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Precipitation of AMP carbamate in CO_2 absorption process

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Abstract

This work presents a novel concept for CO_2 absorption with an amine solution forming a precipitate when absorbing CO_2. The systems consist of the sterically hindered amine, 2-amino-2-methyl-1-propanol, and an organic solvent, N-methyl-2-pyrrolidone or triethylene glycol dimethyl ether. The precipitate is formed when CO_2 is absorbed and reacts with the amine. In order to design an absorption process using precipitating solutions, detailed knowledge on when and where the precipitate will form is needed. The onset of precipitation in four different amine solutions has been investigated in this work, and the composition of the precipitate was also determined using NMR spectroscopy.

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1. Introduction

Sterically hindered amines, such as 2-amino-2-methyl-1-propanol (AMP), are an interesting alternative to conventional amines used for CO_2 capture, because the sterically hindered amines do not form stable carbamates [1, 2]. In aqueous solutions the formation of bicarbonate is favored over carbamate formation [3-5]. If organic solvents are used instead of water the formation of bicarbonate cannot occur and the unstable carbamate is formed instead [2, 6-8]. The carbamate formed is unstable because of the steric hindrance of the amine and is therefore easier to regenerate [5]. For the system presented in this paper, an organic solvent is utilized instead of water. In an organic solvent, with no water present, the hindered amine cannot react further to produce bicarbonate. This limits the loading to 0.5 mol CO_2/mol amine due to stoichiometry. Because the carbamate formed is unstable, there are

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advantages during regeneration of the amine solution. If the components of the mixed solvent are chosen properly, it is possible to obtain a system where the carbamate formed will not be dissolved in the solution but form a precipitate. The formation of a precipitate has been noted in several studies of AMP in organic solvents [2, 6, 9]. This precipitate can be separated from the solution, e.g. by filtration, and regeneration can be achieved with less solvent.

The systems presented in this work consist of an organic solvent, N-methyl-2-pyrrolidone (NMP) or triethylene glycol dimethyl ether (TEGDME), and a reactant, 2-amino-2-methyl-1-propanol (AMP). These systems have shown the potential for sufficient regeneration of the amine at low temperature (70-90°C) compared to conventional amines [10]. Complete desorption of CO_2 could be achieved at 75°C for the solution of AMP in NMP and at 90°C for the solution of AMP in TEGDME. This provides the possibility to use low-grade heat for the regeneration, which makes the CO_2 absorption process more cost effective. Because an organic solvent is used, the AMP carbamate cannot react further and produce bicarbonate. The complex containing amine and carbon dioxide will then precipitate in the organic solvent as previously described. The following reaction mechanism describes the absorption of CO_2 and its consequent reactions, including the precipitation of the carbamate.

$$CO_2(g) \leftrightarrow CO_2(sol) \tag{1}$$

$$CO_2(sol) + RNH_2(sol) \leftrightarrow RNH_2^+COO^-(sol) \tag{2}$$

$$RNH_2^+COO^-(sol) + RNH_2(sol) \leftrightarrow RNH_3^+(sol) + RNHCOO^-(sol) \tag{3}$$

$$RNH_3^+(sol) + RNHCOO^-(sol) \leftrightarrow RNH_3RNHCOO(s) \tag{4}$$

Using a separation unit, the solid particles can be removed from the solvent and the resulting slurry, with a high concentration of precipitate, is pumped to the regenerator. The slurry is heated with waste heat, below 100°C, to regenerate the amine and release the carbon dioxide. As the slurry is highly concentrated, less energy is needed to heat the solvent, which increases the process efficiency. The possibility of obtaining pressurized carbon dioxide after regeneration has also been demonstrated (unpublished data). Heating to 85°C produces carbon dioxide at 6 bars pressure for the solution of AMP in NMP and carbon dioxide at 4 bars pressure for the solution of AMP in TEGDME. Fig 1 shows a simplified flowsheet of the proposed process.

When and where the precipitate will form is crucial for the process design. If the precipitation is formed in a pipe or plugs the packing in the absorption tower it would cause serious problems. It is therefore important to know at what conditions the precipitation will form. For some systems it may be necessary to control the onset of precipitation, by the addition of chemical additives to support crystal formation, so that the process can be operated without problems.

In previous studies the solubility and heat of absorption of CO_2 in solutions of AMP and NMP or TEGDME have been determined [9, 11]. This work is focused on investigating at which conditions the precipitate is formed and what factors affect the onset of precipitation in the studied systems. Experimental data for solutions containing varying amounts of AMP at different temperatures were used and the onset of precipitation was determined [9]. The precipitates were also analyzed using NMR-spectroscopy.

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