

# Chemical Comparative Study of the Chemisorption of Carbon Dioxide in Non-Aqueous and Aqueous Systems

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**ABSTRACT** 

In this article, the chemical comparison of the chemical absorption of carbon dioxide in non-aqueous and aqueous systems was carried out. Investigation in non-aqueous systems 2-amino 2-methyl-1-propanol in aqueous medium used by MEA.

**Keywords:** 

Mea, carbon dioxide, non-aqueous and aqueous systems, 2-amino-2-methyl-1-propnaol (AMP), dimethyl sulfoxide (DMSO).

### Introduction

CO gas belongs to the category of highly toxic gases. Its permissible limit concentration in the workplace - 20 mg/m<sup>3</sup>, in the atmosphere (max) - 3 mg/m3, average per day - l mg/m<sup>3</sup> constitutes CO gas poisons the blood, dizziness, notes causes shortness of breath, tremors, severe poisoning can cause death. CO gas contains the element carbon It is formed due to incomplete combustion of the substance. This gas in black and colored in the process of casting metals, during the operation of engines, blasting operations, nitrogen in production industry of compounds, in the petrochemical industry, ammonia, saltpeter, it is formed in metal, alcohol and similar productions. This gas Absorption and catalytic methods are in industry used neutralization. In the absorption method, CO gas is absorbed into special solutions and CO is separated separately gases are sent for processing. In the catalytic method, CO gas is used as a catalyst oxidized to relatively

harmless CO<sub>2</sub> gas and released into the atmosphere is sent.Release of thousands of tons of waste into the environment, production As a result of the processes, tons of toxic gases and substances are released into the atmosphere release leads to a change in the heat balance. For example, in the composition of air the increase of carbon dioxide gas causes a certain amount of climate warming possible Carbon dioxide gas is a colorless gas that is present in pure, clean air amount is 0.03%.

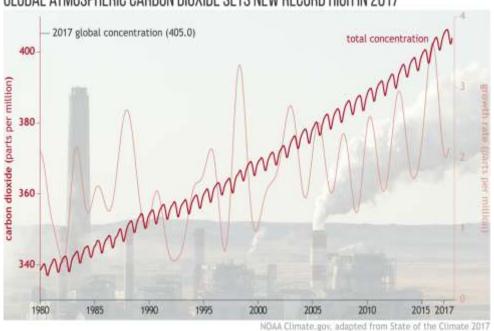
# Materials and methodology

This gas is used in the breathing of living organisms, oil and in gas-fired boilers, steam boilers, thermal power plants, automobiles separates during operation. Over the next hundred years, the air content is choppy the amount of anhydride is increasing by 14%, and at present it is increasing by 0.4% every year. Approximately 140 billion from the 1860s to the present. carbon per ton released into the atmosphere, and currently 8 r year globally

billion about a ton of carbon is released. The air content of this gas increasing the amount creates a certain layer in the atmosphere and heat to space slows down the transmission. This, in turn, can lead to a certain increase in the temperature of the earth's surface. It is known that the air contains carbon dioxide gas As a result of the increase in the amount, it is estimated that the air will increase by 1.5-2.5 °C by 2030 is being done.

Among the toxic gases transported to the environment, mainly CO,  $SO_2$ , NOx (nitrogen oxides),  $C_xH_y$  (hydrocarbon gases) and dust occupy high places. More than 250 million tons of dust, 200 million tons of CO, 150 million tons of  $SO_2$ , 50 million Tons of nitrogen oxides, more than 50 million tons of hydrocarbons substances, as well as more than 20 million tons of  $CO_2$  gas.

Picture.1.
GLOBAL ATMOSPHERIC CARBON DIOXIDE SETS NEW RECORD HIGH IN 2017



The largest production enterprise in Uzbekistan "Shortan Gazkimyo complex" also has a very negative impact on atmospheric pollution (1-table).

Table.1.

Table.1. -Waste released into the atmosphere by "Shortan Gas Chemical Complex" in 1 year composition of gases

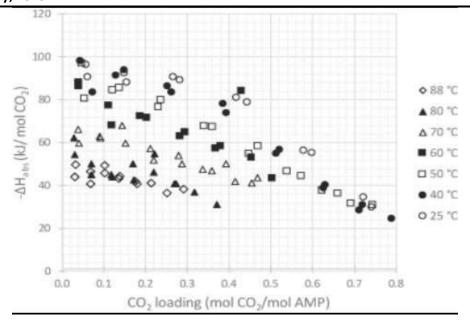
Nº	Exhaust gas name	Quantity,t/y
1	The amount of waste gases released in a year	2561,425
2	Nitrogen (IV) oxide (NO <sub>2</sub> )	448,229
3	Nitrogen (II) oxide (NO)	742,814
4	Carbon (IV) oxide (CO <sub>2</sub> )	1016,569
5	Hydrocarbons (C <sub>n</sub> H <sub>m</sub> )	73,870
6	Sulfur (IV) oxide (SO <sub>2</sub> )	2,930
7	Methane (CH <sub>4</sub> )	6,858
8	Institution	42,596

