



# Simultaneous measurement solubility of carbon dioxide + hydrogen sulfide into aqueous blends of alkanolamines at high pressure



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## ABSTRACT

Treatment of the sour natural gas is a major step in natural gas processing so that the acid gases such as H<sub>2</sub>S and CO<sub>2</sub> are removed from natural gas stream. The acid gases are harmful to environment and destroy the production equipment so that their presence in gas stream leads to corrosion and lowering heating value. On the other hand, for reliable and optimum design of separation equipment, primarily sufficient and accurate equilibrium data of the acid gases solubility in the aqueous alkanolamines is required. In this work, the simultaneous solubility of the H<sub>2</sub>S + CO<sub>2</sub> in the alkanolamine mixtures is measured at 343 K and total pressure range of 0.1–2.1 MPa. The blends are studied as the aqueous mixtures of N-methyldiethanolamine (MDEA) + 2-amino-2-methyl-1-propanol (AMP) + Piperazine (Pz) and the aqueous mixtures of diisopropanolamine (DIPA), AMP and Pz. For the acid gas solubility measurements, a high pressure static apparatus is used through a volumetric method. The mass fraction of the total alkanolamine is fixed at 0.45 and the results are presented as the partial pressure of each acid gas against its loading (mole acid gas/total mole amine) and mole fraction. The influence of the AMP and Pz on the aqueous DIPA-based and MDEA-based systems are studied so that it is observed that the absorption of the CO<sub>2</sub> in the aqueous alkanolamine enhances through separate blending of the AMP and Pz with the aqueous system of MDEA or DIPA and the absorption of the H<sub>2</sub>S reduces in both of the aqueous DIPA-based and MDEA-based systems.

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## 1. Introduction

The natural gas is contaminated with several impurities such as H<sub>2</sub>S and CO<sub>2</sub> that forms an acidic solution in the presence of water. These acid gases should be removed from natural gas because they destroy process equipment and transportation lines; pollute the environment; and reduce heating value of natural gas. Moreover, H<sub>2</sub>S is a poisonous and toxic gas so that both CO<sub>2</sub> and H<sub>2</sub>S are corrosive and damage pipeline, valves, etc. [1]. To remove these gases from natural gas, several processes such as physical and chemical absorption are applied through using an acid gas removal unit which consists of a chemical or physical contactor and a stripper column. Using alkanolamines in a chemical absorption process presents some advantages such as high capacity for absorption, high reaction rate with H<sub>2</sub>S and CO<sub>2</sub>, low vapor pressure, low cost and low corrosiveness [2,3]. An alkanolamine molecule possesses at least one amino group and one hydroxyl group in which these

groups intensify the alkalinity of the solution to improve absorption of the acid gases and reduce the vapor pressure of the solution [4]. The amines are classified in three types, namely primary, secondary and tertiary alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA). MEA and DEA form carbamate in reaction with CO<sub>2</sub>, because stability of carbamate is relatively high and presents a low rate of hydrolysis to bicarbonate so that the loading of CO<sub>2</sub> absorption is limited to about 0.5 mol of CO<sub>2</sub> per mole of amine [5]. Another secondary alkanolamine is diisopropanolamine (DIPA), which uses in the ADIP, Sulfinol and SCOT processes, that the selectivity of DIPA is more toward to H<sub>2</sub>S than CO<sub>2</sub>. In addition, DIPA presents low regeneration steam requirements, great potential for absorption of the other sulfur compounds such as COS and CS<sub>2</sub> that it is less corrosive in comparison to the other primary or secondary alkanolamines [6]. MDEA is known more for its selective removal of H<sub>2</sub>S in comparison to CO<sub>2</sub>, because MDEA does not form carbamate and presents a lower rate of reaction with CO<sub>2</sub> respect to primary and secondary alkanolamines [7] so that MDEA can absorb 1 mol CO<sub>2</sub> per mole of amine stoichiometry. The low enthalpy of the MDEA reaction with H<sub>2</sub>S and CO<sub>2</sub> leads to lower energy requirement for the solvent regeneration that is another feature of MDEA [8]. Both DIPA

