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Studies of N,N-Dibutyltrimethylenediamine and N, N, N'Triethylenediamine for CO_2 Absorption and Desorption

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ABSTRACT

CO_2 gas emissions and their increasing role in global warming have become an issue of much concern. Chemical absorption is preferred for lowering the partial pressure of CO_2. The potential of completely new amines N,N-Dibutyltrimethylenediamine and N,N,N'-Triethylenediamine which are both categorized and widely known as diamine (amine that may contains two active nitrogen atoms without going through any conventional mixing process) were investigated for CO_2 absorption and desorption processes. In order to investigate the potential of these diamines for CO_2 absorption and desorption, experiments and analysis were conducted to determine the absorption rate, absorption capacity, desorption rate and desorption effectivity of CO_2.

Keywords: CO_2, absorption, desorption, diamine, N,N Dibutyltrimethylenediamine, N,N,N'-Triethylenediamine

INTRODUCTION

In recent times, the emission of greenhouse gases and their increasing role in global warming has become a big concern. Amongst the known greenhouse gases, carbon dioxide (CO_2) resulting from combustion of fossil fuels activities such as electricity generation and fuel usage in the transportation sector accounts for around 46% of total CO_2 emissions in Europe alone. CO_2 emissions in European Union (EU) countries are projected to reach 3.8 $GtCO_2$ in 2010 and 4.1 $GtCO_2$ in 2020. These projected growth shows an increment of 1.07% per year between 1995 and 2010 and 0.64% per year between 2010 and 2020 (Viguier, n.d.).

Consequently, this on-going issue with CO_2 emissions has spurred researchers around the world to develop new and effective CO_2 capture technologies that can be implemented strategically in sectors which contribute greatly towards CO_2 emissions.

Removal of CO_2 from fuel gas and hydrogen (H_2) stream has been practiced in many industrial processes such as ammonia manufacture, H_2 production, coal gasification and in oil and gas purification. Aqueous amine solutions are the usual solvents for CO_2 removal. One of the most popular types of aqueous amine solutions is mixed amines systems or 'activated amine solution' which contains small amounts of a primary or secondary amine that acts as an activator (high absorption rate) and a tertiary amine (high absorption capacity). Typical mixed amines systems that are investigated include among others MEA-MDEA, DEA-MDEA and MEA-Piperazine.

MATERIALS AND METHODS

Diamine is an amine which already contains a primary or secondary amine and a tertiary amine in one solution and the supplied diamine solution can be used directly without undergoing conventional or the usual mixing process such as in MEA-MDEA or DEA-MDEA systems. Details about diamines used in this study are shown in Table 1.

TABLE 1
Diamines used

Diamine	Description
1) N,N-Dibutyltrimethylenediamine (Diamine 1) • CAS No.: 102-83-0 • Supplier: Merck, Hohenbrunn, Germany • Purity: ≥ 99%	Possess primary and a tertiary amine properties
2) N,N,N'-Triethylenediamine (Diamine 2) • CAS No.: 105-04-4 • Supplier: Sigma-Aldrich, Steinheim, Germany • Purity: 98%	Possess secondary and a tertiary amine properties

These diamines were selected with due consideration of economic feasibility (price), location of nitrogen atoms in the molecule (primary-secondary-tertiary combination) and the structure of the hydrocarbon group linked to them.

The method for CO_2 absorption and desorption was adapted from Tan (2005) and Zhu (2006). The absorption and desorption experiments were carried out with 1 to 4 M of both N,N-Dibutyltrimethylenediamine and N,N,N'-Triethylenediamine solutions. The volume of all the solutions was 5 ml.

Absorption Experiment

The absorption was carried out in rubber sealed Schott GL 18 test tubes. The required amine solutions were prepared directly inside the test tubes and weighed using a Mettler PT 1200. Reaction gas, CO_2 was supplied to the amine solutions in the test tube by using a PTFE tube (inner diameter = 1/16 inch, outer diameter = 0.04 inch) that penetrates through the test tube cap and rubber seal.

