



IEAGHG Information Paper: 2017-IP37; Water-Lean Solvents for Post-Combustion CO₂ Capture: Fundamentals, Uncertainties, Opportunities and Outlook

Under the growing interest in finding the ideal CO₂ Capture solvent, water-lean solvents can become interesting options due to the lower specific heat of the diluents compared to that of water. However, common perception of high price, poor water tolerance, low CO₂ mass transfer or the need of a complex process configuration have placed those solvents on a secondary level.

Firstly, this paper gives an overview of desired properties of CO₂ capture solvents. Secondly, a review of the types of water-lean solvents is presented (included as a table at the end of this information paper). Advantages water-lean solvents offer are considered and a summary of opportunities is described. An overview of worrying properties of those solvents is also presented. The authors included an analysis at molecular level but that has not been included in this information paper.

There are two controversial properties of water-lean solvents that the authors claim to be misunderstood, thermodynamic profiles and volatility. The thermodynamic profile of solvents has been of interest when finding the ideal CO₂ capture solution. This correlates partial pressure of CO₂ with CO₂ loading and heat of absorption. In this work, it is highlighted the misconception around the heat of reaction needs. Although generally it is considered that a low heat of reaction (CO₂-absorbent solution) is convenient to achieve a low stripping energy penalty, high values can be beneficial to save energy during the CO₂ compression. Regarding water-lean solvent, both thermodynamic profiles can be found, with stripping below and above 100°C. Another sceptical view around water-lean solvents is volatility. However, contrary to some views, the main point of solvent losses would be the absorber but not the stripper. Solvent losses in the stripper will be condensate together with water during compression. As seen in the table below, some water-lean solvents absorb at low temperature and, consequently, high volatility is not an intrinsic characteristic.

Additionally, unique properties that can be misinterpreted during the use of water-lean solvents are:

- CO₂ Mass Transfer: Contrary to expectations, some water-lean solvents, as specific CO₂BOLs, have shown mass transfer coefficients comparable to MEA and PZ solvents, which can be translated as same size absorbers. In that case, mass transfer coefficients are inversely proportional to temperature, which indicates that those water-lean solvents are acting as physical solvents instead of chemical ones. The main advantage of such behaviour is an enhanced absorption at lower temperature. Working at colder temperature will condensate more water and decrease the reboiler duty. However, because that has been studied in limited cases, other water-lean solvents should be examined to confirm that.
- Phase Changes: Although phase changes can be considered inconvenient, those could be advantageous, as only part of the solution would be regenerated (Rich CO₂ phase), reducing the stripper size and potentially cutting down regeneration costs. Three phase changes types can take place: Liquid-solid, solid-liquid and gas-liquid. In the first case, the formation of solid means a lower volatility. However, the water tolerance must be taken into account during the selection of the water-lean solvent and additional mechanical equipment would be needed to avoid accumulation of solids on the bottom of the absorber. Both regeneration temperature ranges, low and high, were observed with this kind of phase change solvents. Secondly, solid-liquid phase change solvents are initially solids and become liquid with the CO₂ intake. The benefit of those is the use of fusion heat to heat up the solution and contribute to the required temperature for stripping. However, as in the previous case, handling solids can be challenging and a removal system would be needed in the stripper. Finally, gas-liquid phase solvents become liquid with the CO₂ loading. Yet, the workability must be studied.



- Changing free energy of solvation: This property, called polarity swing assisted regeneration (PSAR), is only claimed by CO₂BOLs, RIL and NAS solvent platforms and makes easy the release of CO₂ of rich solutions. The advantage associated to this property is lower regeneration temperature, which can reduce thermal degradation and solvent losses. However, further tests are still required.

Apart from those characteristics, there are negative properties of water-based solvents that still are uncertain in the case of water-lean solvents but look initially promising. Example of those are corrosivity, water tolerance and foaming. The absence of water decreases the corrosivity of those solutions. Low corrosion have been confirmed at small-scale, allowing the use of cheaper alloys of steel. Still, the fluegas can contain some water and the tolerance of those solvents must be taken into account. In this review, the majority of water-lean solvents are appreciably water tolerant. Moreover, foaming behaviour observed in water-based solvents have not been studied much with water-lean solvents. A couple of studies claim lower foaming issues than that of water-based solvents. Authors declare that water-lean solvents with similar physical properties (density, viscosity, and surface tension) could also have similar performance.

Complementary aspects as oxidation degradation could be enhanced by the lower reboiler temperature claimed during the use of water-lean solvents and tolerance to SO_x and HCl has been tested, obtaining initial good results. However, the reactions with NO_x are not that clear and toxicity due to continuous exposure to water-lean solvents is still indeterminate.

