

Comparison of Ammonia, MonoEthanolAmine, DiEthanolAmine and MethylDiEthanolAmine Solvents to Reduce CO₂ Greenhouse Gas Emissions

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This paper presents experimental results on the evaluation of ammonia NH₃ solvent for CO₂ absorption. In this novel study, the kinetic and absorption capacity of this solvent is compared with traditional alkanolamine solvents. Experiments have been achieved in range of temperatures 278-303 K and with 2 wt% - 5 wt% for NH₃ and in range of temperatures 303-333 K with 5 wt % - 50 wt % for amines aqueous solutions (MEA, DEA, MDEA). Our results show that carbon dioxide absorption by ammonia is faster than that carried out by MDEA, except for 2% NH₃ at 288K. For 3% NH₃ and 278K, the kinetics of absorption is almost identical compared to the MDEA. The most efficient solvents (absorption capacity) are 5% NH₃ at 278K and 303K. NH₃ (3%, 278K) is three times more reactive than MEA.

1. Introduction

Several techniques have been proposed to reduce the emission of CO₂ into the atmosphere. Among these techniques, chemical solvent absorption methods have been extensively studied and are considered as a reliable and relatively competitive method for reducing carbon dioxide emissions from fossil fuel power plants. Aqueous solutions of alkanolamines are widely used in absorption/desorption processes to separate CO₂ from gas streams. Aqueous blends of a primary or a secondary amine with a tertiary amine or carbonate have received much attention (Bosch et al., 1989; Versteeg et al., 1990; Glasscock et al., 1991; Little et al., 1992). Recent works suggest that a small amount of a primary or secondary amine, such as MEA or DEA, can be added to an aqueous MDEA solution to promote or enhance the absorption rate of CO₂ without significantly affecting the steam stripping equipment. Other work focused on the development of a new solvent based on a blend of N-methyldiethanolamine (MDEA) and triethylene tetramine (TETA). The addition of small amounts of TETA leads to a high increase in the CO₂ absorption rates (Amann and Bouallou, 2008). The MEA scrubbing is so far the most acceptable chemical solvent method to react with CO₂. However, its low absorption capacity, easy degradation and higher energy requirement suggest that future research efforts should be directed toward developing better solvents for removal of CO₂. Ammonia seems to be an alternative solvent for removing CO₂ from flue gases; it has already been used in the DeNO_x process such as selective catalytic reduction and selective non-catalytic reduction in the flue gas systems. The scrub of all acid pollutants in flue gases, including the CO₂, may be possible using the

ammonia. However, limited information on its technical and economical effectiveness is available.

2. Experimental section

A thermostated glass reactor of the Lewis type with a constant gas-liquid interface area was used (figure 1). The reactor is provided with a Rushton turbine in its lower part. The temperature in the reactor is controlled by circulating a thermostatic fluid through the glass double jacket and measured through a 100Ω platinum probe. A tube allows either to evacuate or to introduce CO_2 into the cell.