The flow of CO_2 from the gas tank was regulated using a pressure gauge which maintains the CO_2 flow at 1 bar and then by magnetic valve connected to a Bronckhorst flow controller box. This flow controller box can regulate gas flowrate. For absorption experiments, 20 mlN/min of CO_2 flowrate was used. The water bath temperature for absorption was maintained at 25°C.

Each test tube containing amine solution was weighed every 5 minutes. The absorption was considered to be in complete equilibrium after three consecutive constant weights of the test tubes. The whole process of absorption was about 1 hour to 2 hours at the most. The process flow diagram of absorption experiment is shown in *Fig. 1.*

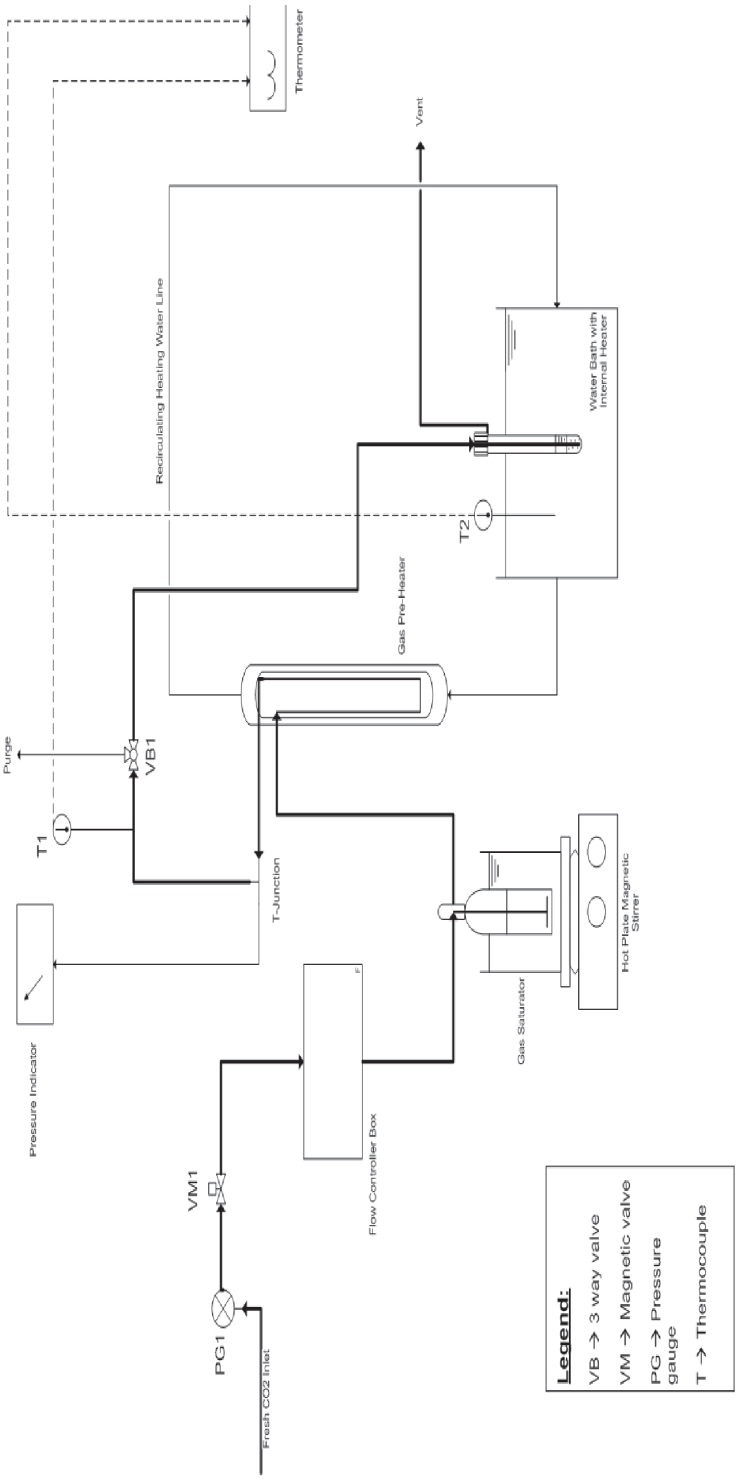

Fig. 1: Process flow diagram of absorption experimental set-up

The operating parameters for absorption experiment were:

