

# INVESTIGATION OF EFFECTS OF THE AMINE SOLUTIONS COMPOSITION ON CARBON DIOXIDE ABSORPTION RATE AND CAPACITY.

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## Abstract

Increasing importance of CO<sub>2</sub> emission reduction cause necessity to find the most effective separation method of this gas from flue gases. The most promising seems to be a chemical absorption in aqueous solutions of alkanolamines. In order to reduce high energy consumption of this process, it is necessary to develop new solutions which will be characterized by the best absorption rate and capacity e.g. through the appropriate composition of amine blends. Experiments were carried out on the solutions containing primary amines, tertiary amines, sterically amines, cyclic amines and organic liquids. The experiments included CO<sub>2</sub> absorption equilibriums and rate determination for temperature range 20-60 deg. C. The results showed a beneficial effect of using blends containing primary amines and sterically hindered amines with organic liquids on both the absorption rate and the absorption capacity.

**Key words:** MEA, MDEA, AMP, CCS, carbon dioxide absorption

## Introduction

The increasing importance of reduction of emissions of greenhouse gases, mainly carbon dioxide from flue gases, is forcing the need to search the most effective methods of carbon dioxide separation. Among the known methods, the easiest to implement is chemical absorption in aqueous alkanolamines solutions. The most widely used compound in this process is monoethanolamine. It has advantages, such as: high absorption rate, a quite high absorption capacity and its cost is relatively low. However, MEA is highly corrosive and has low resistance to thermal and oxidative degradation. It has also a high energy demand in desorption process. Therefore, there is need to search for alternative amine solutions, which do not have monoethanolamine disadvantages. These amines can be divided in four main groups: primary amines, secondary amines, tertiary amines, and recently gaining on importance sterically hindered amines [1]. Primary amines, e.g. monoethanolamine or diglycolamine, reacts quickly with carbon dioxide to form mainly carbamate. In this reaction, two molecules of amine react with one molecule of carbon dioxide. That does not allow to use the full absorption potential of solution. In addition the energy requirement for desorption of carbon dioxide from carbamate is very high. The secondary amines react also rapidly with carbon dioxide, but the heat of absorption is slightly lower than in primary amines. Tertiary amines react with carbon dioxide in different way. The reaction product is not a carbamate but a amine bicarbonate, so the one molecule of amine react with one carbon dioxide molecule. The rate of these reaction is much lower because of slow rate of carbon dioxide dissolution which limitate the reaction rate. Tertiary amines have a low absorption heat and high resistance for degradation. The fourth group is sterically hindered amines – these are primary amines in which the amino group is linked to a tertiary carbon atom or a secondary amine in which the amino group is linked to a secondary or tertiary carbon atom. These amines combine a relatively high absorption rate with a lower desorption heat than primary amines [2]. It is also possible to compose different amines blends to obtain solutions which have features characteristic to a few amine types.

## Apparatus and experimental procedure

The tests were carried out on the following solutions:

- 30% wt. monoethanolamine,
- primary amine/tertiary amine/organic liquid/activator/water (Solvent 1 and Solvent 4),
- sterically hindered amine/ tertiary amine/organic liquid/activator/water (Solvent 3),
- primary amine/sterically hindered amine/organic liquid/activator/water (Solvent 2, Solvent 2.2 and Solvent 5)

On the above solutions were carried out the tests of absorption rates and equilibriums for temperature range 20-60 deg. C. All tests were performed on a specially prepared apparatus, which is shown on Figure 1. To perform the absorption equilibrium test, several portions of solution was added successively to thermostated reactor which was filled before with carbon dioxide. After every addition of

solution the pressure was recorded in state of balance. For kinetics researches the solution was added at one time and the pressure was recorded every 5s.