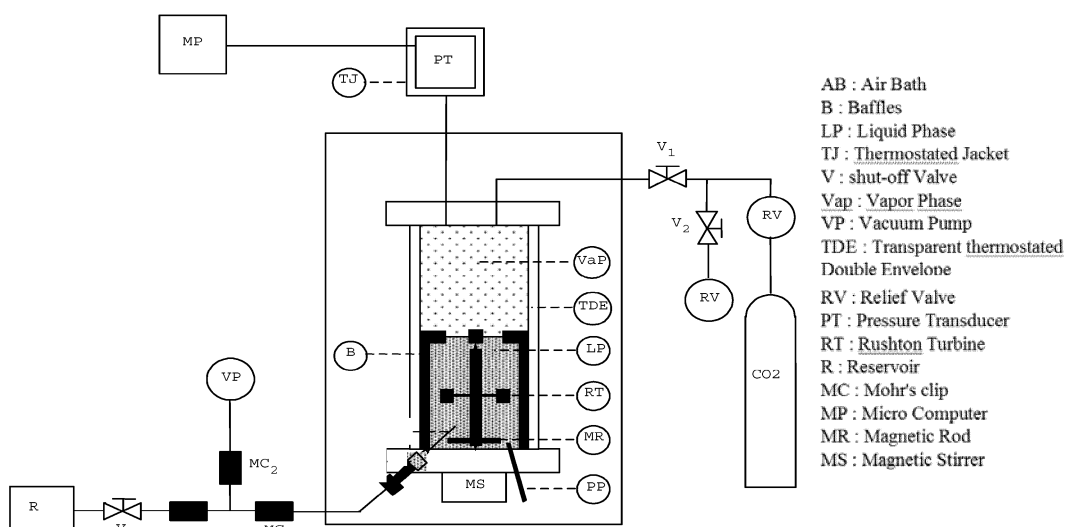


Fig. 1. Flow diagram of the Lewis type apparatus

The kinetics of gas absorption are measured by recording the absolute pressure provided by a pressure transducer, working in the range $(0 \text{ to } 200) \cdot 10^3 \text{ Pa}$. For each temperature investigated T , the transducer is calibrated within 200 Pa against a mercury manometer. A microcomputer equipped with a data acquisition card is used to record the pressure signal as a function of time t .

Water and ammonia or amine are degassed independently and aqueous solutions are prepared under a vacuum. Accurate weightings of the flask before and after the transfer yield the mass of solution present in the cell. The liquid phase volume was calculated using the density correlation. At given temperature and under solution vapor pressure P_1 , pure CO_2 is introduced during a very short time, about 2 s , in the upper part of the cell. Then stirring is started and kept at constant speed.

This procedure corresponds to an initial absorption kinetic study. At the end of this step the solution is loaded by bubbling fresh CO_2 inside the liquid phase, while the Rushton turbine is rotated at full speed to improve the gas dispersion and consequently the solubilization rate. The CO_2 loading circuit is evacuated before the transfer through a vacuum pump. The transferred mass is obtained by weightings the fresh CO_2 reservoir before and after loading.

This equipment where total pressure P_T is recorded as a function of time has been used to determine CO_2 absorption kinetics into loaded and unloaded aqueous solutions of NH_3 at 278 K, 288 K and 303 K and in range of temperatures 303-333 K with 5 wt % - 50 wt % for amines aqueous solutions (MEA, DEA, MDEA) The CO_2 absorption rate φ_{CO_2} is determined from the pressure-time data (dP_T/dt) using the mass balance:

$$\frac{\varphi_{\text{CO}_2} R T A}{V_{\text{CO}_2}} = \frac{dP_T}{dt} \quad (1)$$

where A = interfacial area; T = temperature ; R= gas constant, V_{CO_2} = volume

3. Results and discussion

According to figure 2, we see that for the most of the experiments, 800 to 1000 minutes on average are necessary to reach a maximum loading. Moreover, it is seen that for the 2%wt. NH_3 solutions, this time hardly changes whatever the temperature considered. The 3%wt. NH_3 solutions have a loading much more important than for 2%wt. NH_3 solutions. On the other hand, for 5%wt. NH_3 solutions, the results obtained at 288K does not follow the same tendency as at 278 and at 303K but rather that of the 3%wt. NH_3 solutions. Compared to MEA, NH_3 solvent is superior in its capacity to absorb CO_2 .

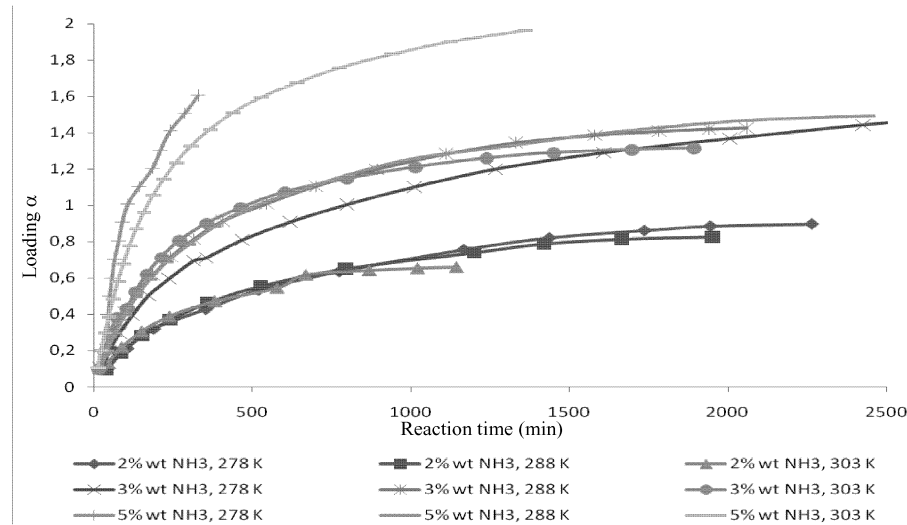


Fig. 2. Maximum CO_2 absorption capacity vs reaction time

In order to represent the absorption of CO_2 into aqueous NH_3 , the gas-liquid chemical reactions can be expressed by the following reaction equation (Bai and Yeh, 1997; Brooks, 1953):