- Volume of amine solution = 5 ml
- Concentration of amine solution = 1 M, 2 M, 3 M and 4 M
- Flowrate of CO_2 = 20 mlN/min
- Pressure = 1.05 bar
- Temperature = 40°C
- Sampling time interval for gravimetric analysis = 5 minutes

Desorption Experiment

The desorption process was carried out subsequently after the absorption process. The desorption process also lasted for about 1 to 2 hours by heating the CO_2 loaded amine solution stepwise from 40°C up to 80°C at 10°C intervals.

The PTFE tube was closed at the tip by using a rubber loop. The test tubes containing CO_2 loaded amine solution were hung by a support up to a depth whereby the amine solution inside the test tube was fully immersed in the heating oil. Additionally, a magnetic stirrer was inserted into each test tube.

As desorption by heating is a non-steady state process and can not reach steady condition, a strictly fixed condition was chosen. First, the temperature of the heating oil was brought to the desired temperatures (40°C to 80°C). Then the test tubes containing CO_2 loaded amine solution were immersed into the heating oil. Every 5 minutes, gas was released from the test tube by detaching the rubber loop at the tip of the PTFE tube and then the rubber loop was attached back to the tip of the PTFE tube. These steps were done for 15 minutes (3 times detaching and attaching the rubber loop). After that, the weight of each tube was recorded. The sketch of desorption experimental set-up is shown in *Fig. 2*.

To achieve the study objectives, the results of the absorption and desorption characteristics of optimized N,N-Dibutyltrimethylenediamine-H_2O system and N,N,N'-Triethylenediamine-H_2O system were analyzed.

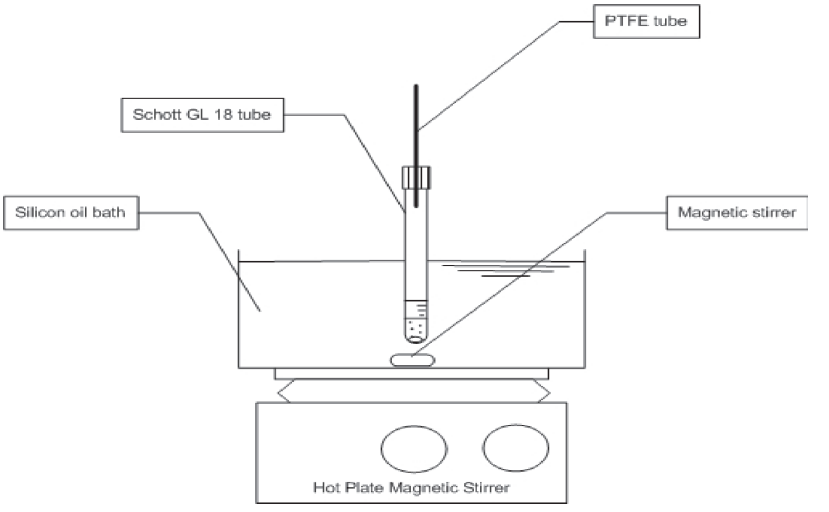

Fig. 2: Desorption experimental set-up

Furthermore, since it was assumed that diamines might have 2 active nitrogen atoms that can react with CO_2 (as this is the main reason why the potential of diamines for CO_2 absorption and desorption was investigated), the results of CO_2 absorption and desorption characteristics were compared between 2 active nitrogen atoms and 1 active nitrogen atom diamine systems.

Optimization of N,N-Dibutyltrimethylenediamine-H_2O System

TABLE 2
Selected results for N,N-Dibutyltrimethylenediamine-H_2O system

Molarity	Max. CO_2 Absorbed (g)	Max. CO_2 Desorbed (g)	n CO_2 Absorbed*n Amine^{-1}	% CO_2 Desorbed	Solid Formation
1	0.32	0.1	1.4545	0.3125	No
2	0.57	0.28	1.2955	0.4912	No
3	0.72	0.35	1.0909	0.4861	No
4	0.69	0.26	0.7841	0.3768	No

Fig. 3 shows the absorption curves of the experiments for different concentrations of the N,N-Dibutyltrimethylenediamine-H_2O system. The results show that the rate of CO_2 absorption is of the order 1 M > 2 M > 3 M > 4 M solution. It is also clear that solutions of lower concentration absorbed more CO_2 per mol of amine.

