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Comparative study on differently concentrated aqueous solutions of MEA and TETA for CO_2 capture from flue gases

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ABSTRACT

Next to IGCC and oxyfuel technology amine scrubbing is one possible process pursued for industrial-scale CO_2 capture from power plant flue gases. Aqueous solutions of Monoethanolamine (MEA) are commonly used for the existing amine scrubbing processes because of their high reaction kinetics during CO_2 absorption. However, the required energy demand for regeneration of the MEA solution is comparably high, requiring improvements in process technology and solvent development. Within this work the results from lab-scale experimental research on the CO_2 absorption from flue gases using differently concentrated aqueous solutions of MEA and Triethylenetetramine (TETA) are presented and discussed. The amine content of the solutions was varied in order to show the influence of concentration on CO_2 loading, cyclic capacity and limitations within physical parameters. The equilibrium CO_2 loading of the concentrated amine solutions was obtained at temperatures from 30 to 95 °C using synthetic flue gas with different CO_2 concentrations of up to 15 vol% CO_2. From these results the cyclic capacities of the different solutions are calculated and discussed with focus on the influence of the amine concentration. Furthermore MEA and TETA will be compared on molar and mass basis specifying the significance of TETA as polyamine and its advantages regarding the scrubbing process.

1. Introduction

Coal fired power plants are regarded as large point sources of CO_2 for which Carbon Capture and Storage (CCS) technologies are being discussed and investigated. Amine scrubbing is one possible end-of-pipe process pursued for industrial-scale CO_2 capture from power plant flue gases. Amine scrubbing can be retrofitted to existing power plants and has so far been used in the chemical industry as well as for enhanced oil recovery (EOR). Although it has proofed technically viable, it has not been installed on a large-scale basis at a power plant so far. The main drawback of the process is its large energy demand causing a reduction to the power plant efficiency of up to 13% points [1]. Therefore improvements in process technology and solvent development are important to minimize the penalty in the power plant efficiency.

Therefore the IFK is investigating new solvents as substitutes for MEA while also developing new process options for CO_2 scrubbing within a national funded research project supported by the German Government and German power companies as well as suppliers. Within the research higher concentrated amine solutions are studied as their usage can possibly reduce the energy demand required by the scrubbing process.

The commonly used aqueous solutions of MEA are characterized through fast reaction kinetics during CO_2 absorption; however they require a comparably high energy demand for regeneration due to their reaction enthalpy. Therefore ongoing research is investigating new solvents as alternatives to MEA requiring less energy for regeneration [1,2]. Specifically designed scrubbing processes have also been developed in which often a combination of a tertiary amine with activators is used [3,4]. Another category of amine solvents are polyamines. They contain two or more amino groups within one molecule and therefore show high affinity to CO_2. Several polyamines such as 2-(2-Aminoethylamino)-ethanol (AEAE), Diethylenetriamine (DETA) or mixtures of TETA with Methyldiethanolamine (MDEA) have recently been studied in the literature [5–9].

The objective of this work is to show the influence of amine concentration on the equilibrium CO_2 loading at different temperatures for Monoethanolamine (MEA) and Triethylenetetramine (TETA). Focusing on the significance of TETA as polyamine and comparing the results on molar and mass basis. Table 1 shows the chemical structures of MEA and TETA. MEA is a primary amine ($-NH_2$) with one functional amino group. TETA as polyamine has four functional groups – two primary amino groups and two secondary amino groups (–NH–). This implies that TETA has four

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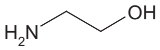
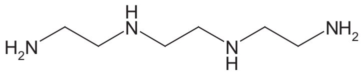
Table 1
Chemical structure, molar mass and concentration of MEA and TETA.

MEA	TETA
	
61.08 g/mol 30 wt.% 4.91 mol MEA/kg solution	146.24 g/mol 18 wt.% 1.23 mol TETA/kg solution

possible reaction sites for CO_2 whereas MEA only has one. In this work, in order to compare both amines with each other, the aqueous solutions of TETA are prepared equivalent in number of amino groups to their corresponding MEA solutions. For instance, a 30 wt.% MEA solution is equivalent to a 18 wt.% TETA solution, having both the same number of amino groups present. Using equivalent concentrations enables a direct comparison of both amines on the average CO_2 uptake per amino group on molar basis.

