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Published in:
Energy Procedia

DOI:
[10.1016/j.egypro.2011.01.040](https://doi.org/10.1016/j.egypro.2011.01.040)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2011

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Citation for published version (APA):

Hamborg, E. S., Derks, P. W. J., Elk, E. P. V., & Versteeg, G. F. (2011). Carbon dioxide removal by alkanolamines in aqueous organic solvents. A method for enhancing the desorption process. *Energy Procedia*, 4(1), 187-194. DOI: 10.1016/j.egypro.2011.01.040

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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 CO₂ in 3 kmol m⁻³ MDEA in methanol–water and ethanol–water solvents were determined. In the current work, experimental values of the CO₂ 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 CO₂ removal plant with 90% CO₂ 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 CO₂ removal processes by alkanolamines in aqueous organic solvents.

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Keywords: post-combustion acid gas removal; alkanolamines; aqueous organic solvents

1. Introduction

Aqueous solutions of alkanolamines are frequently used for the removal of acid gases, such as CO₂ and H₂S, 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 CO₂ and the alkanolamine occurs according to:



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 bonding 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 CO₂ 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 CO₂ 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.

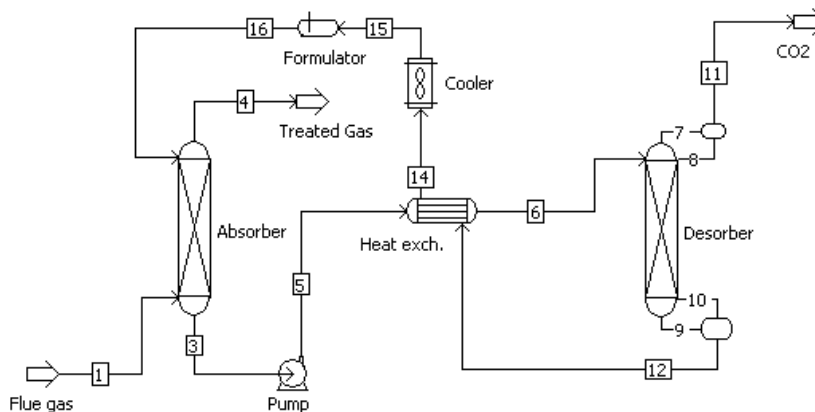


Figure 1: Schematic flowsheet of process concept (1)

Numerous excellent papers and publications exist in the open literature covering the topic of chemical absorption of CO₂ into aqueous alkanolamine solutions. On the contrary, work covering chemical absorption of CO₂ 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.

stirred cell reactor operated with a flat horizontal gas-liquid interface at 25 °C. From the physical absorption measurements, the solubility and mass transfer coefficient were calculated by the following relations:

$$m = \frac{P^0 - P^\infty}{P^0} \frac{V_g}{V_l} \quad (3)$$

$$k_l = -\frac{1}{a} \frac{V_l V_g}{m V_l + V_g} \frac{d}{dt} \ln[P^t - P^\infty] \quad (4)$$

and for the chemical absorption measurement:

$$mk_l E = -\frac{V_g}{a} \frac{d}{dt} \ln P^t \quad (5)$$

where m is the physical solubility, P is the partial pressure of respective N₂O or CO₂, V is the volume, k_l is the mass transfer coefficient, a is the gas-liquid interfacial area, and E is the enhancement factor. The superscripts 0 is the initial time, t is the time, and ∞ is the infinite time, and the subscripts g is the gas phase and l is the liquid phase.

2.1.3. Vapor Liquid Equilibria of CO₂ into a Solution containing Alkanolamines in Aqueous Organic Solvents

The vapor liquid equilibria (VLE) of CO₂ in a solution of alkanolamines in aqueous organic solvents provide information about the chemical solubility and capacity of the solvent. The scope of the work was to quantify the reduced chemical solubility of CO₂ in alkanolamines in aqueous organic solutions with increasing fractions of methanol or ethanol. Vapor liquid equilibria measurements of CO₂ in MDEA-methanol-water and MDEA-ethanol-water mixtures have been conducted. The concentration of MDEA was 3.0 kmol m⁻³ and the methanol and ethanol mole fractions were ranging from 0 to 1 relative to water for all measurements. The measurements were carried out in a vigorously stirred cell reactor at 25 °C.

