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Comparison of the kinetic promoters piperazine and carbonic anhydrase for CO$_2$ absorption

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Abstract

Kinetic promoters that catalyse the absorption and desorption of CO$_2$ can enable the use of solvents with low heat of reaction and slow absorption rate such as MDEA. Mass transfer experiments with 30 wt% MDEA promoted by either 5 wt% piperazine (PZ) or 1.7 or 8.5 g/L enzyme carbonic anhydrase (CA) were conducted in a wetted wall column apparatus at 298 K, 313 K and 328 K for different solvent loadings. The mass transfer of PZ promoted solvents was strongly influenced by the solvent loading as it was steeply decreasing for all temperatures as the solvent loaded; the temperature also increased the mass transfer, the extent was dependent on the solvent loading. CA promoted solvent mass transfer characteristics showed less dependency on the solvent loading and temperature. Lower enzyme concentrations were found to be much slower than MDEA/PZ solvents, whereas high enzyme concentrations were as efficient in capturing CO$_2$ as a 30 wt% MDEA/5 wt% PZ mixture in terms of overall mass transfer, considering change of mass transfer due to solvent loading over the height of a column.

Keywords: piperazine, MDEA, carbonic anhydrase, wetted wall column

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1. Introduction

Carbon capture and storage technology (CCS) has the ability to reduce greenhouse gas emissions with almost immediate impact while ensuring a safe and stable energy supply over the next years, by capturing the carbon dioxide from flue gases exiting fossil fuel burning power plants.

The capture of CO_2 from flue gases is a very energy intensive task. The energy demand of the capture process is offset by combustion of fossil fuels which thus reduces the electricity output of the power plant. In this way the cost of CO_2 free electricity is linked to the energy requirement of the post combustion capture process. The capital costs of retrofitting the post combustion capture unit to the power plant will likewise influence the costs. Clearly, both the capital and operating costs should be minimized for an ideal process. The capital costs can be minimized by reducing the equipment sizes, in mass transfer operations this can be done by intensifying the mass transfer. Likewise, for chemical absorption this can be done by increasing the reaction rate of the solvent with CO_2. Higher reaction rates result in higher mass transfer rates when the other process conditions are kept constant. The current solvents of choice are therefore primary and secondary amines since they have faster kinetics with their direct reaction mechanism with CO_2 forming carbamates. The operating costs of the process can be minimised by limiting the energy requirement for pumps, gas compression, and heat requirement of the desorber. Interestingly, the overall energy demand as a fraction of total energy demand of these tasks is very different. For example, the heat requirement for the solvent regeneration in a post combustion CO_2 capture process makes up between 61 and 70 % of the total energy demand, whereas the compression (up to 110 bar) needs between 25 and 33 % of the total energy [1]. When excluding the compression step the overall energy demand of the desorber rises to 90-93% of the total energy demand. The energy requirement in the desorber can be divided into 3 different parts; part of the energy is needed to reverse the CO_2-solvent reaction, this energy is represented by the heat of desorption. Since the vapor stream consists mainly of CO_2 and water, steam needs to be generated in order to maintain the desorber pressure. The steam leaves the desorber on top and is condensed; the energy demand is referred to as latent heat loss. As the solvent is not brought into the desorber at boiling conditions it has to be heated up to the desired temperature, this energy demand is called sensible heat loss. These latter two heat requirements are strongly dependent on the process design and process conditions. The heat of ab-/desorption is solvent dependent, and so choosing a solvent with a lower heat of absorption can likewise reduce the energy demand of the process.

Fast reaction solvents like primary and secondary amines exhibit a higher heat of ab-/desorption than tertiary amines, the group of primary amines have about 30-40% higher heat of absorption than tertiary amine and the secondary amines about 20 to 30% [1].

On the other hand the kinetics of tertiary amines like MDEA are much slower than primary and secondary amines. The use of aqueous MDEA without additives for a post combustion capture process is not feasible as absorptions towers as high as 300 m would be required to achieve 90% capture [2]. The use of kinetic promoters can help increasing the reaction rate and therefore help taking advantage of the low heat of ab-/desorption.

A very efficient promoter is the secondary diamine piperazine (PZ), which is used in BASF's activated methyldieathanolamine (a-MDEA) solvent. Another very efficient promoter that has gained a lot of interest in recent years is the enzyme carbonic anhydrase which catalyzes the reversible hydration of CO_2 forming bicarbonate.

