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Simultaneous absorption of carbon dioxide and hydrogen sulfide into aqueous blends of 2-amino-2-methyl-1-propanol and diethanolamine

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Abstract

This work presents an experimental and theoretical investigation of the simultaneous absorption of CO_2 and H_2S into aqueous blends of 2-amino-2-methyl-1-propanol (AMP) and diethanolamine (DEA). The effect of contact time, temperature and amine concentration on the rate of absorption and the selectivity were studied by absorption experiments in a wetted wall column at atmospheric pressure and constant feed gas ratio. The diffusion–reaction processes for CO_2 and H_2S mass transfer in blended amines are modeled according to Higbie's penetration theory with the assumption that all reactions are reversible. The blended amine solvent ($AMP+DEA+H_2O$) has been found to be an efficient mixed solvent for simultaneous absorption of CO_2 and H_2S. By varying the relative amounts of AMP and DEA the blended amine solvent can be used as an H_2S-selective solvent or an efficient solvent for total removal of CO_2 and H_2S from the gas streams. Predicted results, based on the kinetics-equilibrium-mass transfer coupled model developed in this work, are found to be in good agreement with the experimental results of rates of absorption of CO_2 and H_2S into ($AMP+DEA+H_2O$) of this work.

Keywords: Absorption; Modeling; Carbon dioxide; Hydrogen sulfide; 2-Amino-2-methyl-1-propanol; Diethanolamine

1. Introduction

The removal of acid gas impurities, such as CO_2 and H_2S, from sour gas streams is a significant operation in natural gas processing. Industrially important alkanolamines for this operation are monoethanolamine (MEA), diethanolamine (DEA), di-isopropanolamine (DIPA) and *N*-methyldiethanolamine (MDEA). While MEA and DEA are widely used today for total acid gas CO_2 and H_2S removal from sour natural gas and industrial gas streams, aqueous MDEA is used very often for selective removal of H_2S from gas streams containing both CO_2 and H_2S. Over the past two decades aqueous amine solvent technology has evolved from total acid gas removal processes for removing H_2S and recently into processes, which can provide any degree of selectivity by using complex blended amine solvents. Blended amine solvents, which consist of a mixture of primary or secondary amine with a tertiary amine, combine the higher CO_2 reaction rates of the primary or secondary amine with the higher CO_2 loading capacity of the tertiary amine. Thus, a blended amine solvent providing both higher CO_2 reaction rate and higher CO_2 equilibrium capacity may result in substantial lower solvent circulation rates compared to a single amine solvent. With respect to economics, solvent circulation rate is the single most important factor in determining the economics of a gas treating process using chemical solvent. A lower circulation rate, besides resulting in lower pumping energy cost, also leads to reduced regeneration energy requirement, which accounts for about 70% of the total operating cost of a gas treating process. Besides these economic advantages of blended amine solvents, another major advantage in the operation of the treating

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process is derived from the degree of freedom that is, the selectivity of a blended amine solvent can be varied as required from high H_2S selectivity to total acid gas removal by varying the relative concentrations of the constituent amines in the blend.

Blends of primary and tertiary amines (such as mixtures of MEA and MDEA) or secondary and tertiary amines (such as mixtures of DEA and MDEA), which combine the higher equilibrium capacity of the tertiary amine with the higher reaction rate of the primary or secondary amine, have been suggested for industrial gas treating processes. As with MDEA, the sterically hindered amine AMP also provides an equilibrium CO_2 capacity about twice that of any primary or secondary amine. Also, similar to CO_2–MDEA reaction, the ultimate product of the CO_2–AMP reaction is bicarbonate. Hence, the regeneration energy requirement when AMP is used as a component of a blended amine solvent will be lower as in the case of using MDEA. On the other hand, AMP offers an additional advantage over MDEA particularly for CO_2 removal due to the fact that the CO_2–AMP reaction is much faster than the CO_2–MDEA reaction. Besides, AMP offers reasonably good H_2S selectivity as well. In view of this, aqueous (DEA+AMP) may be an economically attractive alternative to the blended amine solvent MDEA and DEA for removal of CO_2 and simultaneous removal of CO_2 and H_2S from sour gas streams.