2.2. Simulations of a CO₂ Removal Processes using Alkanolamines in Aqueous Organic Solvents

The aforementioned process concepts were implemented and simulated for indicative purposes in the rate-based Procede Process Simulator. Process concept (1), as shown in Figure 1, was considered, and the effect of the organic compound in the absorber section was investigated by applying a 3.0 kmol m⁻³ MDEA with increasing fractions of methanol. The relation describing the experimentally determined dissociation constants of protonated MDEA as a function of temperature and methanol fraction was implemented in the form of:

$$\ln K_a(T, x_{Alc}) = \frac{a}{T} + b + c \ln T + dx_{Alc}^e \quad (6)$$

The autoprotolysis constant of aqueous methanol was, in addition, implemented according to results of Fonrodona et al. [3], where the temperature dependence was taken to be the same as for pure water. The predicted partial pressures of CO₂ from the Procede Process Simulator were thereafter compared to the experimentally determined VLE of CO₂. The increase of the mass transfer coefficient from the presence of methanol was manually adjusted from a linear interpolation of the determined experimental results. Although the kinetics of aqueous MDEA are too slow for low-pressure CO₂ removal processes and thus resulting in very tall absorber columns, MDEA was considered for a conceptual purpose in the current work because of its well described properties, e.g. kinetics, viscosities, densities, diffusivities, etc., and the relatively simple reaction path of a tertiary alkanolamine with CO₂. The current simulations were carried out based on differences in mass transfer rates and chemical equilibria from the presence of the methanol, and any side / degradation reactions, chemical losses, etc. possibly taking place were not considered. The specifications of the incoming untreated flue gas stream were based on the specification of an 827 MWe pulverized coal fired power plant, and given in Table 1 at a flow rate of 855.2 m³/s at 40 °C and 1 bara. [5] The fraction of removed CO₂ from the flue gas was set to 0.9 in all simulation cases.

Table 1: Composition of the untreated flue gas of an 827 MWe pulverized coal fired power plant based on the mole fraction x

Component	CO ₂	SO ₂	O ₂	H ₂ O	N ₂
x	0.12	0	0.04	0.07	0.77

3. Results and discussion

3.1. Experimental results

3.1.1. Dissociation Constants of Alkanolamines in Aqueous Organic Solvents

Experimental results of the dissociation constants of protonated MDEA at infinite dilution in methanol–water and ethanol–water are given in Figure 3, and show the change of the basic strength of MDEA at different methanol and ethanol mole fractions and temperatures compared to the change of that in pure water at different temperatures. The plots in Figure 3 indicate the cyclic change of the basic strength of MDEA at different methanol or ethanol fractions and temperatures. Ethanol seems to reduce the basic strength of MDEA further than methanol mainly because of its lower dielectric constant (polarity) and higher boiling point. The values given above 50 °C for methanol containing solvents and above 60 °C for ethanol containing solvents were extrapolated using Equation (6) to the respective boiling points of the alcohols.