Cleaning. processing. recuperation and neutralization of waste gases methods are different, they mainly depend on the type of that emits its chemical source gases, concentration. composition, amount. temperature and so on depends on the indicators. To neutralize the gases coming out of production enterprises created interpolymer sorbents harmful to the environment NO<sub>2</sub>, SO<sub>3</sub>, NO, It has the ability to trap HF, HCl type gases, rare and heavy metals. Harmful substances in exhaust gas during catalytic gas purification oxidation. based reduction decomposition processes in the presence of a catalyst rendered harmless. It is in the composition of the exhaust gas that is neutralized there should be no dust and substances toxic to the catalyst. This method exhaust gases from nitrogen, sulfur and carbon oxides and organic solvents It is used for cleaning from vapors. The process is catalytic of various constructions is carried out in reactors. In the thermal method, the exhaust gas content is harmful, bad and the process of neutralizing unpleasant smelling substances is carried out by burning them is increased. The process is carried out in special ovens and torch burners. The advantage of the process is the simple design of the equipment used in the method possession, disadvantage - additional fuel for the implementation of the process (usually natural consumption gas) absorption of gases produced during

combustion or should be retained using adsorption methods.

# **Result and discussion**

a) Non-aqueous amine systems have been suggested as energy-efficient alternatives to conventional aqueous amine systems in postcombustion carbon capture, regeneration temperatures can be achieved. The solubility of CO<sub>2</sub> and heat of absorption in non-aqueous systems were studied using the sterically hindered amine 2-amino-2-methyl-1propnaol (AMP) in the organic solvent dimethyl sulfoxide (DMSO). 13C NMR was used to study the product species in solution as CO<sub>2</sub> reacts with AMP in either DMSO or N-methyl-2pyrrolidone (NMP). The solubility of CO2 in AMP/DMSO showed that low loadings could be achieved at 80-88°C. indicating regeneration can be carried out at lower temperatures than in conventional aqueous systems. Precipitation occurred at 25 wt% AMP in DMSO, increasing the overall capacity of the system. The heat of absorption decreased with increasing temperature, and was explained by physical absorption dominating the absorption mechanism at higher temperatures. This was also confirmed by the results of NMR, as less chemically absorbed species were observed at higher temperatures. The reaction products observed in AMP/DMSO and AMP/NMP were identified as the AMP carbamate, bicarbonate from water impurities, and the AMP carbonate from CO<sub>2</sub> reacting with the hydroxyl group of AMP.



The reaction mechanism proposed for the nonaqueous AMP-NMP system is given below (reactions 1-4), where the reacting amine (AMP) is denoted RNH2 (Svensson et al., 2014a), (g) represents species in gas phase, (sol) species in solution and (s) solid precipitate. CO<sub>2</sub> is first dissolved in the solution (1), and then reacts with the AMP in the solution to form a zwitterion (2). This zwitterion then reacts with another AMP molecule to form carbamate (3). As the CO<sub>2</sub> loading increases in the solution, the AMP carbamate precipitates as solid crystals (4). Thus, two moles of AMP react with one mole of CO<sub>2</sub>, which limits the chemical CO<sub>2</sub> loading of the AMP-NMP system to 0.5 mol CO<sub>2</sub>/mol AMP. However, loadings can exceed 0.5 mol CO<sub>2</sub>/mol AMP due to physical absorption in the organic solvent (NMP).

$$CO_2(g) \rightleftarrows CO_2(sol)$$
 (reaction.1.)  
 $CO_2(sol) + RNH_2(sol) \rightleftarrows RNH_2COO$  (sol)  
(reaction.2.)

 $RNH_2COO(sol)+RNH_2(sol) \rightleftharpoons RNH_3(sol)+RNHCO$  O(sol) (reaction.3.)

RNH<sub>3</sub>(sol) +RNHCOO(sol) ≠RNH<sub>3</sub>+RNHCOO (sol) ( reaction.4.)

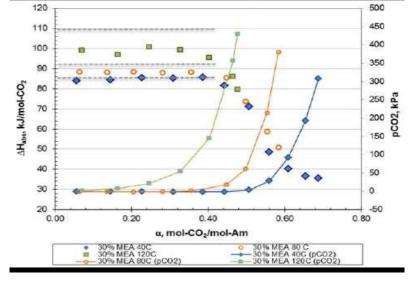
The reaction mechanism above is similar to that in aqueous MEA. However, when water is present in the absorption system, bicarbonate may also be formed (5), increasing the maximum loading capacity to 1 mol CO<sub>2</sub>/mol amine.