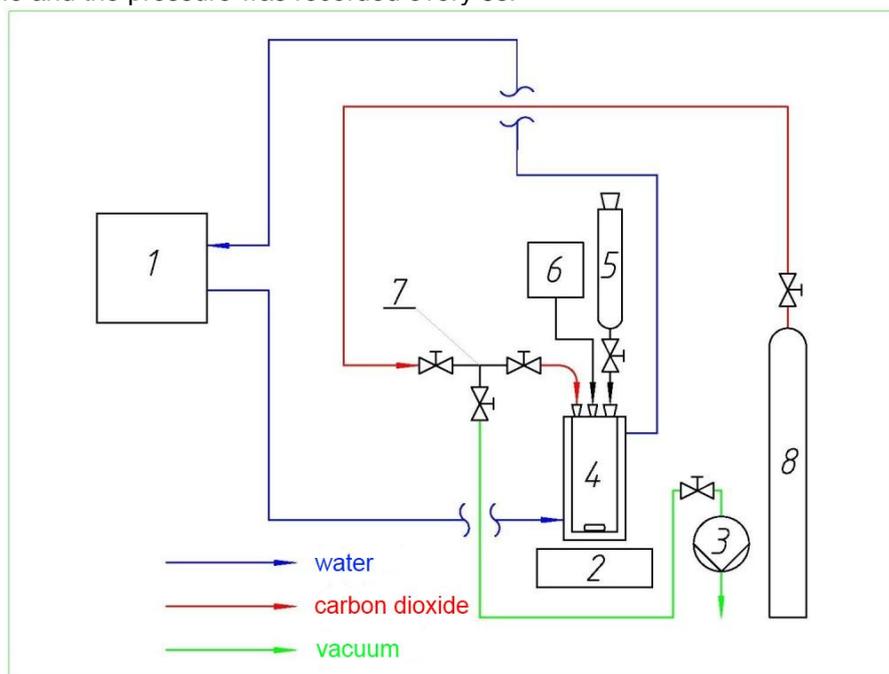


Fig. 1. CO<sub>2</sub> absorption kinetics and equilibria set up - the flow sheet:

1 – refrigerated and heating circulator, 2 – magnetic stirrer, 3 – vacuum pump, 4 – thermostated glass reactor, 5 – cylindrical separatory funnel with graduation, 6 – vacuum gauge, 7 – valve station, 8 – CO<sub>2</sub> bottle.

## Results

The results are presented in the form of carbon dioxide pressure dependence from the number of moles of CO<sub>2</sub> absorbed in one liter of solution and in the form of dependence of amount CO<sub>2</sub> absorbed on the reaction time.

On the basis of carbon dioxide absorption isotherms can be concluded that solutions Solvent 1 and Solvent 3 are characterising by significantly worse sorption capacity than monoethanolamine solution. This may be due to the absence of the fast absorbing primary amines in the solution, which have an activating effect on tertiary amines.

In the case of solution Solvent 2 and its modification – Solvent 2.2. was possible to obtain sorption capacity comparable or even slightly higher than 30% MEA. In these solutions is used a mixture of fast absorbing primary amines, sterically hindered amines and small amount of cyclic amines as an activator. There was completely eliminated tertiary amines additive. In addition, the solution Solvent 2.2. has a minimal amount of water (necessary to dissolve some solution components). This should significantly reduce the heat capacity of solution and as a result reduce energy consumption in desorption process.

Graphs of the amount of CO<sub>2</sub> absorbed versus time shows that the best absorption rate have solutions Solvent 2 and Solvent 2.2. The second of these solutions has a significantly higher absorption rate than 30% wt. monoethanolamine and other solutions. This is most likely the consequence of low water content in the solution. This eliminates almost completely slow reaction to bicarbamate. All amines in the solution reacts only to form carbamate, similar as in the case of monoethanolamine.