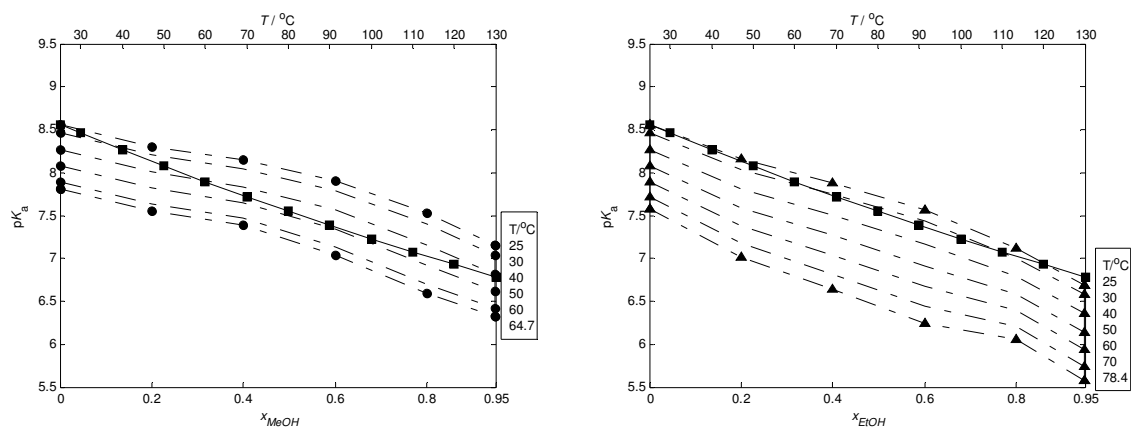


Figure 3: Comparison of the change of the basic strength at infinite dilution of MDEA in; (1) pure water at different temperatures; and (2) different mole fractions of alcohols and temperatures: ■, pure water (upper axis); ●, aqueous methanol (lower axis, text box); ▲, aqueous ethanol (lower axis, text box).

3.1.2. Initial Absorption Rates of CO₂ into a Solution containing Alkanolamines in Aqueous Organic Solvents

Figure 4 shows the increased normalized values of the mass transfer coefficient and the physical solubility of CO₂ into 3.0 kmol m⁻³ MDEA as a function of methanol or ethanol mole fractions relative to water at 25 °C. [4] The plot shows a steep increase of the mass transfer coefficient at alcohol mole fractions lower than 0.1. Figure 5 shows the effect of methanol or ethanol mole fraction relative to water on $m k_1 E$ of CO₂ when absorbed into 3.0 kmol m⁻³ MDEA at 25 °C, which was assumed to take place in the pseudo-first order regime. $m k_1 E$ is proportional to the square root of the overall kinetic rate constant multiplied with the diffusivity of CO₂. Because of the complexity of the current chemical system, the kinetic rate constants were, however, not determined. The values in Figure 4 do however give an indication of the initial mass transfer rate performance of MDEA in aqueous organic solvents. The initial mass transfer rate is seen to increase with increasing fraction of methanol or ethanol, and increases the most in the case of methanol to a factor of about seven at a methanol fraction of unity.

3.1.3. Vapor Liquid Equilibria of CO₂ into a Solution containing Alkanolamines in Aqueous Organic Solvents

Figure 6 shows the CO₂ partial pressure as a function of the loading α_{CO_2} in a 3 kmol m⁻³ MDEA as a function of methanol or ethanol mole fractions relative to water at 25 °C. The results indicate that the chemical solubility is lower in aqueous solutions of ethanol compared to that of methanol, which is to be expected based on the results of the dissociation constants given in Section 3.1.

3.2. Simulations of a CO₂ Removal Processes using Alkanolamines in Aqueous Organic Solvents

The results presented in the previous sections were implemented into the Procede Process Simulator and used to simulate an indicative process for CO₂ removal by alkanolamines in aqueous organic solvents. The predicted partial pressure of CO₂ from the Procede Process Simulator as a function of alcohol fractions, based on the implementation of Equation (6), were at the simulated process conditions found to be within a systematic error of about 30% of the experimentally determined values, as given in Figure 6. This error would decrease if a non-ideal thermodynamic model would be applied. Methanol was chosen as the organic compound because of its better mass transfer characteristics and higher chemical solubility of CO₂ compared to those of ethanol. The mass transfer coefficient in the absorber section

was for simplicity reasons set to 10^{-4} m s^{-1} at a methanol fraction of zero. The increased mass transfer coefficients as a function of increased methanol fractions, as given in Figure 4, were determined in a stirred cell reactor. It is however not clear if this increase also would also occur in a packed absorber column, and a sensitivity analysis was therefore performed. The increased effects on the mass transfer coefficients at increased fractions of methanol, as given in Figure 4, were multiplied with factors of 0.2 to 1.0 at each fraction of methanol.

