Simplified method to describe kinetics of CO₂ absorption into mixed amine solvents

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1. Introduction

Absorption of CO₂ with amine-based absorbents is an established and proven technology and MEA is the most widely used amine solvent for this purpose, however it’s still very energy intensive and has high capital cost. The overall challenge is to bring these two factors down with new and environmentally acceptable solvents. It can be carried out by the process design improvement or by finding a better new solvent, i.e. a better solvent candidate should have a higher capacity, faster absorption rate and lower enthalpy of absorption than those in use recently. Primary and secondary amines are expected to have faster absorption rate but found to have a lower in absorption capacity compared to tertiary amine (Kohl and Nilson, 1997). The use of mixed amine solvents could be another alternative to find a better new solvent for CO₂ absorption. The main purpose of this work is to study the kinetic absorption of CO₂ into mixed amine solvents in a String of a Dics Contactor (SDC) and to develop the simplified method to calculate the kinetic rate constant.

2. Experiment and procedures

2.1. Description of a SDC apparatus

A SDC apparatus was used to perform the kinetic experiments as seen in Fig.1. It comprises an arrangement of \((n_d = 43)\) discs, each with diameter \((d = 1.5 \cdot 10^{-2} m)\) and thickness \((w = 4.0 \cdot 10^{-3} m)\). The actual mass transfer area \(A_{act}\) is calculated by

\[
A_{act} (m^2) = \left[2 \cdot \pi \cdot \left(\frac{d^2}{2}\right) + \pi \cdot d \cdot w - 2 \cdot w^2\right] \cdot n_d
\]  

(1)

A SDC apparatus is operated counter-currently with liquid flowing from top to bottom and gas flowing upwards. The liquid flow rate is adjusted by a peristaltic liquid pump (EH Promass 83). The feed mixture of gases, N₂ and CO₂, was controlled by two Bronkhorst Hi-Tec mass flow controllers and the gas circulated with a Siemens Micro Master Frequency controller. The circulating gas CO₂ concentration was measured with a Fisher-Rosemount BINOS 100 NDIR CO₂ analyzer (i.e., 2 Channels: 2000 ppm and 1 vol % CO₂ for measuring the initial kinetic rate constant while 2 channels 10 vol % and 35 vol % CO₂ for mass transfer measurements). Five K-type thermocouples were used to register the 4 inlet and outlet gas/liquid temperatures and the temperature inside the chamber.
2.2. Principal Procedure of a SDC apparatus

Unloaded and loaded amine solutions were fed to the column at a flowrate which is in the range where the absorption rate is liquid flow rate independent. The experiments were run at low $P_{CO2}$ for unloaded solution but for loaded solution the $P_{CO2}$ was varied to get the desired driving force until steady state was achieved and were terminated when the temperature had reached a stable value at the desired level, and a constant concentration level of $CO_2$ was obtained from the analyzer. The flux of $CO_2$ absorbed into the liquid was calculated from a solute mass balance over the entire system:

$$r_{abs}^{CO2} (kmol \cdot s^{-1}) = Q^{in}_{CO2} - Q^{out}_{CO2}$$ (2)

The amount of $CO_2$ entering ($Q^{in}_{CO2}$) the system can be determined from the $CO_2$ mass flow controller while the amount of $CO_2$ going out ($Q^{out}_{CO2}$) from the system through the constant pressure bleed, can be calculated be calculated from

$$Q^{out}_{CO2} (kmol \cdot s^{-1}) = Q^{in}_{CO2} \frac{y^{out}_{CO2}}{1 - \left(\frac{P_{solution}}{P}\right) - y^{out}_{CO2}}$$ (3)

2.3. Characterization of the SDC apparatus

The liquid-side ($k^a$) and gas side ($k^g$) mass transfer coefficients were characterized by using two different systems, i.e. the absorption of pure $CO_2$ into water and the absorption of $SO_2$ into aqueous NaOH solution (Ma’mun, et al., 2007 and Hartono, et al., 2009). The mass transfer coefficients are expressed as:

$$(k^a \cdot D_A) = 17.92 \cdot (4\Gamma/\mu)^{1.0} \cdot (\mu/\rho D)^{0.5}$$ (4)
\[(k_g d / D) = 0.12 \cdot (\rho v d / \mu)^{0.79} \cdot (\mu / \rho D)^{0.44}\] (5)

**2.4. Determination of Kinetic/Mass transfer constant**

In chemical absorption, the rate of reaction is an important feature of the mass transfer. The absorption flux is enhanced by the chemical reaction and the flux of CO\(_2\) into or out of the solution can be characterized by the overall gas phase mass transfer coefficient as:

\[N_{CO_2} (mol \cdot m^{-2} \cdot s^{-1}) = K_G \cdot LMPD\] (6)

The driving force, (LMPD), however, is often not constant during the experiment, thus a logarithmic mean average was used as an approach to calculate the driving force as:

\[LMPD (kPa) = \frac{(P_{CO_2}^{in} - P_{CO_2}^{in}) - (P_{CO_2}^{out} - P_{CO_2}^{out})}{\log \left( \frac{P_{CO_2}^{in} - P_{CO_2}^{in}}{P_{CO_2}^{out} - P_{CO_2}^{out}} \right)}\] (7)

The \(P_{CO_2}^{*} = f(T, \alpha)\) was obtained from the VLE model, while the \(P_{CO_2}^b\) was taken from the measured pressure in a SDC after correction for the vapour pressure of solvent (amine and water). The overall gas phase mass transfer coefficient \((K_G)\) consists of two resistances, i.e. the gas and liquid resistances (in Eq. 4 and 5), as:

\[1/K_G = 1/k_g + \frac{H_{CO_2}}{E_{CO_2} \cdot k_{l}^*}\] (8)

The enhancement factor \((E_{CO_2})\) can be determined from the known \((K_G)\) (calculated with Eq. 6), the liquid mass transfer coefficient (Eq. 5), and from an experimentally determined Henry’s law constant \((H_{CO_2})\) correlation, as a function of temperature and loading.