2. Materials and methods

Mass transfer experiments were carried out in a wetted wall column apparatus with MDEA promoted by piperazine or carbonic anhydrase. The experiments were conducted at 298, 313 and 328 K at different solvent loadings.

2.1. Chemistry

Amine solvents are generally used in aqueous mixtures. In an aqueous MDEA solution the following reversible reactions are rate limiting for the reaction with CO_2

$$CO_2 + OH^- \leftrightarrow HCO_3^- \tag{1}$$

$$CO_2 + MDEA + H_2O \leftrightarrow HCO_3^- + MDEAH^+ \tag{2}$$

The first is a hydroxide reaction and the second is a base catalyzed CO_2 hydration which is the reaction mechanism for tertiary amines [3]. There are more reactions ongoing in the liquid phase, but most of them are proton transfer reactions which are thought to be much faster and therefore at equilibrium.

Piperazine as a diamine has two active nitrogen groups, the two main reactions that are rate limiting in a solvent containing PZ is the carbamate and dicarbamate formation [4]:

$$CO_2 + PZ + H_2O \leftrightarrow PZCOO^- + H_3O^+ \tag{3}$$

$$CO_2 + PZCOO^- + H_2O \leftrightarrow PZ(COO^-)_2 + H_3O^+ \tag{4}$$

The enzyme carbonic anhydrase is catalyzing the following reaction:

$$CO_2 + H_2O + B \overset{CA}{\leftrightarrow} HCO_3^- + BH^+ \tag{5}$$

B represents any buffer which acts as a proton acceptor. It can be seen that the main reactions of PZ and CA differ significantly. Another big difference is that PZ as an organic chemical changes the thermodynamic and chemical of the solvent, whereas the addition of CA leaves the thermodynamic properties unchanged [5].

The speciation of ions in the solvents for the experiments are calculated with the extended Uniquac activity model [6].

2.2. Wetted wall column

A wetted wall column as shown in Figure 1 was used for the mass transfer experiments. It is a gas liquid contacting device with well-defined flowing conditions and dimensions. The gases carbon dioxide and nitrogen are mixed from gas bottles with mass flow controller; the gas is then passed through two saturators, on standing in a water bath at reaction temperature, the gas is then either bypassed or send through wetted wall column where it is in contact with the liquid phase, in both cases the gas was then analyzed for CO_2 content, pressure and temperature after it was conditioned in a condenser at 15 ℃. The liquid phase is pumped from a liquid reservoir through a rotameter and a heating coil that is immersed in the same water bath as the saturator; it then enters the reaction chamber in the bottom in the inside of a metal pipe. On top of the open pipes the liquid flows down on the outside creating a thin complete liquid film. The thickness of the liquid film can be calculated from a momentum balance for a free falling liquid film on a surface. The mass transfer area can then be calculated from the dimensions of the wetted wall column in Figure 1 adding the liquid film thickness on top. A mole balance over the gas phase from the bypass and wetted wall column experiments gives the mass transfer flux of CO_2.

The general expression for a chemical absorption process using the Enhancement factor model is as a ratio of driving force and resistance:

$$N_{CO_2} = \frac{(P_{CO_2}^{gas} - H_{CO_2} \cdot C_{CO_2}^{liq})}{\dfrac{1}{k_{CO_2}^{gas}} + \dfrac{H_{CO_2}}{k_{CO_2}^{liq0} \cdot E}} \tag{6}$$

The mass transfer of CO_2 N_{CO_2} (mole m^{-2} s^{-1}) through the interface from one phase into the other can be described using the partial pressure of CO_2 in the gas phase bulk $P_{CO_2}^{gas}$ (Pa), the concentration of CO_2 in the liquid bulk $C_{CO_2}^{liq}$ (mole m^{-3}), the apparent Henry coefficient for CO_2 in the solvent H_{CO_2} (Pa m^3 mole^{-1}); the product of H_{CO_2} and $C_{CO_2}^{liq}$ is the equilibrium partial pressure of the solvent. The mass transfer resistance is the sum of gas side mass transfer resistances which are the reciprocals of the gas side mass transfer coefficient $k_{CO_2}^{gas}$ (mol Pa^{-1} s^{-1} m^{-2}) and the liquid side mass transfer resistance consisting of the Henry coefficient, the physical mass transfer resistance $k_{CO_2}^{liq0}$ (m s^{-1}) for mass transfer in absence of chemical reaction and an Enhancement factor E (-) accounting for the intensification of mass transfer due to chemical reaction. The product of Enhancement factor E and physical mass transfer coefficient $k_{CO_2}^{liq0}$ is regarded as chemical liquid side mass transfer coefficient $k_{CO_2}^{liq}$.