Fig. 4 shows the desorption curves of the experiments for different concentrations of the N,N-Dibutyltrimethylenediamine-H_2O system. The highest CO_2 desorption occurs at 80°C for all concentrations. The desorption efficiency was as follows; 1 M < 3 M < 4 M

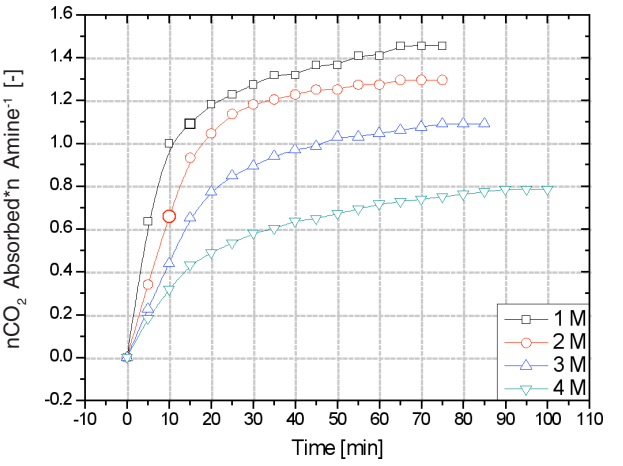

Fig. 3: Mol CO_2 absorbed / mol amine [-] vs. time [min] for N,N-Dibutyltrimethylenediamine-H_2O system

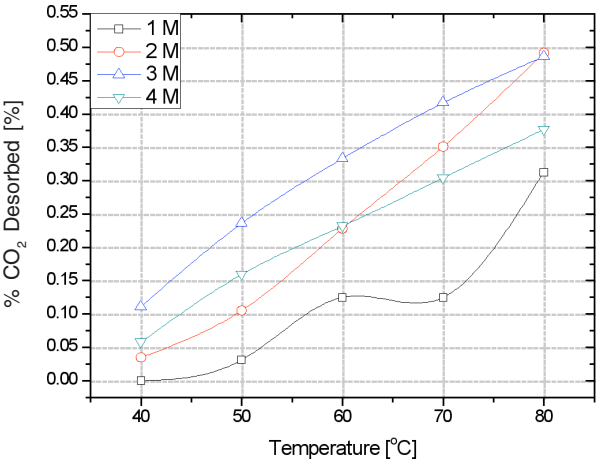

Fig. 4: % CO_2 desorbed [%] vs. temperature [°C] for N,N-Dibutyltrimethylenediamine-H_2O system

< 2 M. The 2 M solution desorbed CO_2 better than 3 M and 4 M solutions because increase in viscosity was not significant in the 2 M solution as compared to 3 M and 4 M solutions.

The optimum concentration for N,N-Dibutyltrimethylenediamine-H_2O system was 2 M. The 1 M solution was ruled out due to low CO_2 desorption capability. The 3 M and 4 M solutions were ruled out because the significant increase in viscosity had an effect on CO_2 absorption and desorption capabilities.

Optimization of N,N,N'-Triethylenediamine-H_2O System

TABLE 5
Selected results for N,N,N'-Triethylenediamine-H_2O system

Molarity	Max. CO_2 Absorbed (g)	Max. CO_2 Desorbed (g)	n CO_2 Absorbed*n Amine^{-1}	% CO_2 Desorbed	Solid Formation
1	0.28	0.07	1.2727	0.25	No
2	0.51	0.09	1.1591	0.1765	No
3	0.74	0.2	1.1212	0.2703	No
4	0.93	0.45	1.0568	0.4839	No

Fig. 5 shows the absorption curves of the experiments for different concentrations of the N,N,N'-Triethylenediamine-H_2O system. The rate of CO_2 absorption was 1 M > 2 M > 3 M > 4 M solutions. The results showed that solutions with lower concentration absorbed more CO_2 per mol of amine.

