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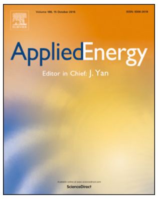

Performance of sulfolane/DETA hybrids for CO_2 absorption: Phase splitting behavior, kinetics and thermodynamics

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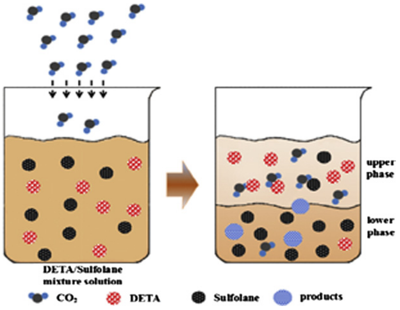
HIGHLIGHTS

- The phase splitting occurred upon CO_2 absorption into DETA/sulfolane hybrid.
- Most of the absorbed CO_2 was concentrated in the upper layer and the lower layer was sulfolane.
- DETA/sulfolane achieved an absorption rate 100% higher than that of MEA.
- DETA/sulfolane-based process reduced the heat duty by 19% compared with MEA.
- The viscosity of DETA/sulfolane was over 20 times lower than the other phase splitting absorbents.

GRAPHICAL ABSTRACT



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ABSTRACT

The phase splitting solvent as a promising alternative to MEA for CO_2 capture has received an increasing attention due to its low energy consumption. In this paper, the mixture of diethylenetriamine (DETA) and sulfolane was employed to absorb CO_2 from the simulated flue gas. Its phase splitting behavior was investigated. The species in each separated phase were identified using nuclear magnetic resonance (NMR), revealing that the upper layer was a CO_2-rich phase and mainly consisted of DETA and DETA-carbamate. Whereas, the lower layer was CO_2-lean phase with the sulfolane presented individually. The CO_2 absorption kinetics was also measured in a wetted-wall column as a function of temperatures, CO_2 loadings, and gas flow rate. Their impacts on the enhancement factor and mass transfer resistance were calculated by the Vapor-Liquid Equilibria (VLE) model, implying that the main CO_2 mass transfer resistance gradually transferred from the gas side to the liquid side with the CO_2 loading increasing from 0 to 2.21 mol L^{-1}. During the CO_2 absorption process, sulfolane acted as an inert solvent for substituting the role of water and separated from the absorption product. Consequently, the sensible heat and vaporization heat were substantially decreased by 59% and 12%, respectively. Hence the total heat duty was lowered by 19% which might noticeably advance the CO_2 capture technology.

1. Introduction

The increasing energy demand arouses large amounts of CO_2 emission from the power plants which has become a critical environment issue [1–3]. As a conventionally employed technology for CO_2 capture, monoethanolamine (MEA)-based absorption technology is suffering from the high energy consumption, which increases the cost of electricity generation by approximately 80% [4,5]. Among the energy

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consumption, it has been reported that the regeneration heat accounts for approximately 50% [6] of the total heat duty. To address this issue, development of the alternatives to MEA with a lower regeneration heat is receiving more and more attention [7]. As a promising candidate, the phase splitting solvents comprise of two or more compositions coexisting in a homogeneous solution at the initial stage. After a large amount of CO_2 is absorbed by this blend, two different phases are formed and separated with each other [8]. It is caused by the fact that the product of CO_2 absorption is insoluble in the original solvent. As a result, the total volume of rich phase needed for regeneration is substantially decreased compared with the conventional MEA absorbent. Therefore, both of the sensible heat and latent heat were markedly reduced, resulting in a decline of the total heat duty by 20% to 30% [9].

The phase splitting solvent can be categorized into liquid–solid and liquid–liquid phase splitting behavior [10]. During the liquid–solid phase splitting process, the CO_2 absorption product precipitates as the solid form, which is then separated from the absorbents and transferred to the stripping devices for regeneration [11]. Shen et al. developed a liquid–solid phase splitting solvent, ProK/ethanol hybrid, in which 55–60% of the absorbed CO_2 was concentrated in the solid phase [12]. Because the CO_2-rich solid was sent for the stripping, a substantial decrease of the energy consumption was archived due to that the water evaporation during the absorbent regeneration was lowered. However, the issues related to solid handling and heat exchange during desorption of solid should be addressed.

Developing the liquid–liquid phase splitting absorbent is also a promising strategy, in which the reaction product, existing in another liquid phase, is able to separate from the bulk of absorbents after an adequate amount of CO_2 is absorbed. Typically, the absorbed CO_2 is concentrated in the lower layer because its density is much higher than that of the upper layer. Arshad [13] developed a liquid–liquid phase splitting absorbent comprised of DEEA and MAPA and its thermodynamics was investigated by the Extended UNIQUAC Framework model. Zhang et al. [14] reported a liquid–liquid splitting absorbent named as CPCAs (CO_2 phase change absorbents) for CO_2 capture, in which 1-propanol, 2-propanol and tertiary butanol was used as the diluents. However, the viscosity of the reported CO_2-rich phase was gradually increased due to a large amount of carbamate generated from CO_2 absorption and transmission. Consequently, it became difficult to circulate the CO_2-rich absorbent in the stripper which weakened the feasibility of its regeneration. The mass transfer coefficient would decrease accordingly, resulting in a further drop in the absorption rate based on a modified Stokes–Einstein equation [15]. To address that issue, the hybrid of a highly efficient amine in less presence, and a non-volatile solvent is expected to show high capacity for CO_2 capture and phase splitting after absorption.