RNHCOO-(sol)+ $H_2O \rightleftharpoons RNH_2$  (sol)+ $HCO_3$ -(sol) The combination of AMP and NMP in aqueous solutions has been studied by Pakzad et al. (2018) using water concentrations of about 50 wt%. They found that at 60 °C, the solubility of CO<sub>2</sub> was highest in the AMP-H<sub>2</sub>O system, lower in the AMP-NMP-H2O system, and lowest in the non-aqueous AMP-NMP system. These findings are in agreement with the reaction mechanism described above. It should also be noted that in the systems studied by Pakzad et al. (50 wt% water, temperatures between 40 and 80 °C and AMP concentrations up to 30 wt%) solid precipitation was only observed in some of the experimental runs, and only when the partial pressure of CO<sub>2</sub> exceeded 300 kPa in the vapour-liquid equilibrium cell.

b)... 2 removal using solvent systems is the most widely used technology at present and 21 large-scale CCS projects reported to be under construction or in operation around the world can capture up to 40 million tons of CO<sub>2</sub> annually [1]. Lot of efforts are currently made to develop novel solvent systems in order to overcome the main drawback of this technology - high energy consumption for solvent regeneration. One of the important thermodynamic parameters necessary for the estimation of the energy consumption is a heat

of absorption of CO<sub>2</sub>," H abs . The exothermic reaction taking place when CO2 is bound to the amine in the absorber generates a strong temperature bulge in the absorber. Basically, in flue gas treatment, all the reaction enthalpy leaves the plant with the treated flue gas, as solvent vapour, and is lost in the water wash knockout cooler. This implies that the reaction enthalpy must be supplied at stripper temperature in order to regenerate the solvent. In addition comes the need to generate stripping steam as sweep gas for the solvent, as given by the molar ratio between water and at the desorber top. This contribution to reboiler duty is given by the difference in between heat of absorption and heat of vaporization, where a high heat of absorption gives a stronger effect of temperature swing and may contribute in a reduced total reboiler duty. This always depends on the solvent properties and the chosen process configuration. Earlier work on measurement of the heat of absorption have shown that the values seen for amines considered in post combustion solvents have values within a relatively narrow range. However, recent work shows that there are still large differences arising through temperature effects. This was also discussed in early literature as e.[2], where the heat of absorption for H<sub>2</sub>S in MEA is shown to increase strongly with temperature. Two types of calorimeters are used in literature for measuring the heats of absorption of CO<sub>2</sub> in different solvents.

Experimental heats of absorption measured using flow calorimeters differential in temperature, since experiments are performed at constant temperature. However, they are integral in loading, since the measurements are done by mixing fresh amine solution (zero loading) and CO2 to a certain loading point. These data show little or no effect of loading on the heat of absorption [3]. Reaction calorimeter allows measurements of the heats of absorption differential both in temperature and loading by conducting experiments at constant temperature and adding CO<sub>2</sub> in several steps. The same set-up has been used in this work after some modifications and new experimental data are presented in this work. Ethanolamine (MEA, 99%, CAS 141-43-5) from Sigma Aldrich and CO<sub>2</sub> (5.0) from YARA were used as received. Aqueous solutions were prepared by gravity using distilled de-ionized water. experimental set-up (Fig. 1) and procedure have been described in detail.[4] and only briefly described here. The reaction calorimeter CPA 122 (Chemisens) is mechanically agitated reactor of 2 L volume. The same set-up was used in this work after a small modification: the CO2 in this work has been fed through the bottom of the reactor directly into the liquid phase instead of feeding through the reactor top into the vapour phase as has been done earlier.



Also the  $CO_2$  flow-meter was recalibrated and the amount of  $CO_2$  fed to the reactor was calculated from the flow-meter data in addition to the estimation of the  $CO_2$  amount based on the pressure drop in the CO cylinders using EOS. The temperature in the reactor is measured with a Pt100 temperature sensor (accuracy  $\pm 0.1$  K at 273 K,  $\pm 0.027$  K at 373 K); pressure transducer OMEGA (0-10 bara, 0.15% FS) is used.

#### Conclusion

The solubility of  $CO_2$  and heat of absorption in non-aqueous systems were studied using the sterically hindered amine 2-amino-2-methyl-1-propnaol (AMP) in the organic solvent dimethyl sulfoxide (DMSO). When  $CO_2$  binds with the amine in the absorber, the exothermic reaction that occurs causes a strong temperature rise in the absorber. The data in Figure 3 show that loading has little or no effect on the heat of absorption.

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