Fig. 6 shows the desorption curves of the experiments for different concentration of the N,N,N'-Triethylenediamine-H_2O system. The highest CO_2 desorption occurred at

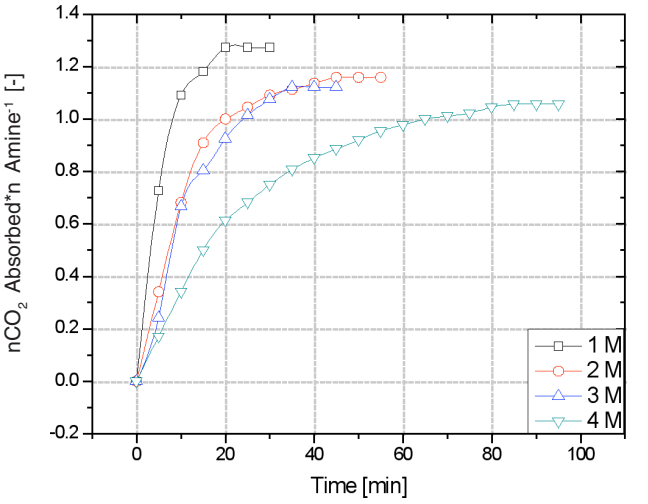

Fig. 5: Mol CO_2 absorbed / mol amine [-] vs. time [min] for N,N,N'-Triethylenediamine-H_2O system

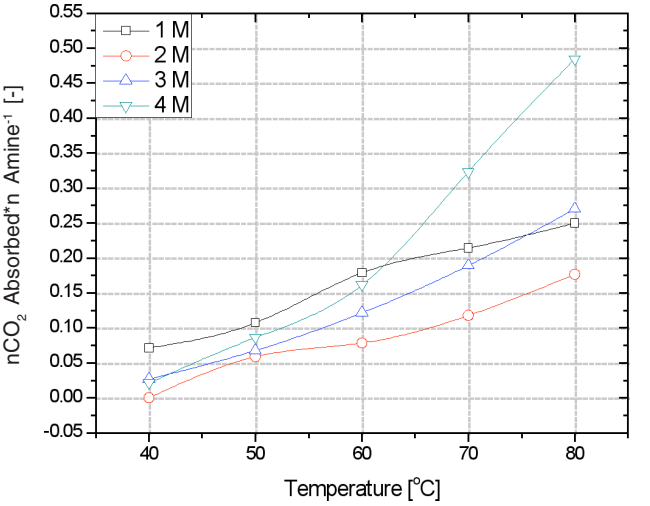

Fig. 6: % CO_2 desorbed [%] vs. temperature [°C] for N,N,N'-Triethylenediamine-H_2O system

80°C for all concentrations. The desorption efficiency was 2 M < 1 M < 3 M < 4 M. The 4 M solution desorbed CO_2 better than 1 M, 2 M and 3 M solutions because of higher amine content available in the 4 M solution in comparison to the other solutions.

The optimum concentration for N,N-Dibutyltrimethylenediamine-H_2O system was 4 M solution. The 1 M, 2 M and 3 M solutions were ruled out due to low CO_2 desorption capabilities.

Comparison of Both Optimized Systems (Two Active Nitrogen Atoms in Diamines)

TABLE 6
Selected results for two active nitrogen atoms in diamines comparison

Amine Solutions	Max. CO_2 Absorbed (g)	Max. CO_2 Desorbed (g)	n CO_2 Absorbed*n $Amine^{-1}$	% CO_2 Desorbed
2 M N,N-Dibutyltrimethylenediamine-H_2O system	0.57	0.28	1.2955	0.4912
4 M N,N,N'-Triethylenediamine-H_2O system	0.93	0.45	1.0568	0.4839

Fig. 7 shows the comparison of absorption curves for the different optimized systems involved. The rate of CO_2 absorption for all optimized systems is as follows; 2 M N,N-Dibutyltrimethylenediamine-H_2O>4 M N,N,N'-Triethylenediamine-H_2O. The CO_2 absorption capacity per mole of amine for 2 M N,N-Dibutyltrimethylenediamine-H_2O was greater than 4 M N,N,N'-Triethylenediamine-H_2O.

