

REACTIVE ABSORPTION OF CO₂ INTO AQUEOUS SOLUTIONS OF N,N-DIETHYLETHANOLAMINE (DEEA)

Monteiro, J.G.M.-S.¹, Pinto D.D.D.¹, Hartono A.¹, Svendsen H.F.¹

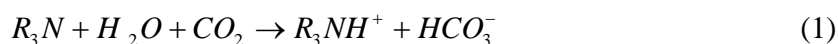
¹The Norwegian University of Science and Technology (NTNU)

julianag@chemeng.ntnu.no

Keywords Post-combustion capture, N,N-diethylethanolamine, kinetics, absorption

Introduction

The research on amines used for CO₂ absorption has recently focused on proposing novel solvents or solvents blends that can lead to lower energy requirements in the regeneration process. In this context, the reactive absorption of CO₂ by tertiary amines solutions has been investigated. As first proposed by Donaldson and Nguyen (1980), tertiary amines promote the reaction of hydration of CO₂, leading to bicarbonates formation (reaction 1):



The reaction heat of formation of bicarbonates is lower than that of carbamates (formed when using primary and secondary amines). Hence, tertiary amines lead to lower energy demand for the amine regeneration (Vaidya and Kenig, 2009). Part of the steam required for amine regeneration stems from the heat of absorption of CO₂ into the desired amine solution, and Kim and Svendsen (2010) have shown, in a study involving primary, secondary and tertiary amines, diamines, triamines and cyclic amines, that the tertiary amines gives the lowest heats of absorption. If this can be combined with high equilibrium sensitivity and thereby low requirement for stripping steam, this could be a major improvement to the absorption process.

Studies on the kinetics of the reactions between CO₂ and various tertiary amines, such as triethanolamine (TEA), methyldiethanolamine (MDEA), triethylamine (TREA), dimethylaminoethanol (DMMEA) and N,N-diethylethanolamine (DEEA) can be found in literature. Versteeg *et al.* (1996) compiled literature information on the kinetics of the reaction between an aqueous solution of DEEA and CO₂ and showed that the values presented for the second order reaction constant, k_2 , were in very poor agreement. By the time the work was published, only four studies were available. Now, the results from the studies of Li *et al.* (2007) and Vaidya and Kenig (2009) can also be compared with those older ones but there is still little agreement between the available data.

Experimental

In this work, the reactive absorption of CO₂ into aqueous solutions of DEEA was studied. The study was conducted in a string of discs contactor, in which a mixture of N₂ and CO₂ and the aqueous DEEA solution flow in countercurrent mode. The equipment was previously described by Ma'mun *et al.* (2007), Knuutila *et al.* (2009) and Hartono and Svendsen (2009). In those works, it was used for measuring the kinetics of reactive CO₂ absorption by different amines and carbamates solutions.

The inlet flow rates of N₂ and CO₂ were set using mass flow controllers, while the CO₂ composition on the outlet gas was determined by a CO₂ analyzer. There are indicators for the inlet and outlet temperatures of liquid and gas streams, and the inlet liquid flow rate is set by a mass flow controller. The equipment comprises also pressure and pressure drop indicators, so all information needed for establishing the kinetics are readily available. The densities, viscosities and vapor pressures of DEEA solutions were measured to enable calculations of Henry's law constant, diffusivity, liquid and gas-film mass transfer coefficients (k_L and k_G), k_2 (considering both pure CO₂ flow and a mixture of CO₂ and N₂) and the kinetic rate of the reaction.

The reaction was performed within the temperature range of 25°C to 60°C. The tested values for DEEA concentration were: 1M, 3M and 5M.

Acknowledgements

Financial support from the EC 7th Framework Programme through Grant Agreement No : iCap-241391, is gratefully acknowledged.

References

- Donaldson, T.; Nguyen, Y. N. *Carbon Dioxide Reaction Kinetics and Transport in Aqueous Amine Membranes*. Ind. Eng. Chem. Fundam. 1980, 19, 260-266.
- Hartono, A.; Svendsen, H. F. *Kinetics reaction of Primary and Secondary Amine Group in Aqueous Solution of Diethylenetriamine (DETA) with Carbon Dioxide*. Energy Procedia. 2009, 1, 853-859.
- Kim, I.; Svendsen, H. F. *Comparative study of the heats of absorption of post-combustion CO₂ absorbents*. International Journal of Greenhouse Gas Control. 2010. Article in Press
- Knuutila, H.; Svendsen, H. F.; Juliussen, O. *Kinetics of carbonate based CO₂ capture systems*. Energy Procedia. 2009, 1, 1011-1018.
- Li, J.; Henni, A.; Tontiwachwuthikul, P. *Reaction Kinetics of CO₂ in Aqueous Ethylenediamine, Ethyl Ethanolamine, and Diethyl Monoethanolamine Solutions in the Temperature Range of 298-313 K, Using the Stopped-Flow Technique*. Ind. Eng. Chem. Res. 2007, 46, 4426-4434.
- Ma'mun, S., Dindore, V. Y., Svendsen, H. F. *Kinetics of the Reaction of Carbon Dioxide with Aqueous Solutions of 2-((2-Aminoethyl)amino)ethanol*. Ind. Eng. Chem. Res. 2007, 46, 385-394.
- Vaidya, P. D.; Kenig, E. Y. *CO₂ capture by Novel Amine Blends*. Proceedings of the 1st Annual Gas Processing Symposium 2009, 239-246.
- Versteeg, G. F.; van Dijck, L. A. J.; van Swaaij, W. P. M. *On the kinetics between CO₂ and Alkanolamines both in Aqueous and Nonaqueous Solutions. An Overview*. Chem. Eng. Commun. 1996, 144, 113-158.