importance between each pair without considering the relations to the other indicators. The process to define the weights for each indicator is developed in Supporting Information.

For this selection, a matrix has been built summarizing all the pairwise comparisons for 6 indicators (Table S2), giving the weight of each indicator in the last column. The yellow cells are filled using the relative importance levels presented above. The other cells and, particularly, the weight of each indicator is calculated using the AHP method (see SI for more details).

The most important indicator in this techno-economic step of the methodology is the regeneration energy indicator, measured or estimated through various methods. Indeed, the regeneration energy, also called specific reboiler duty, is overwhelmingly the main part of the operative costs and is therefore the major penalty of the carbon capture absorption-regeneration process. This disadvantage is the main reason for the research of new innovative solvents. The regeneration energy includes multiple parameters such as the CO_2 desorption heat or the heat capacity of the solvent, but also the latent heat of vaporization of the solvent which is linked to its volatility.

On the other hand, the volatility of the organic compounds and the solvent cost have the lowest weights. The volatility of the organic compounds is present in this methodology to consider the potential loss of the organic compounds mainly in the absorption part of the process, resulting in their emissions into the atmosphere. Nevertheless, the contribution of the volatility of the solvent for the regeneration part is already included in the regeneration energy. The solvent cost, as an economic indicator, is also related to the make-up of solvent after the loss of some of its compounds. Nevertheless, the cost of an absorption-regeneration process is composed of capital and operative costs and the make-up of solvent generally remains a minor part of the operative costs.

After the weighing of each indicator, a scoring scale from 1 to 5 must be associated to each indicator in order to score each demixing solvent and to allow a classification of them. The scoring scales for the six key indicators (see Table S3) have been defined to ensure a quite homogeneous repartition of the scores from one to five between the reviewed mixtures. The indicators for the regeneration energy, the absorption capacity, the absorption rates, the volatility of the organic compounds and the solvent cost are relative to the values for the MEA (30 wt.%) solvent.

For this first step of the methodology, the final score attributed to each solvent is calculated by summing each indicator contribution (w_i) multiplying the indicator score (s_i) with its corresponding weight (see Eq. 9).

$$Score = \sum_{i=1}^{6} w_i * s_i \tag{9}$$

3.2 Health, Security and Environment (HSE) evaluation

For this second step, the data are related to the pure chemical components and come from the European Chemical Agency (ECHA) database. The data selected for this step includes two classifications of hazards. The first one comes from the harmonized classification and labelling in accordance with the CLP Regulation and in which multiple chemical substances are defined[93]. The second one is the notifications submitted to ECHA by the producers and importers themselves according to the Registration, Evaluation, Authorization and restriction of CHemicals

(REACH) legislation. These notifications have to be supported by data and studies[94]. The hazards can be divided into three categories: health, physical and environmental hazards. Each hazard category is identified by an H-code associated with a hazard statement. These codes and statements have been harmonized and classified, among others, in the REACH legislation of the European Union (EC 1907/2006 and EC 1272/2008) or the Globally Harmonized System of Classification and Labelling of Chemicals of the United Nations.

As for the techno-economic step, each reported hazard is scored from 1 (the least dangerous) to 5 (the most dangerous). However, contrary to the first step of the selection, the selection method is here governed by the direct elimination of mixtures containing a chemical component that presents at least one very serious hazard (score 5). For example, in the present work, a deadly hazard as well as an important danger for reproduction are considered as "very serious health hazards". The same category is applied for chemicals which show potential corrosion to metals (H226) as it would lead to premature degradation of the plant, or which are harmful to aquatic environment in the long term (H412).

Indeed, the presence of a component with a very high risk for environmental or health safety, can lead to a risk for the whole process, especially during the storage of the pure components and the mixture preparation. After the solvent preparation, the risk could be considered lower because the dangerous chemical compound has been diluted. However, there is no indication of the real decreasing of the reported hazard during the storage or the preparation of the aqueous mixture. Therefore, for the present methodology, a single dangerous chemical compound results in the exclusion of the solvent of which it is part.

Nevertheless, the hazard statements also cover less serious dangers. Therefore, a complete classification of all the reported hazards has been established to get a more accurate view of the dangers related to the potential solvents even if it is not redhibitory in the selection methodology. As for the exclusion of some mixtures, the score of a solvent is the worst score of one of its components. The scaling of the hazards structured in health, physical and environmental hazard is presented in Supporting Information (Table S4).