Fig. 8 shows the comparison of desorption curves for the different optimized systems involved. The highest CO_2 desorption occurred at 80°C for all the systems involved. The desorption efficiency of 4 M N,N,N'-Triethylenediamine-H_2O was smaller than that for 2 M N,N-Dibutyltrimethylenediamine-H_2O. Both diamines systems desorbed almost 50% CO_2 due to the presence of the two active nitrogen atoms.

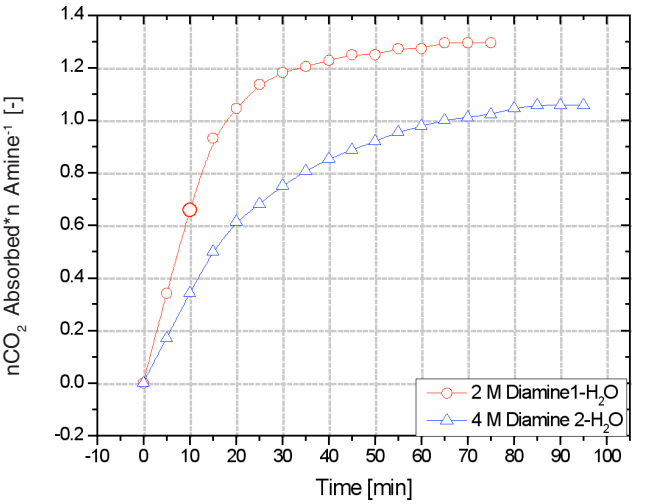

Fig. 7: Mol CO_2 absorbed / mol amine [-] vs. Time [min] for two active nitrogen atoms comparison

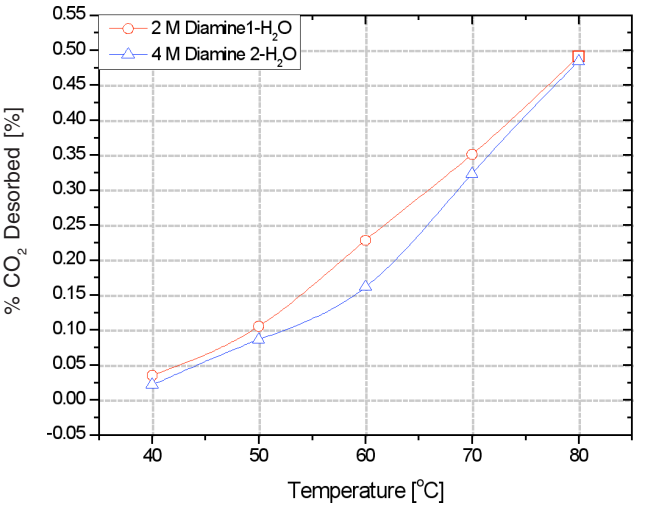

Fig. 8: % CO_2 desorbed [%] vs. temperature [°C] for two active nitrogen atoms comparison

Comparison of All Optimized Systems (One Active Nitrogen Atom in Diamines)

TABLE 7
Selected results for one active nitrogen atom in diamines comparison

Max. CO_2 Amine Solutions	Max. CO_2 Absorbed (g)	Max. CO_2 Desorbed (g)	n CO_2 Absorbed*n Amine^{-1}	% CO_2 Desorbed
2 M N,N-Dibutyltrimethylenediamine-H_2O system	0.1425	0.07	0.6478	0.1228
4 M N,N,N'-Triethylenediamine-H_2O system	0.2325	0.1125	0.5284	0.121

Results from the screening of N,N-Dibutyltrimethylenediamine-H_2O and N,N,N'-Triethylenediamine-H_2O systems presented earlier reveal the optimum concentration of each system. Here, the results for N,N-Dibutyltrimethylenediamine-H_2O and N,N,N'-Triethylenediamine-H_2O systems are assumed to have only one active nitrogen atom that can react with CO_2. These results are shown in Table 7.