The mass transfer coefficients for the gas phase have been determined experimentally for this setup by SO_2 absorption experiments into 1 M NaOH as described in our previous study [7], the other values can be correlated or measured during experiments, leaving the chemical liquid side mass transfer coefficient $k_{CO_2}^{liq}$ the only unknown.
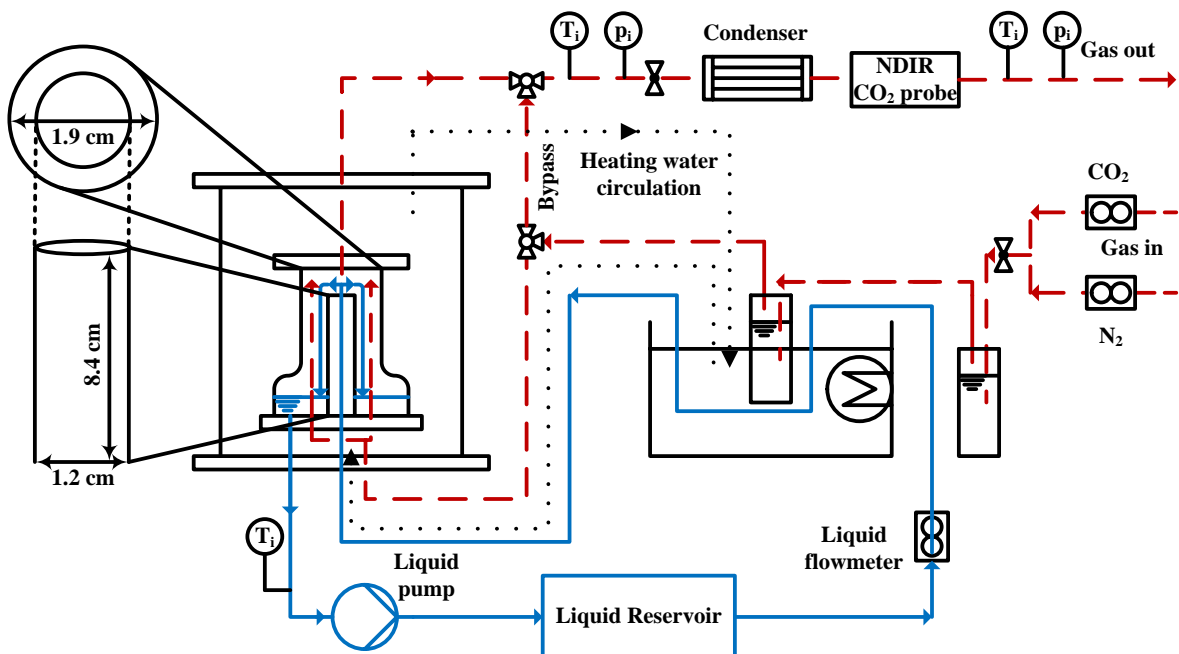

Figure 1: Wetted wall column setup

2.3. Chemicals

The solvents were prepared mixing MDEA from BASF (99% purity) with DIwater. For the piperazine experiments 5wt% PZ was added and the amount of water was reduced, resulting in a solvent consisting of 30 wt% MDEA and 5 wt% PZ. For the loaded solvents, preloaded MDEA solution was mixed with PZ and different dilutions were made with unloaded MDEA with PZ. In the solvents with carbonic anhydrase, some of the water was

replaced with enzyme solution. The solvent loading of all experiments was determined using a BaCl2 titration method [8]. The solvent loading of MDEA with PZ will be reported as mole CO_2 per mole MDEA to make the value comparable to experiments with MDEA and CA.