The simulation results are given in Figure 7 and Figure 8. Figure 7 shows the normalized effect on the reboiler duty as a function of methanol fractions at 90% removal of CO_2 from the flue gas. The total solvent flow rate was set to 9542 kg/s in every simulation cases, and methanol thus replaced water on a mass basis in order to achieve the mole fractions of methanol relative to water. The result shows the effect of the increasing mass transfer coefficient and the decreasing chemical solubility of CO_2 with increasing methanol fraction, i.e. a higher total absorption of CO_2 with the presence of methanol in the absorbent. The results show a decreased energy use if the mass transfer coefficient is increased by a factor of about 0.4 or higher in an absorber column compared to the increase in a stirred cell reactor if methanol is added to the solvent. A maximum decrease of the reboiler duty of the desorber of about 7.5% is obtained at a methanol fraction of about 0.06. Figure 8 shows the effect on the reboiler temperature as a function of methanol fractions at 90% removal of CO_2 from the flue gas. A sensitivity analysis with regard to the mass transfer coefficients, as described above, was carried out. The temperature is shown to decrease with increasing fractions of methanol and mass transfer coefficients.

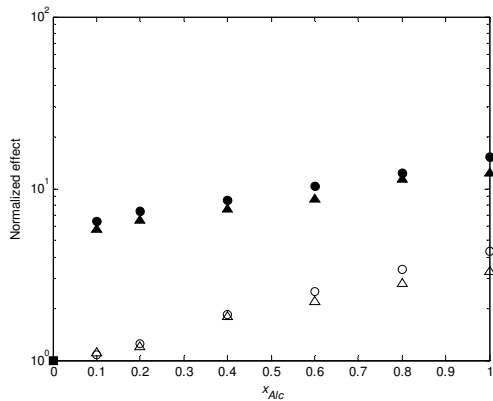


Figure 4: Semi logarithmic plot of the normalized effect of methanol or ethanol on m and k_f of CO_2 into 3 kmol m^{-3} MDEA in aqueous organic solvents at 25°C : ■, k_f and m in pure water; ●, k_f in aqueous methanol; ▲, k_f in aqueous ethanol; ○, m in aqueous methanol; △, m in aqueous ethanol

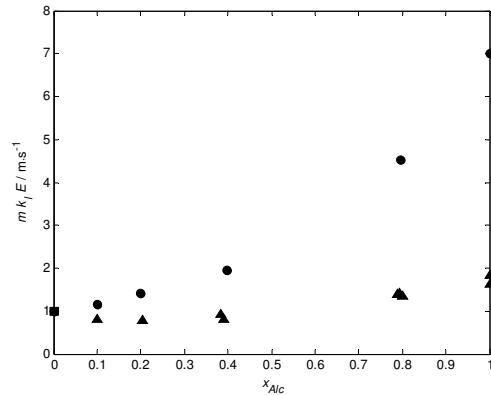


Figure 5: The normalized effect of methanol or ethanol on $m k_f E$ of CO_2 into 3 kmol m^{-3} MDEA in aqueous organic solvents at 25°C : ■, pure water; ●, aqueous methanol; ▲, aqueous ethanol.

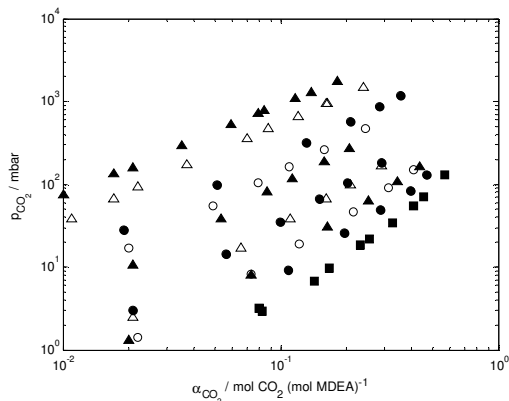


Figure 6: The effect of methanol and ethanol on the VLE of 3 kmol m^{-3} MDEA in aqueous organic solvents at 25°C : ■, pure water; ● or ○, aqueous methanol at fractions of 0.2, 0.4, 0.8, and 1.0; ▲ or △, aqueous ethanol at fractions of 0.2, 0.4, 0.8, and 1.0.