Density and the viscosities of water and ammonia solutions are determined experimentally in our laboratory. We also determined a correlation giving the CO_2 Henry's law constant H_{CO_2} from our experimental measurements with an accuracy of 7% based on the correlation proposed by Zhenhao (2003):

$$\ln(H_{CO_2}) = c_1 + c_2 T + \frac{c_3}{T} + c_4 T^2 + \frac{c_5}{630 - T} + c_6 P + c_7 P \ln(T) + c_8 \frac{P}{T} + c_9 \frac{P}{630 - T} + c_{10} \frac{P^2}{(630 - T)^2} \quad (3)$$

with $c_1 = 2.8945 \cdot 10^{+01}$; $c_2 = -3.545810^{-02}$; $c_3 = -4.770710^{+03}$; $c_4 = 1.027810^{-05}$; $c_5 = 3.3813 \cdot 10^{+01}$
 $c_6 = 9.0404 \cdot 10^{-03}$; $c_7 = -1.1493 \cdot 10^{-03}$; $c_8 = -3.0741 \cdot 10^{-01}$; $c_9 = -9.0730 \cdot 10^{-02}$; $c_{10} = 9.3271 \cdot 10^{-04}$

Diffusivity data for CO₂ in NH₃ aqueous solutions is not available, therefore and since the maximum NH₃ mass concentration is lower than 5%, we supposed that the CO₂ diffusion coefficient in the aqueous ammonia solution is that of CO₂ in water.

The mass transfer correlation between dimensionless quantities (Reynolds, Schmidt and Sherwood numbers) used in this work has been established by Amararene and Bouallou (2004) for the apparatus from N₂O absorption experiments by the MDEA-water solutions to determine the physical mass transfer coefficient k_L of the CO₂.

The experiments of CO₂ absorption by ammonia were performed at the reaction temperatures of 278, 288 and 303 K. The plot of $\ln(k)$ as a function of $1/T$ and the slope coefficient of the regression line is equal to the rate (k) of the chemical reaction. CO₂ absorption by ammonia conforms to Arrhenius law in the range of experimental temperature as follows:

$$k_{NH_3} = 292.2 \times e^{-\frac{3379}{T}} \quad (4)$$

The activation energy of the chemical reaction is 28.1 kJ/mol, and the exponential factor A is 292.2 m³/(mol.s). Our results are to be compared with the single work that we found in the open literature: 26.73 kJ/mol and 240 m³/(mol.s) but these values depend certainly and significantly on the vapor-liquid equilibrium data used.

For the absorption of CO₂ into unloaded mixtures of amines, MDEA - MEA or MDEA - DEA, it is found that the pressure of CO₂ follows an exponential decay, which means that the rate of absorption is first order with respect to the pressure of CO₂. Initial kinetics in blend of amines at 296 K are compared to those achieved with MDEA aqueous solutions. The respective time-pressure acquisition data show that the addition of a small amount of MEA or DEA to a MDEA aqueous solution increases the CO₂ absorption rate (figure 5).

The zwitterion mechanism, originally proposed by (Caplow, 1968), is the most widely accepted mechanism for primary and secondary amine reaction with CO₂. This mechanism comprises two steps: formation of the CO₂-amine zwitterion, followed by a base-catalysed deprotonation of the zwitterion. (Rinker et al., 1996) have considered the overall reaction as a first order in both the amine and the CO₂ concentrations.