3. Results and discussion

The mass transfer coefficients of 30 wt% MDEA enhanced with 5 wt% PZ and 1.7 g/L CA are shown in Figure 2. Compared to 30 wt% MDEA alone, both promoters increase the mass transfer significantly. The mass transfer of MDEA with 5 wt% PZ is higher than for CA for loading lower than 0.34. Loading does effect the mass transfer of MDEA-PZ as we can see a steep decline for all three temperatures, the decrease is more profound the higher the temperature is in the experiments. The mass transfer at low solvent loadings is higher with higher temperature. When the solvent loaded the difference between the 3 temperatures diminishes, at a solvent loading of around 0.2 there is almost no effect of temperature on the mass transfer. At loadings than higher 0.2 there seems to be a difference between the different temperatures, mass transfer here is higher when temperature is lower. Mass transfer in chemical absorption is dependent on the reactions between the solvent and CO_2 at the interface. In case of PZ promoted MDEA the most important reactions are the reaction of free PZ with CO_2 described Eq. (3) and the reaction of PZ-carbamate with CO_2 described in Eq. (4). The reaction rates are linked to the concentrations of the free species PZ and $PZCOO_3^-$. The reaction kinetics of PZ and $PZCOO_3^-$ are following Arrhenius dependency [9], resulting in higher reaction rate constants for higher temperatures. For the concentration of the species PZ and $PZCOO_3^-$, the trend is reverse; here higher temperature favors product formation, thus lower concentration of reactants. The solvent loading itself has a distinct effect on the concentration of active promoters PZ and $PZCOO_3^-$; at higher temperature the higher reaction rate constant cannot compensate the lower concentration of active promoters when the solvent loading is about 0.2 mole of CO_2 per mole of MDEA.
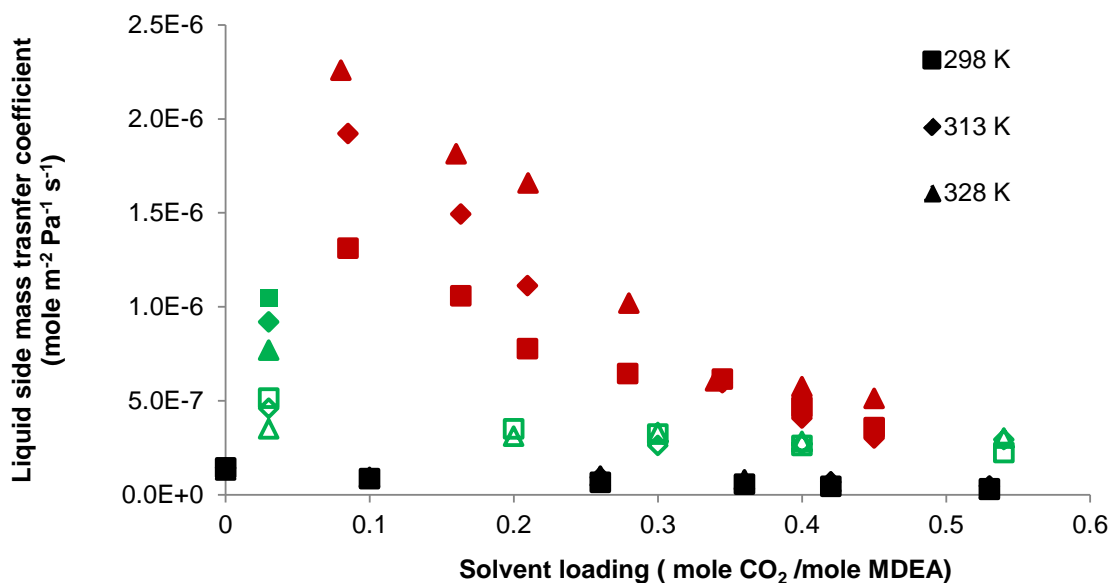

Figure 2:Chemical liquid side mass transfer coefficient of 30 wt% MDEA enhanced with either 5 wt% PZ or CA (8.5 and 1.7 g/L) at different temperatures and solvent loadings; red symbols correspond to MDEA/PZ, green symbols to MDEA/CA, filled (8.5 g/L) and empty (1.7 g/L); black symbols are MDEA without promoter

Mass transfer in experiments with carbonic anhydrase is also declining with increasing solvent loading. The extent is not as distinct as in experiments with PZ promoted MDEA. The reason for this decline is most likely a product inhibition by bicarbonate ions for the enzyme [10]. The mass transfer for enzyme promoted MDEA in case of a low loading is also higher at lower temperatures, this might be an indicator, that the enzyme kinetics are not following a Arrhenius type reaction.