Aqueous diethanolamine (DEA) is a common chemical absorbent used in refineries to remove hydrogen sulfide from refinery off gases (Kohl and Riesenfeld, 1985). Aqueous MDEA is used to accomplish selective removal of H_2S (Mandal et al., 2004a). Besides MDEA, diisopropanolamine (DIPA) has also been reported to have a greater selectivity for H_2S over CO_2 than either MEA or DEA. Since the introduction of sterically hindered amines as important absorbents for the gas sweetening processes by Sartori and Savage (1983), a number of hindered amine-based processes have been commercialized. It is also indicated that hindered amines, e.g., 2-amino-2-methyl-1-propanol, may have very good selectivity towards H_2S in the presence of CO_2 in the sour gas streams (Saha et al., 1993; Mandal et al., 2004a). Recently, hindered amine-based H_2S-selective gas treating processes have been commercialized by Exxon Research and Engineering Company. It is claimed that the new hindered amine-based processes are potentially attractive replacements for the existing selective H_2S removal processes including MDEA-based and direct conversion processes. Haimour and Sandall (1983) modeled the simultaneous absorption of H_2S and CO_2 into diethanolamine using penetration theory. Say et al. (1984) have presented a process development work using hindered amine as the promoter of hot carbonate solutions for simultaneous absorption of H_2S and CO_2. Rascol et al. (1997) numerically interpreted the simultaneous mass transfer of CO_2 and H_2S into aqueous blends of MDEA and DEA. They have used the film and approximate film theories to describe the mass transfer phenomena within the liquid phase. Rinker (1997) studied theoretically and experimentally the simultaneous absorption of CO_2 and H_2S into aqueous blends of MDEA and DEA.

However, in spite of the immense commercial significance of the aqueous blended amine solvent (AMP+DEA) for simultaneous removal of CO_2 and H_2S from sour natural gas streams, studies on simultaneous absorption of H_2S and CO_2 into aqueous blends of AMP and DEA have not been reported in the open literature so far.

In this work, the simultaneous absorption of CO_2 and H_2S into aqueous blends of AMP and DEA is studied theoretically and experimentally. The effect of contact time, temperature and amine concentration on the rate of absorption and the selectivity were studied by absorption experiments in a wetted wall column. The diffusion-reaction processes for CO_2 and H_2S mass transfer in the blended amine solvents are modeled according to Higbie's penetration theory with the assumption that all reactions are reversible.

2. Reaction scheme and mathematical model

2.1. Reaction scheme

The following reactions may take place when CO_2 and H_2S are absorbed into an aqueous blended amine solution of AMP (RNH_2) and DEA ($R'R'NH$) (where $R = C(CH_3)_2CH_2OH$ and $R' = CH_2CH_2OH$).

$$CO_2 + RNH_2 + H_2O \overset{K_1,k_{21}}{\longleftrightarrow} RNH_3^+ + HCO_3^-, \tag{1}$$

$$CO_2 + OH^- \overset{K_2,k_{22}}{\longleftrightarrow} HCO_3^-, \tag{2}$$

$$R'R'NH + CO_2 \overset{K_3,k_{23}}{\longleftrightarrow} R'R'NCOO^- + H^+, \tag{3}$$

$$HCO_3^- \overset{K_4}{\longleftrightarrow} H^+ + CO_3^{2-}, \tag{4}$$

$$H_2S + RNH_2 \overset{K_5}{\longleftrightarrow} RNH_3^+ + HS^-, \tag{5}$$

$$H_2S + R'R'NH \overset{K_6}{\longleftrightarrow} R'R'NH_2^+ + HS^-, \tag{6}$$

$$RNH_2 + H^+ \overset{K_7}{\longleftrightarrow} RNH_3^+, \tag{7}$$

$$R'R'NH + H^+ \overset{K_8}{\longleftrightarrow} R'R'NH_2^+, \tag{8}$$

$$H^+ + OH^- \overset{K_9}{\longleftrightarrow} H_2O, \tag{9}$$

where K_i $(i = 1, \ldots, 9)$ is the equilibrium constant for the reaction (i), and k_{2j} $(j = 1, \ldots, 3)$ is the second order forward rate coefficient for reaction (j). Reactions (1)–(3) have finite reaction rates and are reversible and reactions (4)–(9) are considered instantaneous and reversible and at equilibrium.

2.2. Reaction mechanism

The proposed mechanism for the reaction between CO_2 and AMP (RNH_2), a sterically hindered amine, involves