As a promising non-volatile and neutral physical solvent with excellent stability and low corrosiveness, sulfolane featured high capability of combining with CO_2 which was frequently deployed to improve the ability of CO_2 absorption. More important, sulfolane might separate from the bulk of amine-based absorbent after a number of CO_2 was loaded, so that the energy consumption for absorbent regeneration was markedly reduced [16]. Meanwhile, the total concentration of amine in the CO_2-rich phase was lowered due to the replacement by sulfolane, resulting in a substantial decrease of its viscosity. Although the previous researches provided useful references for exploiting novel phase splitting absorbents, little information was yet available on systematic investigation on their kinetics and thermodynamics, which incurred less understanding of the feasibility with respect to the novel sulfolane-based absorbent in real practice.

In brief, it is still the key point to develop new phase splitting solvents with high CO_2 loading capacity and high absorption rate [17,18] in order to overcome the shortcomings of MEA technology. In the current research, a novel DETA-sulfolane hybrid serving as the liquid–liquid phase splitting absorbent for CO_2 capture was exploited. The absorption kinetics was investigated by a wetted-wall column (WWC) [19]. The thermodynamics was studied by revealing the phase splitting behavior and calculating the heat duty by the Vapor-Liquid Equilibria (VLE) model [20,21]. The results can advance a novel absorption-based technology for CO_2 capture with higher removal efficiency and less energy requirement than the conventional MEA absorption.

2. Experiments

2.1. Chemicals and apparatus

Diethylenetriamine (DETA, ≥99 wt%, ρ = 0.963 g/ml), sulfolane (≥99 wt%, ρ = 1.109 g/ml), monoethanolamine (MEA, ≥99 wt%, ρ = 1.019 g/ml), 2-(diethylamino)-ethanol (DEEA, ≥99 wt%, ρ = 0.88 g/ml), dioxane (≥99.5 wt%) and deuterium oxide (D_2O, ≥99.96 wt%) were obtained from Aladdin Biochemical Technology Co., Ltd., in Shanghai. The nitrogen (N_2, ≥99.99%, volume fraction) and CO_2 (≥99.9%, volume fraction) were purchased from Baoding North Special Gases Co., Ltd. All reagents were used without further purification.

The phase splitting behavior of DETA/sulfolane was investigated by bubbling pure CO_2 into this hybrid in 50 ml at a gas flow rate of 500 ml/min. The CO_2 loading levels would gradually increase with the bubbling time. After 5 min, the liquid–liquid phase splitting phenomenon was observed. The volume of the upper and lower layers at different bubbling time was measured respectively as well as the density. The viscosity was determined by the rotary viscometer with the type NDJ-5S. The species involved in the two phases were identified by nuclear magnetic resonance (NMR). Fig. 1 was used to depict the structure of DETA and sulfolane.

A wetted-wall column (WWC) was employed in this study to investigate the reaction kinetics of CO_2 absorption [22–24] as shown in Fig. 2, in which the gas–liquid interface area was available definitely. WWC was constructed of a stainless steel tube with 9.1 cm in height and 1.26 cm in diameter being protruded from a fixed base. The phase splitting absorbent with a certain CO_2 loading was prepared in a total volume of 1.5 L and placed in a thermostatic water bath for preheating to 303–348 K. The absorption rate of CO_2 by three potential candidates, including 2 M DETA + 3 M sulfolane, 5 M DETA, and 1 M DETA + 4 M DEEA, were compared to 5 M benchmark MEA solution in the WWC reactor.

After the reaction was initiated, the prepared absorbent was pushed up through the inside of the tube, which evenly distributed across the outer surface of the tube and then overflowed towards the base of the column. The flow rate of absorbent was controlled to maintain a smooth liquid film. After that, the absorbent was collected and circulated back to the reservoir by a peristaltic pump. Because the total amount of absorbent is much higher than that of absorbed CO_2 within the reaction time less than 1 h, the concentration of the absorbent is regard equal to its initial concentration. The reaction region for absorbent and CO_2 contacting was enclosed by a thick-walled glass tube with the outside diameter of 2.6 cm. The temperature of the chamber is controlled by the water bath.

Regarding the simulated flue gas comprised of CO_2 and N_2, it was introduced from the bottom of WWC and contacted with the absorbent

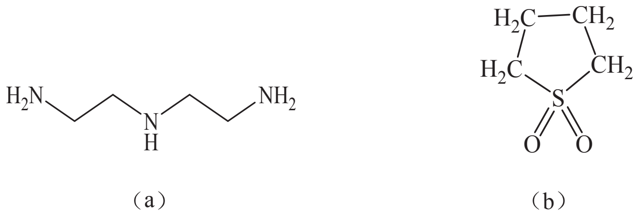

Fig. 1. Chemical structure: (a) DETA; (b) Sulfolane.