Calorimetric analysis of CO_2 absorption in an aqueous N-methyldiethanolamine solution using H.E.L.'s Simular

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Abstract

The study of the CO_2 absorption process in alkanolamines is crucial for enhancing gas sweetening and carbon capture technologies, which are essential in reducing greenhouse emissions. Alkanolamines, such as N-methyl diethanolamine (MDEA), are favored because of their thermodynamic and kinetic properties that improve CO_2 capture efficiency. Understanding the calorimetry of these processes aids in optimizing absorption capacity and energy efficiency. Here, we show the thermodynamic behavior of CO_2 absorption in a 30% MDEA solution using H.E.L's Simular isothermal reaction calorimeter operated in power compensation mode. The heat liberated during CO_2 absorption in a 30% MDEA solution was determined to be 77.07 kJ/mol on CO_2 basis. This result demonstrates the capability of Simular to generate calorimetric data for the gas adsorption process. This finding highlights the potential of Simular as a powerful tool for optimizing CO_2 absorption processes, contributing to effective and safe carbon capture technologies, and supporting global climate change mitigation efforts.

Introduction

The study of CO_2 absorption in alkanolamines is critical for the optimization of industrial processes – e.g., gas sweetening and carbon capture. These processes are essential in the battle against global warming for their capabilities to reduce greenhouse emissions. Alkanolamines, like N-methyl diethanolamine (MDEA) (Figure 1), are frequently used due to their favorable thermodynamic and kinetic properties, which enhance the efficiency of CO_2 capture from industrial waste gases[1,2]. Understanding enthalpy changes using the calorimetry of these absorption processes provides insight into the processes, enabling its optimization in terms of both absorption capacity and energy efficiency.[3]

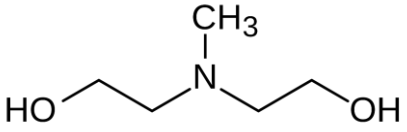

Figure 1. N-methyldiethanolamine molecule

Direct calorimetric measurements of this process provide accurate values on the enthalpy of absorption, reflecting both

the heat effects due to the physical dissolution of gas in the solvent and the chemical reaction between CO_2 and amine. The key reactions that take place during the process are shown in Figure 2. The heat of absorption of CO_2 in aqueous solutions of 27% MDEA (w/v) has been previously investigated, resulting in an average value of 61.4±2.8 kJ mol^{-14}. High pressure has been shown to increase the solubility of CO_2. These studies highlighted the importance of detailed calorimetric analysis in developing efficient and cost-effective carbon capture technologies. The aim of this application note was to use H.E.L's Simular with a MDEA solution and analyze the thermodynamic behavior of the absorption of CO_2 in the aforementioned alkanolamine.

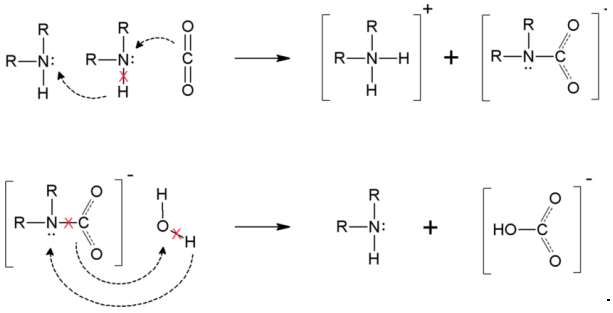

Figure 2. Chemical reaction steps involved in the absorption of CO2 in alkanoamines.

Simular

H.E.L's Simular (Figure 3) is a highly configurable reaction calorimeter designed for precise monitoring and control of reaction parameters. This equipment is designed for the determination of heat generation during a process; calorimetric data can be further used for process optimization and hazard assessment to investigate the thermal properties of a chemical reaction under defined operating conditions. In this application note, a 1-liter stainless steel reactor was used. Brooks Mass Flow Controller (MFC SLA 5850S) was used to feed the CO2 into the reaction mass as well as to maintain the constant reaction pressure inside the reactor. A Druck pressure transducer with a 250 bar pressure rating was used to monitor high-resolution pressure.