For absorption of CO\(_2\) into amine solution (both single and mixed amine), the CO\(_2\) overall reaction can be expressed as follows:

\[r_{CO_2}^{Obs} = r_{CO_2-Am} + r_{CO_2-OH^-}\] (9)

For the fast kinetics, the term of \(r_{CO_2-OH^-}\) can be neglected without substantial loss of accuracy. This indicates that the bicarbonate reaction has no significant effect on the observed kinetic rate constant.

In this work a pseudo-single or combined amine approach was used and it was assumed that the kinetic rate of CO\(_2\) can be expressed as a second-order reaction:

\[r_{CO_2}^{Obs} = r_{CO_2-Am} = k_2 \cdot [Am] \cdot [CO_2]\] (10)

The apparent second-order rate constant \((k_2)\) can be calculated from the enhancement factor \((E_{CO_2})\) (Eq. 8) according to:

\[Ha = Ea = \frac{k_{obs} \cdot D_A}{k_l} = \frac{k_2 \cdot C_{freeAm} \cdot D_A}{k_l} \] (11)

Where the free amine is taken to be \(C_{freeAm} = C_{Am}^* \cdot (1 - \alpha)\) where the blended amine was assumed as a single amine.
3. Results and Discussion

In Fig. 2 is shown the fluxes obtained for CO₂ against LMPD from the experimental runs. The transfer flux of CO₂ increases with increased driving force, as expected. However, at higher loadings and subsequently partial pressures CO₂, the flux of CO₂ remains almost constant due the increase in loading. At constant loading, an increase in temperature leads to an increase in CO₂ flux at low loadings (0.2-0.3). At high loadings, an increase in temperature may lead to a decrease in flux because of the equilibrium effect.

![Fig. 2](image)

**Fig. 2** The fluxes of CO₂ as a function of driving force (LMPD) for different temperatures and loadings (Points are taken out from the experimental data and solid lines represent the soft model).

The overall gas phase mass transfer coefficient ($K_G$) was calculated from the slope of the transfer flux of CO₂ as a function of LMPD and can be seen in Fig. 3. It increases with increase the temperature but tends to decrease with increasing loading. However, at the highest loadings, an increase in temperature leads to a decrease in mass transfer coefficient ($K_G$).

![Fig. 3](image)

**Fig. 3** The overall gas phase mass transfer ($K_G$) as a function of driving force (LMPD) for different temperatures and loadings (Points are calculated from the experimental data and solid lines represent the soft model).
The calculated enhancement factors \( (E_{CO_2}) \) as a function of temperature and loading and were sorted for approximately constant loading and temperature as seen in Fig. 4.

**Fig. 3** The enhancement factors \( (E_{CO_2}) \) as a function of the driving force (LMPD) for different temperatures and loadings (Points are calculated from the experimental data and solid lines represent the soft model).

The enhancement factors \( (E_{CO_2}) \) are expected to increase with increase in temperature, but tend to decrease with increasing loading. The highest value of the enhancement factor \( (E_{CO_2}) \) is found for the lowest loadings due to the highest rates of absorbed CO\(_2\). The \( k_2 \) values calculated in this way are shown in Fig. 4 and are seen to increase with temperature at low loadings and decrease with temperature at high loadings. This is an artefact caused by the way the data are treated. Since the system consists of two amines, one fast and one slow, the decrease in \( k_2 \) at high loadings is a result of the slow amine, tertiary amine, starting to dominate the mass transfer.

**Fig. 4** The second-order kinetic rate constant \( (k_2) \) as a function of loading for different temperatures (Points are calculated from the experimental data and solid lines represent the soft model).
The soft model of the second-order kinetic constants \( k_2 \) as a function of loading and temperature can be expressed as:

\[
k_2(m^3 \cdot mol^{-1} \cdot s^{-1}) = k_2^0 \cdot (1/\exp((\Theta - \alpha)^{-1}))
\]

\[
k_2^0 = -2.9647 \cdot 10^4 + 2.0044 \cdot 10^3 \cdot t - 45.04 \cdot t^2 + 3.441 \cdot 10^{-1} \cdot t^3
\]

\[
\Theta = 0.6523 + 4.675 \cdot 10^{-3} \cdot t - 8.75 \cdot 10^{-5} \cdot t^2
\]

The second-order kinetic rate constant \( k_2 \) of the soft model can be used together with the diffusivity \( D_{CO_2} \) and the Henry’s law constant \( H_{CO_2} \) model to calculate back the fluxes and compared with the experimental data as seen in Fig. 5.

![Parity plot of the fluxes \( N_{CO_2} \) from the experimental data and the model](image)

**Fig. 5** Parity plot of the fluxes \( N_{CO_2} \) from the experimental data and the model

### 4. Conclusion

The string of disc contactor was used for measuring the kinetics CO\(_2\) absorption in mixed amine solvents for different loadings and temperatures. The simplified method to calculate the second order rate constant \( k_2 \) was developed and gave a reasonable good to calculate back the CO\(_2\) fluxes, however artefacts occurred when treating the mixed amine solvents as a pseudo-single component.

### 5. Acknowledgements

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### 6. References

Journals:

Books: