



Solubility of carbon dioxide in mixtures of 2-amino-2-methyl-1-propanol and organic solvents



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ABSTRACT

Sterically hindered amines, such as 2-amino-2-methyl-1-propanol (AMP), are an interesting alternative to the amines used in conventional CO₂ absorption processes in industrial applications. One reason for this is because the carbamate formed is not stable, which may be beneficial during the regeneration of the amine solution in terms of a reduced energy requirement.

This paper presents experimental data on the solubility of CO₂ in solutions of AMP in one of two organic solvents: N-methyl-2-pyrrolidone or triethylene glycol dimethyl ether, at different amine concentrations (15 wt% and 25 wt%) and temperatures (25 °C and 50 °C). A solid precipitate was observed during some of the experiments. The absorption capacity of the solution increased with AMP concentration and was higher at lower temperatures.

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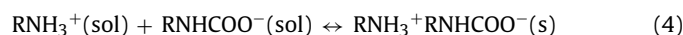
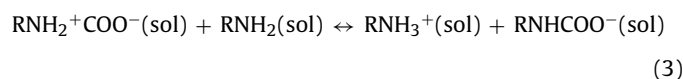
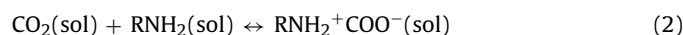
1. Introduction

Sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) have been widely studied as an alternative to commercial systems employing, for instance, monoethanolamine (MEA) and diethanolamine (DEA) for the absorption of CO₂ (Chakraborty et al., 1986; Xu et al., 1996). The main reason for this is the higher loading capacity of the aqueous AMP solutions, and the problems associated with the use of aqueous MEA solutions concerning corrosion, volatility, and the high regeneration temperature of the amine (Bougie and Iliuta, 2012; Park et al., 2003; Sartori and Savage, 1983).

A number of reaction mechanisms have been suggested for the reaction of CO₂ with AMP, mainly for aqueous solutions (Barzagli et al., 2013; Bougie and Iliuta, 2012; Camacho et al., 2005; Chakraborty et al., 1986; Dash et al., 2011; Gabrielsen et al., 2006; Kumar et al., 2012; Kundu and Bandyopadhyay, 2006; Mehdizadeh et al., 2013; Park et al., 2003; Samanta and Bandyopadhyay, 2009; Sartori and Savage, 1983; Xu et al., 1996; Yamada et al., 2011; Zheng et al., 2012, 2013). The general consensus is that the carbamate

is formed through the zwitterion mechanism. In aqueous solutions the formation of bicarbonate is suggested to proceed through hydrolysis of the carbamate and through direct formation of bicarbonate in the solution, with direct formation of bicarbonate being more important. Sartori and Savage (1983) also suggested a reaction pathway with the zwitterion and water to form bicarbonate rather than hydrolysis of the carbamate. In non-aqueous solvents there is no hydrolysis of the carbamate, although the solvent used may act as a base in the carbamate instead of the amine, thus increasing the loading capacity of the solution (Barzagli et al., 2013; Xu et al., 1996; Zheng et al., 2012, 2013).

A simplified reaction mechanism for the absorption and reaction of CO₂ with the amine, AMP (denoted RNH₂), in organic solvents can be described by the following reactions (1)–(4):



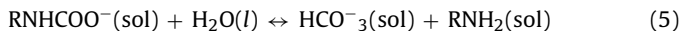
Each mole of CO₂ thus reacts with two moles of AMP to form carbamate, which is unstable due to the steric hindrance of the amine.

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This is advantageous during regeneration of the amine solution as less energy is required (Park et al., 2003).

In aqueous solutions, bicarbonate formation can also occur according to reaction (5).



The formation of bicarbonate increases the loading capacity of the amine solution from 0.5 mole CO₂/mole amine to 1 mole CO₂/mole amine, thus doubling the stoichiometric absorption capacity of the solution. If an organic solvent is used instead of water, no bicarbonate is formed, and the loading is limited to 0.5 mole CO₂/mole amine.

High amounts of carbamate, formed during absorption and reaction with CO₂, as described by reaction (4), may be precipitated in the solution. The formation of a solid carbamate increases the absorption capacity of the solution, as the reactions described above are shifted to the right. When and if precipitation occurs depends on which solvent is used. The presence of a solid precipitate has been noted in previous studies. Xu et al. (1996) noted a white carbamate precipitate in solutions of AMP in 1-propanol, at high concentrations of AMP and at high CO₂ loadings, and found that it was readily dissolved in water. Barzagli et al. (2013) studied solutions of AMP in DEA, N-methyldiethanolamine, methylethanolamine, or diisopropanolamine dissolved in alcohol mixtures (1,2-propanediol/ethanol, ethylene glycol (EG)/methanol or EG/ethanol) or in pure 1-propanol or diethylene glycol monomethyl ether. Precipitation was only observed in solutions of AMP and DEA in 1-propanol. The solid precipitate was identified as the AMP carbamate [RNH₃⁺RNHCOO⁻], and they concluded that the AMP carbamate was less soluble than the DEA carbamate, and was in fact more stable in the solid state than in solution. The precipitate was instantly dissolved in other solvents, such as methanol, ethanol, and ethylene glycol, where the AMP carbamate reacted with the solvent to form monoalkyl carbonate. Barzagli et al. (2013) also showed that a high CO₂ desorption efficiency (94%) could be achieved at low desorption temperatures (50–65 °C). Brüder et al. (2011) noted a solid precipitate in some aqueous solutions of AMP and piperazine loaded with CO₂. No experiments could be carried out on these solutions as the crystals clogged the experimental setup.

If a precipitate is formed, it can be separated from the solution and the amine can be regenerated with less solvent present. Energy can thus be saved, as a smaller volume of solvent must be heated to the desorption temperature. Barzagli et al. (2013) showed that a low desorption temperature could be used for regeneration of the solid AMP carbamate, as found in our preliminary desorption studies (unpublished data). This provides further advantages in the regeneration of the amine solution, as the amount of energy required for regeneration of the amine is reduced further. If a low desorption temperature can be used for the regeneration of the amine, low-grade heat can be used instead of high-grade steam, which makes the desorption process even more cost-efficient. A low desorption temperature will also lead to less thermal degradation of the amine, and smaller amine and solvent losses due to evaporation.

This study presents solubility data for the absorption of CO₂ in organic solutions of AMP. Two organic solvents were used: N-methyl-2-pyrrolidone (NMP) and triethylene glycol dimethyl ether (TEGDME). The solvents were chosen after rigorous screening to find an organic solvent that, together with AMP, produced a solid carbamate during the absorption of CO₂. The objective was to determine how the absorption capacity of the amine solution was influenced by the organic solvent, the concentration of AMP, and the temperature.

Table 1

Composition of the amine solutions used in the experiments (weight fractions).

Amine solution	AMP	NMP	TEGDME
1	0	1	0
2	0	0	1
3	0.15	0.85	0
4	0.25	0.75	0
5	0.15	0	0.85
6	0.25	0	0.75

2. Materials and methods

2.1. Materials

The chemicals used were CO₂, NMP, TEGDME and AMP. CO₂ was obtained from AGA (≥99.99% pure), while NMP, TEGDME and AMP were obtained from Merck (purity min. 99%) and used as received without further purification. The solvent mixtures were prepared by weight, on a scale with an accuracy of 0.05 g for weights up to 2000 g.

2.2. Experimental procedure

Experiments were conducted on three solutions with different concentrations of amine (AMP) and solvent (NMP or TEGDME). The solutions used are presented in Table 1. The experimental procedure, true heat flow reaction calorimeter, and uncertainties have been described in detail previously (Svensson et al., 2013). Therefore, only a brief description is given here.

All experiments were performed using the CPA202 Chemical Process Analyzer from ChemiSens AB. A reactor made of glass and stainless steel with an effective volume of 250 cm³ was used in the experiments. The experimental setup is depicted in Fig. 1. Before each experiment, the reactor was loaded with approximately 100 g of the amine solution. The reactor was then pressurized with nitrogen, to about 5 bar, to ensure that the reactor had been properly assembled and that no leaks would occur during the experiment. The solution was degassed by lowering the pressure in the reactor to near vacuum, at approximately 25 °C, with a filter pump before each experimental run. This process took 10–12 s and the reactor was then closed, and the system was allowed to reach equilibrium. No solvent trap was used during the lowering of the pressure. The maximum amount of solvent loss during the lowering of the pressure was estimated to be below 1 mg. This falls well below the margin of error of the scale used to prepare the samples and was therefore considered negligible. The vapor pressure of amine and solvent in the gas phase of the reactor is assumed to be constant and equal to the total equilibrium pressure before the first addition of CO₂ to the reactor. The experiment was conducted at a constant temperature of 25 or 50 °C. CO₂ was introduced into the reactor via a Bronkhorst Hi-Tec mass flow controller. The dosing of CO₂ took approximately 25–170 s. The CO₂ flow rate during dosing was 0.8 g CO₂/min. An automation script was used to control the experiments. This script seeks stability in pressure and true heat flow between each addition of CO₂. The maximum deviation in the pressure and true heat flow were required to be below ±0.01 bar and ±0.02 W, respectively, for 30 min, in order for the system to be considered to be at equilibrium.

Two independent experiments were performed with each solution at each temperature. The pressure in the reactor, the amount of CO₂ added to the reactor and the heat flow from the reactor were continuously logged during the experiments. Each experiment consisted of 5–8 equilibrium points. The main sources of uncertainty in the experimental data are associated with the amount of CO₂ added to the reactor. The amount of CO₂ added to the reactor is recorded by the mass flow controller, which has an accuracy

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