The Simular offers the flexibility to operate between traditional Heat Flow or, for quicker results, Power Compensation Control (PCC), which eliminates the need for pre and post-calibration. Simular uses WinISO software with the real-time display and logging of all the process parameters such as reactor temperature, jacket temperature, pressure, power, gas feed flow rate, total gas feed, etc. WinISO integrates operation and data management, providing an intuitive interface to run, monitor, and control the reaction calorimeter experiment. Raw data captured using WinISO can be analyzed separately using the iQ interface to determine the heat of the reaction.

Material and Methods

A solution of 30% MDEA (w/v) in distilled water was prepared using 98 % MDEA procured from Loba Chemie Pvt Ltd., Mumbai. CO_2 gas used was procured from Sandesh Gases Pvt. Ltd., Pune, with 99.99 % purity. 400 ml of 30% MDEA solution was taken into Simular pressure reactor made by SS316L. Simular was operated in power compensation, maintaining the reaction in isothermal conditions at 50 °C temperature. CO_2 gas was fed with a regulator and Mass Flow Controller until the pressure reached 6 bar (absolute). Once the desired pressure of 6 bar was reached,

CO_2 feeding was stopped while maintaining the reaction at constant temperature of 50 °C. The heater power which is the representative data of actual reaction power was monitored and recorded throughout the reaction. Once the heater power reached a stable value, the reaction was considered to be complete.

Figure 3. High-Pressure Simular Reaction Calorimeter

Results and discussion

Figure 4 shows the reactor temperature, jacket temperature (Oil in Temp), heater power, and pressure profile of the CO_2 absorption in the 30% MDEA solution experiment. In this experiment, the reaction temperature was 50 °C, and the initial reaction pressure was 6 bar. During the first step, the heater did not supply any heat, and the reactor temperature was solely maintained at 50 °C by the circulator. In the second step, the temperature of the circulator was reduced to 40 °C as this was power compensation calorimetry, and a compensation drop of 10 °C was chosen. This temperature difference was compensated by the heater in order to maintain the reaction temperature of 50 °C. Once CO_2 is added to the vessel and the chemical reaction starts, energy is released. In order to maintain the reaction temperature at 50 °C and handle the energy released, cooling needs to be provided which was done using the heater, as heater power decreases. Heater power automatically reaches its initial value once the reaction ends and there is no further energy released. Pressure data shows a continuous drop because after reaching the reactor pressure at 6 bar, the CO_2 feed was stopped, and due to the CO_2 consumption during the reaction, pressure started dropping.

Figure 5 shows the CO_2 feed rate and total CO_2 feed profiles from the Simular experiment. In order to reach a reactor pressure of 6 bar, MFC releases a fixed amount of CO_2 gas for a certain time only; once 6 bar pressure is reached, MFC automatically stops. That is why after reaching a certain value of total CO_2 feed, this profile is completely horizontal with no change with respect to time (pink color).

The heater power profile obtained was integrated using iQ software to estimate the total heat released; it was again converted into molar heat in kJ/mol on a CO_2 basis based on the CO_2 moles consumption in the process. The value of heat obtained from Simular experiment is the combination of CO_2 interaction with MDEA, CO_2 interaction with water, heat of mixing, heat loss to the environment, stirrer energy, etc. Hence, the obtained experimental value in the presented work may have some deviation from the theoretical values based on either heat of formation or bond energy methods.