The process described and simulated above shows the effect of methanol in an absorber limited process configuration. Hence, the lack of high temperature experimental data of the mass transfer coefficient and VLE of CO_2 in the respective solvents, as given in Figure 4 and Figure 6, is justified in the simulations. For a similar simulation using other alkanolamines such as monoethanolamine, piperazine, or others, further experimental work has to be conducted.

Process concept (2), as shown in Figure 2, cannot at the current stage be simulated because of lack of high temperature experimental data, such as VLE of CO_2 , etc. In this case, the separation unit of the organic compound after the desorber also has to be considered, and the type of organic compound added will determine which type of separation unit can be used. Low-temperature boiling organic compounds such as methanol, ethanol, or similar, can be removed by vacuum distillation for low-temperature heat input. In that case, the separation unit should be positioned at the cold side of the heat exchanger. In the case of ethanol,

pervaporation/membrane units might be an attractive option. Long-chain alcohol such as *n*-butanol or higher are partially immiscible in water, but becomes miscible at temperatures higher than 100 °C. [6] The long-chain alcohol can be added to the desorber, which is kept above 100 °C, and after the desorber easily separated from the remaining solvent by the formation of two liquid phases with decreased temperature. The presence of alkanolamines and / or ionic species will however influence the phase diagram of aqueous long-chain alcohols. Simulation of these types of process concepts warrants further experimental studies.

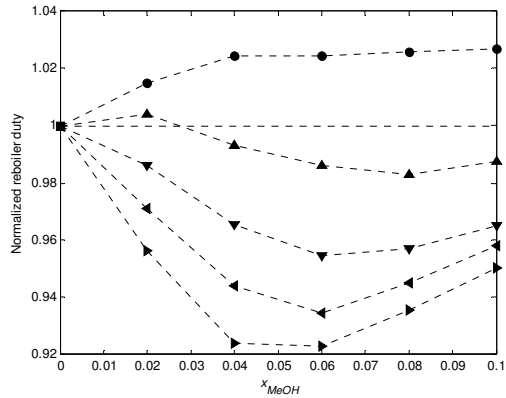


Figure 7: Simulated results of the normalized reboiler duty of process concept (1) with 3 kmol m^{-3} MDEA in aqueous organic solvents with increasing methanol fractions and 90% CO_2 removal from the flue gas: ■, pure water. The results of a sensitivity analysis of the increased effect on k_1 with addition of methanol multiplied by factors of: ●, 0.2; ▲, 0.4; ▼, 0.6; ◀, 0.8; ▶, 1.0.

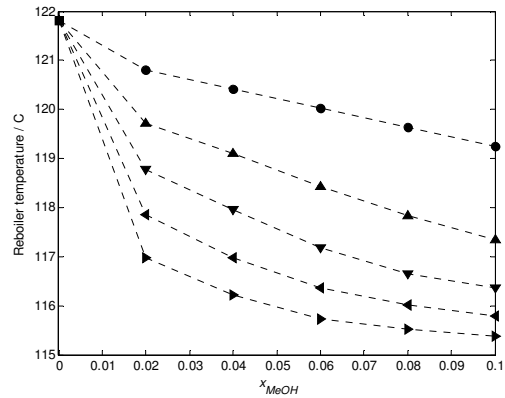


Figure 8: Simulated results of the reboiler temperature of process concept (1) with 3 kmol m^{-3} MDEA in aqueous organic solvents with increasing methanol fractions and 90% CO_2 removal from the flue gas: ■, pure water. The results of a sensitivity analysis of the increased effect on k_1 with addition of methanol multiplied by factors of: ●, 0.2; ▲, 0.4; ▼, 0.6; ◀, 0.8; ▶, 1.0.

4. Conclusion

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.

(Previous) 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% compared to purely aqueous solutions at a methanol fraction of about 0.06 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.

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Acknowledgements

This research is part of the CAPTECH program, a Dutch national research program on CO₂ capture. CAPTECH is financially supported by the Dutch government (EOS) and the consortium partners. (www.co2-captech.nl) The authors would like to express their gratitude for their financial support.