4 Results and discussion

The 30 reviewed solvents presented in Section 2 are classified and selected through the methodology presented in Section 3.

4.1 Techno-economic step

4.1.1 Key indicators

A. Regeneration energy (RE)

The summary for the regeneration energy indicator is presented in Supporting Information (Table S5). When it is available, this table includes the values of the three contributions to the estimation of the regeneration energy. An analysis of the proportion of each contribution in the total regeneration energy estimation shows that the CO_2 absorption heat weighs between 60% and 88%, with an average of 72% of the total required energy. Therefore, when only the absorption heat was available, this value is divided by 0.72 to estimate the total regeneration energy. For some solvents, the CO_2 absorption heat is also missing. To solve this issue, an estimation for each type of reaction mechanism is used, corresponding to 1.93 GJ/tCO_2 for primary and secondary amines and to 1.25 GJ/tCO_2 for tertiary amines[95].

B. CO_2 absorption capacity (AC)

The CO_2 absorption capacities of the 30 studied solvents are listed in Supporting Information (Table S6) with the experimental conditions of the measurements. The table also includes the same parameter of the CO_2 absorption rate under similar conditions for the reference solvent

(MEA 30 wt.%). When the value is not available in the literature, the score was set by analogy with another solvent with a similar composition (same amine compounds with only a slight difference of the concentration or additional amine in small concentration compared to a known solvent). It concerns six solvents, and the detailed analogy used is reported in the Supporting Information.

C. CO_2 absorption rate (AR)

The specific data characterizing the absorption rates for each solvent reacting with CO_2 are reported in Supporting Information (Table S7) with the same parameter measured for the reference solvent in the same kinetic study. The ratio between the value and the reference as well as the corresponding score is also presented. However, there are still 8 solvents of the 30 for which there is no precise information in the literature. For them, an analysis of the types of the amines present in the blends provides an estimated score even without a literature value.

D. Demixing volume ratio (DR)

The demixing volume ratio values found in the literature are reported in Supporting Information (Table S8) with the respective score. The conditions of the demixing ratio are indicated in the same table. 10 of the 30 identified solvents have no information available. For three of them, analogies with similar solvents have been implemented to provide an estimated score. Seven solvents remain without any information and therefore get the worst score (5) according to the scoring scale for this demixing indicator.

E. Volatility of the organic compounds (OV)

The volatility results ($K_{solvent}$) simulated by the AspenPlus™ software as well as the related key indicator (OV) calculated as the relative value to the MEA 30 wt.% are reported in the

Supporting Information (Table S9). The corresponding scores (from 1 to 5) using the scale presented above are also added to this table.

F. Solvent cost (SC)

The solvent cost per liter or kilogram is reported in Supporting Information (Table S10) with the relative indicator to the cost of MEA 30 wt.% (SC) and the corresponding score. The calculation is based on the prices of the pure organic compounds, weighted by the concentration of each compound and considering the water as costless.

4.1.2 Global scores of the techno-economic evaluation

From the scores of each solvent and the weight of each indicator, the global score of each solvent for the techno-economic selection can be calculated (Table S11) by a weighted average of the indicator scores using the indicator weights reported in Table S2. These results show that the five first solvents according to this classification are solvents 21, 22, 25, 15 and 8, respectively TETA (30 wt.%) – PROP (50 wt.%), DETA (30 wt.%) – PROP (50 wt.%), DEEA (46 wt.%) – TETA (14 wt.%) – SULF (24 wt.%), TEPA (30 wt.%) – DGME (30 wt.%) and TETA (15 wt.%) – DMCA (35 wt.%).

The importance of all the six indicators in the global score has also been tested by alternatively suppressing the weight of the two smallest indicators: the solvent cost and the volatility of the organic compounds. In this case, the weights of the five remaining parameters are normalized to assure their sum is still equal to one. The classifications of the 30 solvents for these cases as well as for the full methodology are displayed in Supporting Information (Table S12). Even if the first solvent has not changed between the three classifications (TETA 30 wt.% – PROP 50 wt.%), the evaluation without considering the solvent cost shows that the position of 16 solvents has moved from one to two places relatively. For the classification without the volatility of the organic compounds, it is 20 solvents that moved from their position. In this case, the solvent DMCA (13 wt.%) – MCA (35 wt.%) gains 5 positions from 19 to 14 while the two solvents containing DETA and SULF loses 4 positions from positions 14 and 15 to positions 18 and 19. This analysis shows that even indicators weighted for less than 10% of the total evaluations, can change the classification of more than the half of the tested solvents and reinforces the need to take an interest in all indicators, including those whose weight is less than that of the main indicators.