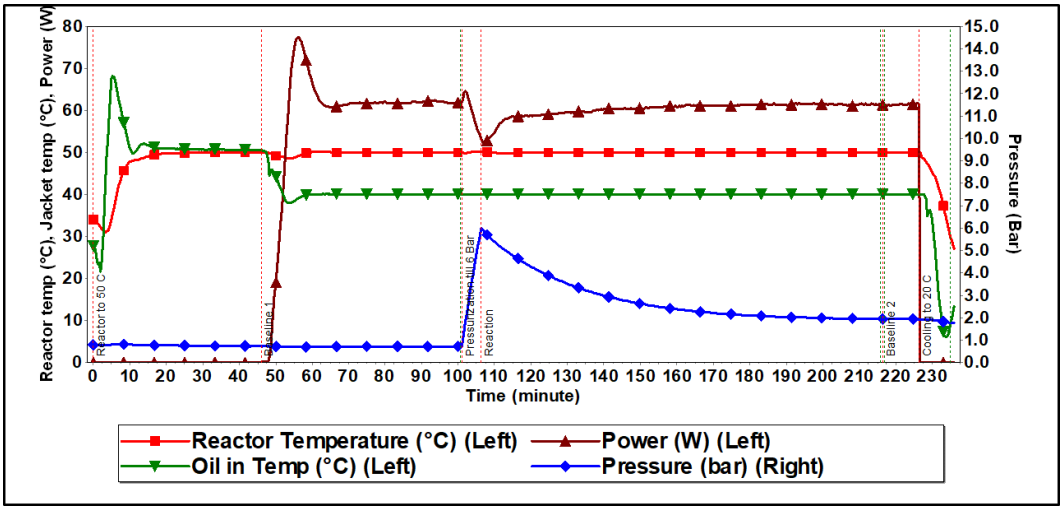

Figure 4. Reactor temperature, jacket temperature, heater power, and CO_2 pressure profile from reaction calorimeter experiment of CO_2 absorption in a 30% N-methyldiethanolamine solution

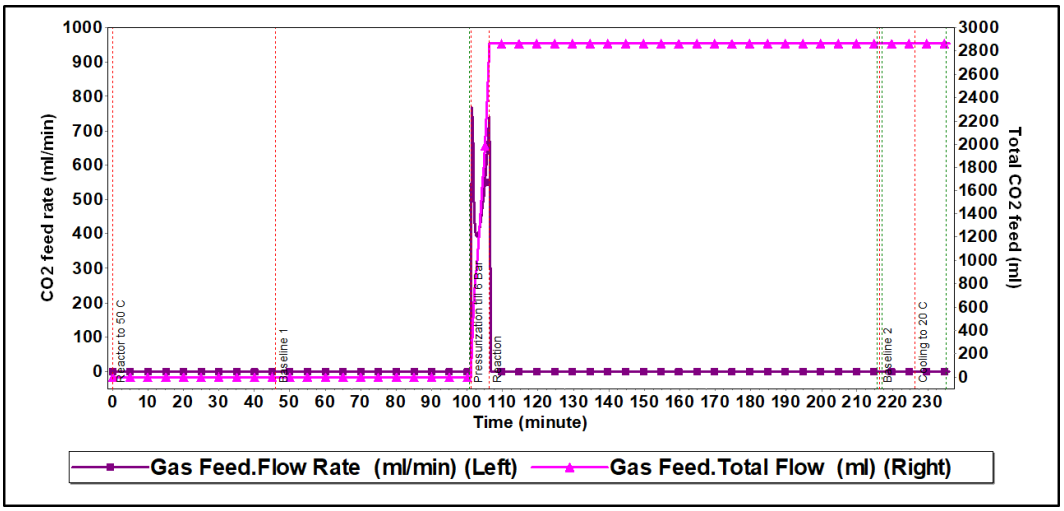

Figure 5. CO_2 feed rate and total CO_2 feed profiles from reaction calorimeter experiment of CO_2 absorption in a 30% N-methyldiethanolamine solution

Conclusion

Alkanolamines are highly promising molecules in our battle against climate change due to their capacity to absorb CO_2. As this is an exothermic process, hence quantification of its heat of reaction is a must for the process understanding and safe scale-up. The presented experiment and obtained results demonstrate the capability of Simular for the use of this process. A 30 % MDEA solution was used for the presented work. However, a similar result can be obtained for other MDEA concentrations and other industrial alkanolamines. For the presented study, the heat of reaction of 77.07 kJ/mol was obtained for the CO_2 absorption process on 30 % MDEA solution. Moreover, Simular has the capacity to operate in Power Compensation, a method that has been shown to provide faster results with no loss in accuracy or precision[5]. Simular is, therefore, a very powerful tool for obtaining thermal change data while reducing experiment time and increasing the efficiency of research.

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