For the representation of the absorption of CO₂ into blends of amines, we have considered the case of absorption into unloaded aqueous solutions. The water dissociation is neglected, as the concentration of hydronium ion is very low at the conditions of the simulation and not needed in the reaction rate expressions. The

carbamate to bicarbonate reversion is neglected because the rates of this reaction is very low and would not have a significant effect (Hagewiesche et al. 1995). Density, viscosities, solubilities, diffusion coefficients and equilibrium constants for reactions are obtained by the same correlations previously used by Cadours, 1998. From our absorption experiments (Cadours, 1998), our model (Cadours and Bouallou, 1998) was used to estimate the kinetic parameter of the reaction between CO_2 and MEA by interpreting CO_2 absorption rate data into unloaded MDEA-MEA aqueous blends.



The kinetic law is determined by:

$$k_{\text{MEA}} = 6.138 \times 10^{-6} \times e^{-\frac{4187}{T}} \quad (6)$$

The values of the reaction rate constants of ammonia are higher than those of the MEA, which indicates a reaction rate more important up to nearly 308 K. The reaction temperature plays a key role in the CO_2 absorption. NH_3 (3%, 278K) is three times more reactive than MEA (figure 4).

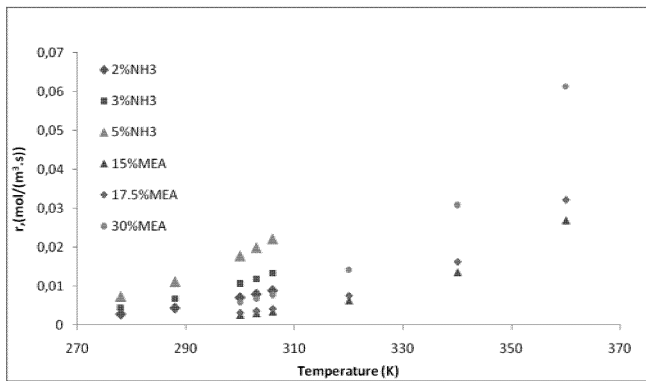


Fig.4 Comparison of MEA and NH_3 reaction rates for CO_2 absorption

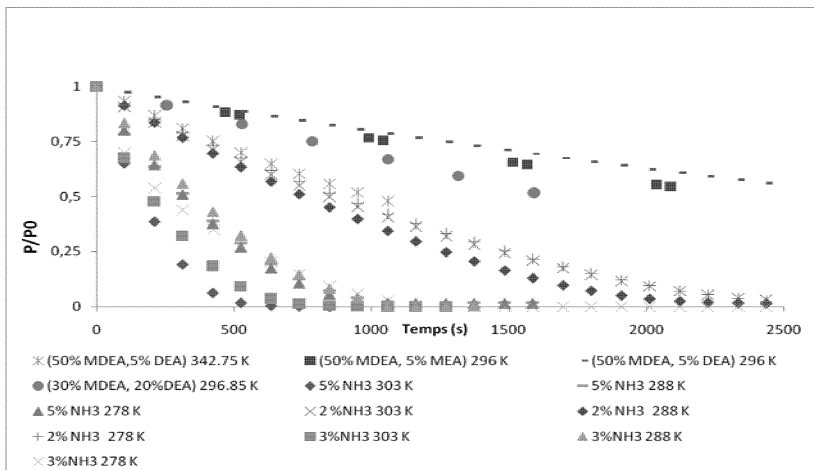


Fig. 5 comparative study on NH_3 and unloaded amines aqueous solutions

Figure 5 shows that carbon dioxide absorption by ammonia is faster than that carried out by MDEA, except for 2% NH₃ at 288K. For 3% NH₃ and 278K, the kinetics of absorption is almost identical compared to the MDEA.

4. Conclusion

CO₂ absorption rates into NH₃ aqueous solutions were measured into a thermoregulated constant interfacial area Lewis-type cell. The experimental temperature ranged from 278 - 303 K and NH₃ concentration ranging from 2 - 5 wt %. The kinetic parameters from experimental data were determined. No significant difference could be found between reaction constants estimated in this work and those from literature. However, these values depend certainly and significantly on the vapor-liquid equilibrium data used. The comparative study on NH₃ and amines aqueous solutions (MEA, DEA, MDEA) is also performed. Our results show that carbon dioxide absorption by ammonia is faster than that carried out by MDEA, except for 2% NH₃ at 288K. For 3% NH₃ and 278K, the kinetics of absorption is almost identical compared to the MDEA. The most efficient solvents (absorption capacity) are 5% NH₃ at 278K and 303K. NH₃ (3%, 278K) is three times more reactive than MEA.

Acknowledgements

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