4.2 Health, Safety and Environment step

The scales for the three categories of identified hazards with the corresponding H-code of the ones involved in this selection, meaning that they are at least reported for one chemical, is presented in Supporting Information (Table S13). The HSE score for the 30 solvents involved in this selection methodology is also presented in Supporting Information (Table S14). Contrary to the first step of the selection, the selection method is here governed by the direct elimination of mixtures containing a chemical component that presents at least one very serious hazard. 17 solvents are therefore eliminated as they contain at least one of the seven following chemicals: AEEA, SULF, DETA, DGME, MCA, EAE, DGM. These are phase-splitting agents like sulfolane or ether (DGME and DGM) as well as polyamine molecules such as DETA or MCA. 12 of the remaining solvents have an HSE score of 4, which means that some of their components still require precautions (in particular, safety equipment) to be handled. Among the five best-ranked solvents from the first step, only the first (TETA 30 wt.% – PROP 50 wt.%) and the fifth (DMCA 35 wt.% – TETA 15 wt.%) pass this HSE analysis to become the first and second best-ranked solvents in the final ranking.

4.3 Final ranking and discussion

The final classification includes 13 solvent compositions over the 30 reviewed in the literature (**Figure 3**). They present various techno-economic score from 1.49 to 4.14 and represent two main categories of the aqueous biphasic solvents. The first one is the mixture of amines, mainly composed of one primary/secondary amine as absorption activator and one tertiary amine working as regeneration promoter. The second large group of solvents includes one amine molecule (primary, secondary or tertiary) with an alcohol as phase-splitting agent. Indeed, the other agents (sulfolane and ethers) exhibits important hazards (notably for reproduction), and their mixtures have been eliminated during the second step of the selection process. The solvent 5 (including TETA 15 wt.%, DEEA 47 wt.% and PROP 17 wt.%) in position 9 brings together both categories of solvents.

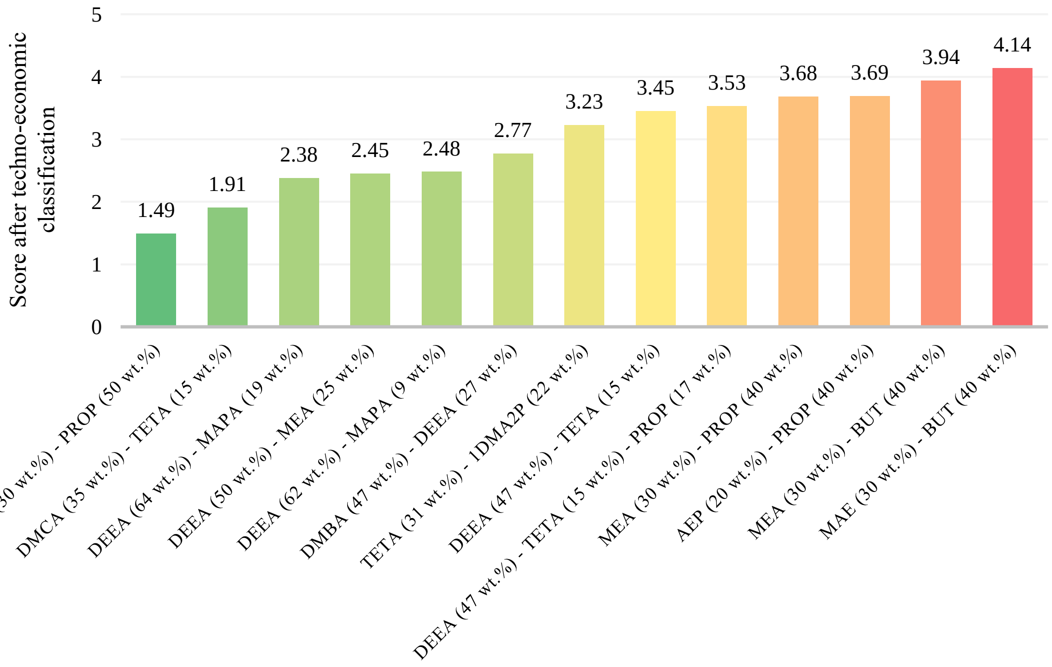

Figure 3. Classification of the demixing solvents after the complete selection methodology with their respective techno-economic score.