The experiments showed that the PZ as a promoter resulted in higher mass transfer than MDEA promoted with 1.7 g/L CA. Fivefold increase of the enzyme concentration resulted in higher mass transfer for the CA promoted solvent as shown in Figure 3 where the liquid side mass transfer as a function of temperature is depicted. Mass transfer of MDEA promoted with CA at both enzyme concentrations follows similar temperature behaviour, with higher mass transfer at lower temperature. A solvent of 30 wt% MDEA promoted with 1.7 g/L CA is slightly slower than 30 wt% MDEA promoted by 5 wt% PZ at a solvent loading of 0.34 mole CO_2 per mole of MDEA, surprisingly both solvents follow a similar decline in mass transfer with temperature. A 30 wt% MDEA solvent promoted with 8.5 g/L is as fast as 30 wt% MDEA/5wt% PZ solvent at a solvent loading of 0.16 at 298 K and comparable to the PZ promoted solvent with a loading of 0.28 at 313 and 328 K.
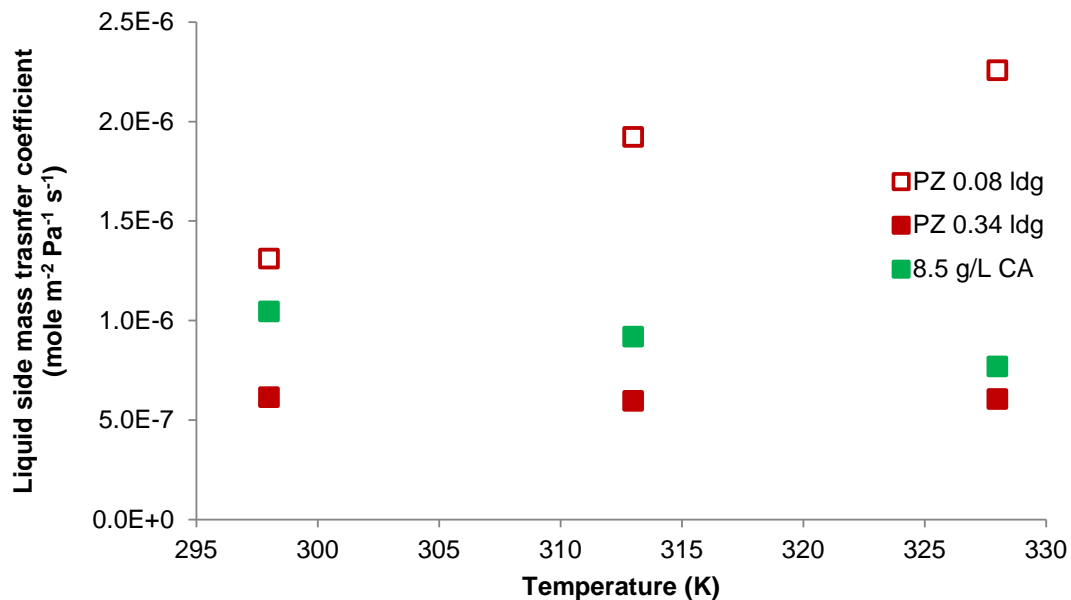

Figure 3: Chemical liquid side mass transfer coefficient of 30 wt% MDEA as a function of temperature, for PZ activated solvent at different loadings and CA promoted solvent at different enzyme concentrations

4. Conclusion

Addition of both carbonic anhydrase and piperazine can increase the mass transfer of CO_2 to MDEA significantly. A mixture of 30 wt% MDEA with 5 wt% PZ has the highest mass transfer at low loading. The chemistry of the MDEA/PZ mixture results in a rapid decrease of mass transfer as the concentration of reactive species is reduced. This decrease is even more distinct at higher temperature. The influence of solvent loading and

temperature on enzyme enhanced solvents is rather different, since the mass transfer does not decline so strongly with loading, and the mass transfer is higher at lower temperatures. Hence a solvent with high enzyme concentration is still slower than 30 wt% MDEA/ 5wt% PZ mixture at low loading, but given the smaller decrease in mass transfer with loading it has the potential to compete with a PZ enhanced solvent in terms of overall mass transfer over the total height of a column.

Acknowledgements

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