Fig. 9 shows the comparison of absorption curves for the optimized systems involved. The rate of CO_2 absorption for 2 M N,N-Dibutyltrimethylenediamine-H_2O was greater than that for 4 M N,N,N'-Triethylenediamine-H_2O. The CO_2 absorption capacity per mole of amine for 2 M N,N-Dibutyltrimethylenediamine-H_2O was greater than for 4 M N,N,N'-Triethylenediamine-H_2O.

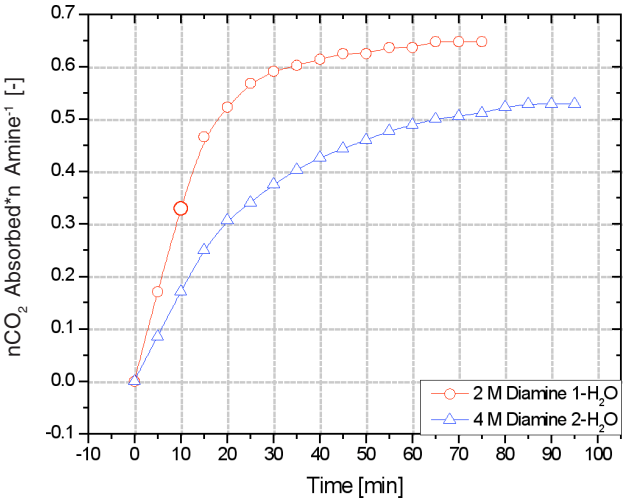

Fig. 9: Mol CO_2 absorbed / mol amine [-] vs. temperature [°C] for one active nitrogen atom comparison

Fig. 10 shows the comparison of desorption curves for the optimized systems involved. The highest CO_2 desorption occurs at 80°C for all the systems involved. The desorption efficiency for 2 M N,N-Dibutyltrimethylenediamine-H_2O was less than that for 4 M N,N,N'-Triethylenediamine-H_2O. Both diamine systems desorbed less CO_2 than systems with 2 active nitrogen atoms due to the lack of 1 active nitrogen atom.

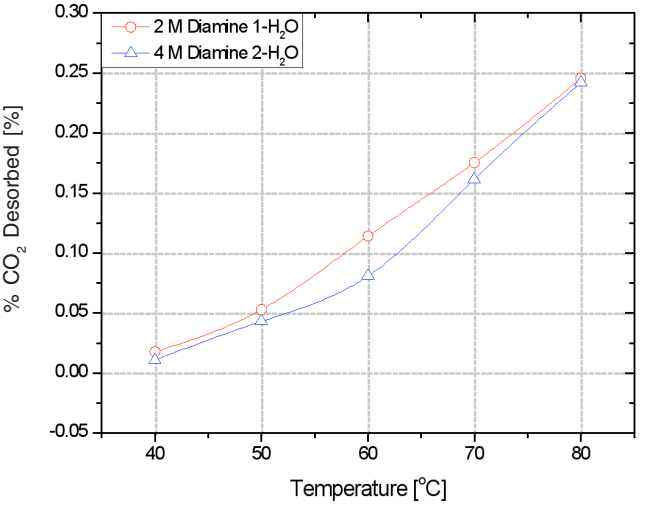

Fig. 10: % CO_2 Desorbed [%] vs. temperature [°C] for one active nitrogen atom comparison

CONCLUSIONS

After thorough investigation and analysis, it was found that both aqueous diamines (N,N-Dibutyltrimethylenediamine-H_2O and N,N,N'-Triethylenediamine-H_2O) systems have the potential to be used as a chemical solvent for CO_2 absorption and desorption. This statement is valid provided that there are 2 active nitrogen atoms within the diamines molecules that can react with CO_2.

Other conclusions that can be drawn are as follows:

1. The optimized concentration for N,N-Dibutyltrimethylenediamine-H_2O system at 40°C and 80°C CO_2 absorption and desorption temperatures respectively is 2 M.
2. The optimized concentration for N,N,N'-Triethylenediamine-H_2O system at 40°C and 80°C CO_2 absorption and desorption temperatures respectively is 4 M.

The assumption regarding 2 active nitrogen atoms reacting with CO_2 needs validation with further investigations.

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