According to this final ranking, the most promising aqueous biphasic solvent combines triethylenetetramine (30 wt.%) and propan-1-ol (50 wt.%) with a score of 1.49. This mixture presents very good characteristics in 5 indicators used in the techno-economic evaluation (with three scores of 1 and two scores of 2). The exception is the volatility of the organic compounds and can be related to the presence of propan-1-ol. The second most promising solvent also includes TETA but with a cyclic amine, DMCA, for a global score of 1.91. It also presents good performances for the regeneration energy and the CO_2 absorption capacity (two scores of 1) but also shows mean features for the other indicators (four scores of 3). The solvents ranked from the 3rd to the 5th position are close to each other regarding the techno-economic score (from 2.38 to 2.48). The three solvents contain diethylethanolamine (DEEA) with a primary amine (MAPA or MEA). This similarity in the composition combined with similar concentrations for each type of molecule, leads to comparable performances as demixing solvents for carbon capture. The 6th solvent includes DMBA and DEEA and its relatively good global score (just better than the mean score) is mainly driven by its excellent value of regeneration energy as shown in **Figure 4**.

Figure 4. Indicator scores for the six most promising solvents.

5 Conclusions

The present study focused on the development of a selection methodology, specifically applicable to the liquid-liquid aqueous demixing solvents used for carbon capture already studied, at least at laboratory scale. This method includes two steps: one techno-economic step and one health, safety and environmental step. The process based on six techno-economic indicators (regeneration energy, CO_2 absorption rates, demixing volume ratio, CO_2 absorption capacity, volatility of the organic compounds and solvent cost), for the first part, and on the hazard statements, for the second part. The technical characteristics of each solvent have been found in the literature or estimated using other similar solvents or general rules. The estimation of the missing values is one of the main advantages of this method as it allows to use this method even when multiple parameters are not reported in the literature (which remains the best option when it is available). Specific experiments could be carried out to get the currently unknown data or replaced the simulated ones (e.g., for the volatility of organic compounds). Adding or replacing estimated parameters by literature values will be an improvement if such data become available in the future. The evaluation of the solvent behaviour under degradative performance (through experiments or simulations) should be one of the most interesting further steps to refine the selection methodology by adding this parameter, which impacts both economic and environmental aspects. Indeed, the few data currently available on the degradation of demixing solvents do not enable to include the degradation behaviour in the current selection methodology.

Until now, the methodology implemented in this work delivers as the most promising solvent, an aqueous mixture of triethylenetetramine (30 wt.%) with propan-1-ol (50 wt.%) as phase-splitting agent. This solvent is part of the solvents made with only one amine (usually containing primary and/or secondary amine) and an alcohol, which have been studied only in the recent years. This alcohol (propan-1-ol) is the inducer of the phase-splitting behaviour but also causes the main disadvantage of this solvent through its volatility. The second-best aqueous solvent contains TETA (15 wt.%) and DMCA (35 wt.%). All the three next promising solvents include DEEA as regeneration promoter with MAPA or MEA as an absorption activator. This type of mixture containing two different categories of amines has now been experimented for longer but remains very interesting to study. Using the results of this study, the next steps for developing liquid-liquid biphasic solvents to industrial scale should focus on experiments at micro-pilot scale for these solvents to confirm their status as one of the solutions to reduce global CO_2 emissions and, so, tackle the effects of climate change.

ASSOCIATED CONTENT

Supporting Information.

Comparison between physical and chemical solvents (Figure S1); conventional absorption-regeneration CO_2 capture process (Figure S2); Molecules of the reviewed solvents (Table S1); literature review with ether and sulfolane; discussion on the solvent degradation; AHP method; weighing and scoring scales for the six indicators (Tables S2 and S3); HSE analysis (Table S4); application of the techno-economic evaluation (Tables S5 - S12); application of the HSE evaluation (Tables S13 and S14) (PDF).

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