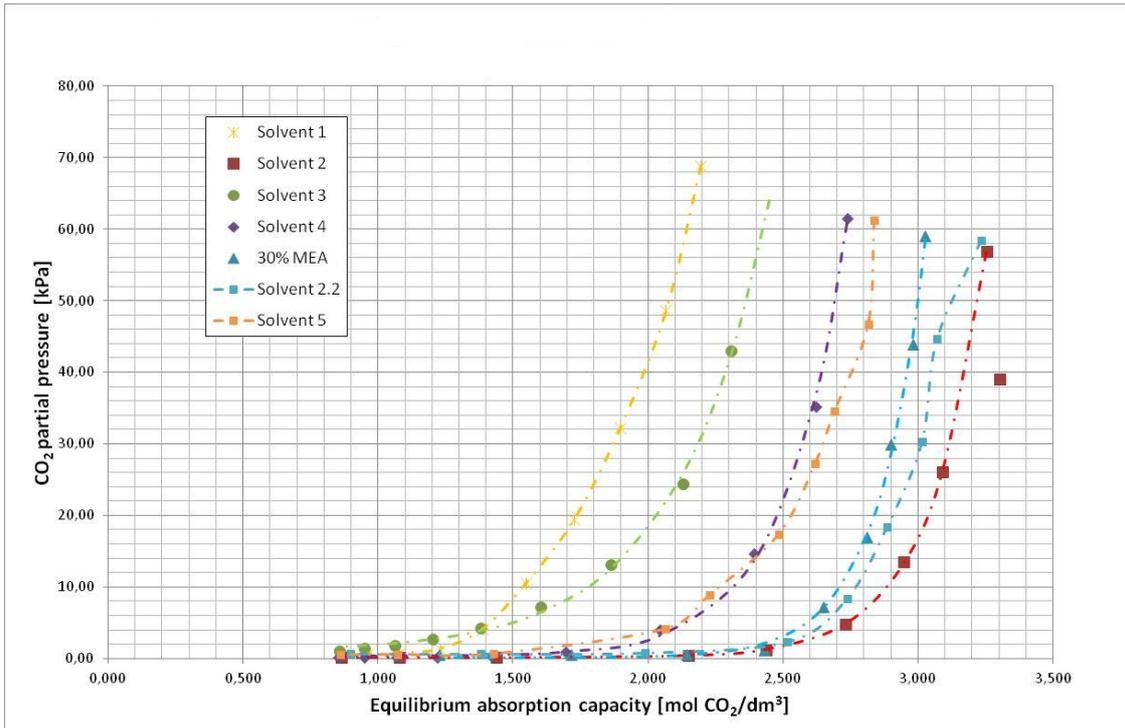


Fig. 2 Dependence on partial CO<sub>2</sub> pressure of over the solutions versus number of moles of CO<sub>2</sub> absorbed in one dm<sup>3</sup> of solution for temperature 30 deg. C.

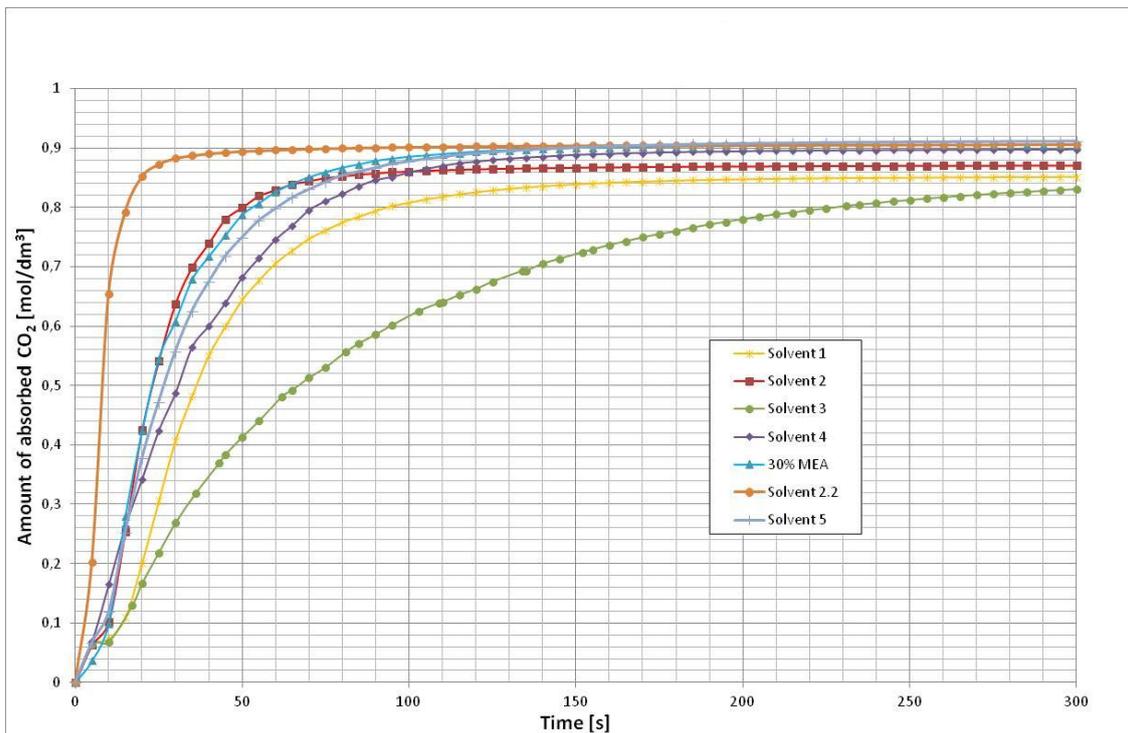


Fig. 3. Dependence of amount of CO<sub>2</sub> absorbed in one dm<sup>3</sup> of solution versus reaction time at temperatures from 30 deg. C.

**Summary**

The data obtained during the research shows that by an appropriate amine blends composition, we are able to obtain solutions which are alternatives to monoethanolamine solution. Selected during the tests solutions – Solvent 2, Solvent 2.2 and Solvent 5 – were characterized by parameters similar or even slightly better than 30% wt. monoethanolamine. In addition, these solutions showed a greater increase in the carbon dioxide partial pressure with increasing temperature than 30% wt. MEA. This indicates a potentially lower desorption heats of these solutions.

The results showed the necessity to use in a mixtures fast reacting primary amines due to their favorable influence on both the kinetics and the sorption capacity. In addition, all of the additives used in the study had a higher resistance to oxidative and thermal degradation [3],[4].

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