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Carbon dioxide removal by alkanolamines in aqueous organic solvents. A method for enhancing the desorption process

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Abstract

Process concepts of using alkanolamines in aqueous organic solvents have been evaluated by experimental work and process simulations using the Procede Process Simulator. N-methyldiethanolamine (MDEA), methanol, and ethanol were chosen as the respective alkanolamine and organic compounds in the current work.

In previous work, the dissociation constants of protonated MDEA at infinite dilution in methanol–water and ethanol–water solvents and the initial mass transfer rates of CO_2 in 3 kmol m^{-3} MDEA in methanol–water and ethanol–water solvents were determined. In the current work, experimental values of the CO_2 vapor liquid equilibria in 3 kmol m^{-3} MDEA have been determined in methanol-water and ethanol-water solvents.

The experimentally determined results have been implemented into the Procede Process Simulator, which has been used to simulate a CO_2 removal plant with 90% CO_2 removal based on the specification of the flue gas of an 827 MWe pulverized coal fired power plant. A solvent of 3 kmol m^{-3} MDEA in aqueous methanol solution was considered for conceptual purposes. The results indicatively show a maximum decrease in the reboiler duty of the desorber of about 7.5% at methanol fractions of about 0.06 compared to purely aqueous solutions and a reboiler temperature decrease with increasing methanol fractions. Further experimental results are, however, necessary in order to more precisely simulate CO_2 removal processes by alkanolamines in aqueous organic solvents.

1. Introduction

Aqueous solutions of alkanolamines are frequently used for the removal of acid gases, such as CO_2 and H_2S, from a variety of gas streams. [1] A conventional acid gas removal plant is operated with an acid gas absorption / desorption cycle of the acid gas. In the absorber, the acid gas is (chemically) absorbed by the basic absorbent. At an elevated temperature in the desorber, the acid gas is released. The acid gas is released because of lower chemical solubility of the acid gas at elevated temperatures as a combined result of several factors such as the shift of the governing chemical equilibria, etc. For an alkanolamine of tertiary structure, the reversible reaction between CO_2 and the alkanolamine occurs according to:

$$B + CO_2 + H_2O \rightleftarrows BH^+ + HCO_3^-$$
{1}

where *B* is an alkanolamine. The reversible Reaction {1} is shifted towards the right side of the equation in the absorber and towards the left side of the equation in the desorber by the respective temperature changes. Shifting of the governing chemical equilibria, such as Reaction {1} in the case above, may also be achieved by changing the polarity of

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the solvent by the addition or removal of an organic compound. The organic compound would then act as a part of the solvent in which the alkanolamine is dissolved. Water as a solvent has a relatively high polarity, extensive hydrogen bounding abilities, and a low molar mass. These factors have contributed to the significance of water as a widely used solvent. The polarity of water and an organic compound can differ substantially. The degree of (non-)polarity of a compound can generally be described by the dielectric constant. In a mixture of water and an organic compound, the dielectric constant will usually be a numeric value in between those of the pure compounds. The dielectric constant of a solution, either a single compound or mixture, is a measure of the ratio of stored electrical energy when a potential is applied to the solution relative to vacuum. In more applied terms of engineering, the dielectric constant of a solution is a measure of what type of compounds it can dissolve. As a rule of thumbs, polar compounds dissolve polar compounds the best and non-polar compounds dissolve non-polar compounds the best. Strongly polar compounds such as salts dissolve easily in a polar compound like water, but less in a less-polar compound like an alcohol. By such, the dielectric constant can be a measure of the ability of the ionic form of a compound, rather than the molecular, to be present in a solution. Reactive acid gas treating processes (often) involves the conversion of CO_2 from molecular structure to ionic structures in the form of bicarbonate, carbonates, or carbamates following the reaction path with an alkanolamine. Additionally the alkanolamine might also exist as an ionic structure in terms of a protonated alkanolamine. The polarity, and thus also the chemical equilibria, of the solvent can thus (to a degree) determine whether CO_2 and the alkanolamine will exist as molecular structures or ionic structures at a given operating condition. The chemical equilibria may thus shift without any increase or decrease of the temperature, yet temperature change will lead to a further shift. Two process concepts are introduced and shown schematically in Figure 1 and Figure 2:

(1) The addition of an organic compound as part of the solvent mixture throughout an absorber / desorber cycle. Because an organic compound has different physical and chemical properties than the alkanolamine and water, the addition of such a compound may lead to favourable effects in both the absorber and the desorber section.

(2) The addition of an organic compound to the incoming acid gas loaded absorbent at the start of the desorption process in the desorber, and removal by evaporation, pervaporation, liquid phase-split, or any other separation process before the lean absorbent is directed back to the absorber. The organic compound is returned to the beginning of the desorption process, and by such an additional organic compound cycle is added to the conventional absorption / desorption cycle. The acid gas may then be released from the absorbent at lower temperatures in the desorber section.
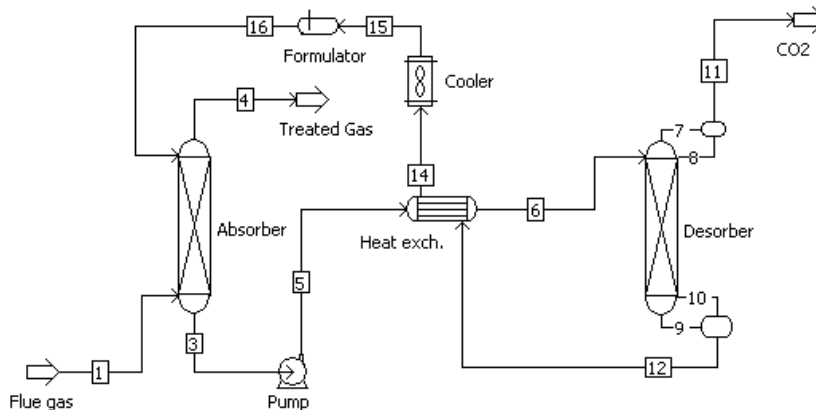

Figure 1: Schematic flowsheet of process concept (1)

Numerous excellent papers and publications exist in the open literature covering the topic of chemical absorption of CO_2 into aqueous alkanolamine solutions. On the contrary, work covering chemical absorption of CO_2 into solutions of alkanolamines in mixtures of aqueous and organic solvents is limited, even though several processes using these types of solvents have been developed, e.g. the Sulfinol process, etc. Although these processes were developed for the treatment of high pressure acid gas streams, it is generally concluded that the initial gas-liquid mass transfer rates of carbon dioxide are increased, mainly because of higher diffusivities and/or physical solubilities if an organic compound is present in the solution, whereas the reaction kinetics and chemical solubilities are reduced as a result of the absence of water and reduced solvent polarity. The optimal fraction of an organic compound in the absorber section would hence be determined by a trade-off between absorption rates and solvent capacities. The increased mass transfer rate and lowered chemical solubilities would lead to an enhancement of the mass transfer limited desorption process at elevated temperatures.