Regarding the CO₂ capture process configuration, it is important to highlight that the typical configuration has been originally designed for water-based solvents. New configurations could be more convenient to optimize the CO₂ capture with water-lean solvents. For example, due to their high viscosity, high-G columns and indirect hollow-fibre or sheet membrane contactors can be more convenient. Differences in surface tension, contact angle, thermal conductivity, density and polarity would impact on the optimum design too. Additionally, as mentioned above, absorption at lower temperature can be optimum for those solutions. A faster mass transfer and higher condensation of water prior to the absorption would be advantageous although additional energy for cooling would be required.

Finally, as the main parameter to scale –up and commercialize a new capture process, cost should also be taken into account for a proper comparison of water-lean and water-based solvents. As expected, water-lean solvents would be more expensive but process performance should be evaluated in detail to prove if that could be compensated. Moreover, as with water-based solvents, cost may be irrelevant if there is not enough capacity to manufacture at adequate scale.

As conclusion, this study is a review of types of water-lean solvents and the main objective is not only to report the properties of those but to clarify some misunderstanding on their characteristics. Contrary to water-based solvents, water-lean solvents cover a wider range of properties due to the use of different diluents instead of one unique diluent, water, as in the case of aqueous solutions. For this reason, it is possible to design the water-lean solvent with a higher degree of freedom. However, water is a cheap diluent, and manageable in terms of viscosity and density. The use of other co-solvents can also increase the viscosity, what will increase pumping costs and make more difficult the manageability. Still, some water-lean solvents claim not that high viscosity.

Regarding absorption characteristics, there is a misconception about CO₂ mass transfer on water-lean solvent and neither that can be assumed to be lower than that on water-based solvents. Water-lean solvents have been proved in some cases as physical solvents and higher mass transfer at low temperature can be beneficial to work at a lower absorption temperature. Still, the cost of additional



cooling down must be evaluated in such case. Moreover, water-lean solvent can suffer phase changes during absorption/desorption, what could be advantageous. However, managing different phases during the capture process can be difficult.

Generally, little information is known about CO₂ diffusion and bonding in those solvents. Moreover, still an extrapolation of observed properties on few solvents to others can be optimistic, and specific studies with each combination would be more convenient. Although the properties of water-lean solvents have been reported in the literature, most of them have not been tested at large scale. Higher scale tests should be performed to confirm the claimed enhanced properties.

For more information: Heldebrant et al., *Water-Lean Solvents for Post-Combustion CO₂ Capture: Fundamentals, Uncertainties, Opportunities and Outlook*, Chemical Reviews (2017) <http://pubs.acs.org/doi/abs/10.1021/acs.chemrev.6b00768>

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Type	Absorption temperature (°C)*	Absorption capacity*	Stripping temperature (°C)*	Heat of absorption*	Viscosity*	Volatility*	Other
Nonaqueous organic amine blends	20	Higher	Lower, reaching values below 100 (65-80)		Higher	Lower	High concentration of amines can be used with less corrosivity issues than those of water-based solvents; High CO ₂ solubility
Aminosilicones	-	-	-	Between 20000 and 2500 KJ/Kg CO ₂ Secondary	Higher	-	Combination of physical and chemical absorption
Switchable carbamates (reversible ionic liquids, RILs)	-	-	-	Some formulations have shown heat of absorption from -21KJ/mol to -152 KJ/mol	Can be higher	Can be higher	Some can have low chemical durability
Amines with Superbase Promoters	65-90 45-90 when included co-solvent	130 mol % per primary amine base	120	-	High viscosity without the use of co-solvents	-	-
Amino Acids in Organic Solvents	-	High	40-50 (N ₂ bubbling), 90 (thermically)	-	-	-	Intrinsic basicity, high water solubility, good thermal stability, excellent CO ₂ selectivity, good biodegradability and commercial availability
Alkylcarbonates	-	-	Room temperature-60 (under N ₂ flow gas)	-	High (non-linear relation with CO ₂ loading).	Low	High pKa; reduced mass transfer; those compounds can become solids at specific conditions, limiting CO ₂ intake; low cyclic capacity
N-Heterocyclic Azoles	-	High	-	-	High	Low	Higher CO ₂ selectivity and solubility; water tolerance
Hybrid solvents	-	Enhanced/comparable and high in other cases	Reported low energy penalty for regeneration	-	High (can be solved by decreasing the bulk of inert material)	Negligible	Enhance thermal stability; easy tunability; high CO ₂ solubility; good cyclic capacity

*Note: Values included in this table are the reported ones in the paper. Due to the large combination of components and/or diluents, those values can vary