During CO_2 absorption the main reaction of primary and secondary amines is the formation of carbamate according to Eq. (1). The carbamate formation takes either place by the zwitterion or the termolecular mechanism. The zwitterion mechanism was first introduced by Caplow [10] and reinforced by Danckwerts [11] suggesting a zwitterion as intermediate to carbamate formation. The direct reaction of the amine with CO_2 called termolecular mechanism was proposed by Crooks and Donnellan [12]. Calculations have shown that preferably the direct reaction of CO_2 with amine occurs, however the formation of a zwitterion can be temporarily possible [13].

$$CO_2 + 2HNR_1R_2 \leftrightarrow R_1R_2NCO_2^- + R_1R_2NH_2^+ \tag{1}$$

$$CO_2 + HNR_1R_2 + H_2O \leftrightarrow R_1R_2NCO_2^- + H_3O^+ \tag{2}$$

(R_1, R_2 carbon side chains, e.g. MEA: $R_1 = H$, $R_2 = C_2H_4\text{–}OH$)

Da Silva [13] states that bicarbonate formation according to Eqs. (3)–(6) [12] – usually attributed to tertiary amines –can also take place with primary and secondary amines. The absorption of CO_2 is thereby catalyzed by the amine molecule acting as a base forming hydroxide-ions. However, carbamate formation is by far the faster reaction. Therefore if only Eq. (1) is taken into account the maximum loading of primary and secondary amines is $0.5\ mol_{CO_2}/mol_{amine}$. Yet practical experience has shown that higher loadings are achieved due to bicarbonate formation even for primary amines.

$$H_2O + HNR_1R_2 \leftrightarrow OH^- + R_1R_2NH_2^+ \tag{3}$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \tag{4}$$

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \tag{5}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{6}$$

The CO_2 absorption with polyamines offers several more reaction pathways to occur. Thereby the primary and secondary amino groups are expected to react according to Eqs. (1) and (2) with additional formation of polycarbamate. One polyamine molecule with n amino groups can form polycarbamates consisting of a maximum of n molecules of CO_2 bound as carbamate. NMR spectra analysis were done by [8,6] for AEAE- and DETA–H_2O–CO_2 systems with two and three amino groups respectively. The studies suggest that in fresh solutions the primary amino groups react first. At higher loading, $0.4\text{-}0.5\ mol_{CO_2}/mol_{amine}$, the secondary amino groups start forming carbamate. Exceeding $0.5 - 0.7\ mol_{CO_2}/mol_{amine}$ polycarbamates can form as well as bicarbonate or carbonate at loadings close to the theoretical maximum loadings of $1.0 - 1.5\ mol_{CO_2}/mol_{amine}$. [6,8] have not identified polycarbamate species where all n amino groups are present as carbamates. In consequence DETA with 3 amino groups is not reported to form tricarbamate whereas the presence of dicarbamate was detected. The reaction kinetics of the primary amino group is reported in [5] to exceed that of the secondary amino group by a factor of 100. This can indicate that the reaction enthalpy of the primary amino group is higher than the reaction enthalpy of the secondary amino group. In [14] the reaction enthalpies of a 30 wt.% AEAE and approx. 30 wt.% DETA solution were determined to 80 and $84\ kJ/mol_{CO_2}$ respectively. This is only a small difference, but may show a trend towards decreasing reaction enthalpy with increasing relative amount of secondary amino groups to primary amino groups. Concluding from the literature results the two primary amino groups of TETA are expected to react at first with CO_2, followed by the two secondary amino groups. Considering the presence of two secondary amino groups with reported lower reaction kinetics the reaction enthalpy of TETA with CO_2 is suggested to be lower than that of MEA.

2. Experimental setup

The laboratory experiments were performed using the experimental setup illustrated in Fig. 1. The equilibrium CO_2 loadings of the concentrated solutions of MEA and TETA were determined

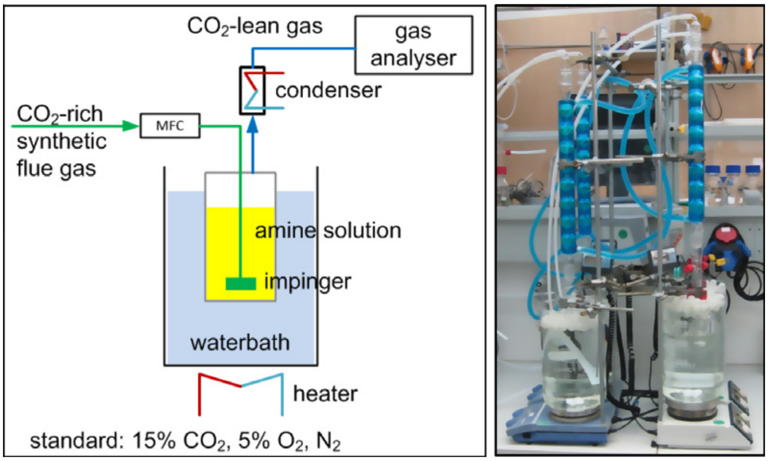


Fig. 1. Experimental setup.