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### Nomenclature

|     |                            |
|-----|----------------------------|
| $n$ | number of mole             |
| $P$ | pressure                   |
| $R$ | gas constant               |
| $T$ | temperature in Kelvin      |
| $u$ | uncertainty                |
| $V$ | volume                     |
| $x$ | liquid phase mole fraction |
| $y$ | vapor phase mole fraction  |
| $Z$ | compressibility factor     |

### Subscripts

|                      |                  |
|----------------------|------------------|
| $\text{CO}_2$        | carbon dioxide   |
| $\text{H}_2\text{S}$ | hydrogen sulfide |
| inj                  | injection cell   |
| g                    | gas phase        |
| l                    | liquid phase     |
| tot                  | total            |
| v                    | vapor            |
| 1                    | before injection |
| 2                    | after injection  |

### Greek letters

|          |  |
|----------|--|
| $\alpha$ | $\text{CO}_2$ or $\text{H}_2\text{S}$ loading in liquid phase, mole of gas/mole of amine |
| $\rho$   | density  |

and MDEA present fast reactivity with  $\text{H}_2\text{S}$  so that the protonation reaction can proceed immediately without controlling the reaction kinetically [9,10].

Another class of alkanolamines is sterically hindered amines such as AMP so that a sterically hindered amine is a primary alkanolamine structure in which amino group is attached to a ternary carbon atom. Moreover, a hindered amine can be as a secondary alkanolamines that the amino group is attached to a secondary or a ternary carbon atom. Because of AMP forms bicarbonate through  $\text{CO}_2$  absorption, thus, the acid gas loading is about 1 mol  $\text{CO}_2$  per mole of amine so that for its regeneration lower energy is required [5]. AMP also reacts with  $\text{CO}_2$  faster than MDEA that it is an advantage over MDEA. Aroua et al. [11] showed that the solubility of  $\text{CO}_2$  in the aqueous MDEA + AMP with equal ratio is greater than the aqueous MDEA so that its loading value is between the aqueous AMP and aqueous MDEA.

In the recent years using the aqueous alkanolamines blended with some additive, which is known as chemical activator, is widely used to enhance the loading of the acid gases in solvent. Piperazine (Pz) is most commonly used as a chemical activator and in comparison to the other chemical activators is resistant to thermal and oxidative degradation and presents a higher rate of reaction. Additionally, the blended alkanolamines with Pz has low amine volatility because of non-ideality of the solvents [12].

Recently, the blended alkanolamines are widely studied to overcome the disadvantage of using a single alkanolamine. The mixed-alkanolamines consisting of a primary or secondary alkanolamine is blended with a tertiary alkanolamine that allows one to combine higher  $\text{CO}_2$  loading of primary or secondary amines with higher selectivity of tertiary alkanolamines toward  $\text{H}_2\text{S}$ . Thus, using the mixed-solvent allows one to remove  $\text{H}_2\text{S}$  from the  $\text{H}_2\text{S} + \text{CO}_2$  mixture so that  $\text{CO}_2$  reaction with alkanolamine is taking place kinetically, because of the slow absorption of  $\text{CO}_2$  [9]. Using a mixed-solvent of alkanolamines with appropriate molecular structure, an unstable carbamate ion may be formed in which it hydrolysis to bicarbonate ion so that the  $\text{CO}_2$  gas loading of unity

is achieved [4]. For selective removal of  $\text{H}_2\text{S}$  in the presence of  $\text{CO}_2$ , a molecular structure for solvent may be designed that repress the formation of carbamate without influencing on the  $\text{H}_2\text{S}$  absorption [4].

At a gas sweetening process, absorption of sour gases is taking place in an absorption column at high acid gas partial pressure and low temperature so that the desorption for regeneration of the solvent occurs at high temperature and low acid gas partial pressure. So far a lot of data are given on the solubility of single acid gas in the one or mixed aqueous alkanolamines at the different pressure and temperature so that the available solubility data for  $\text{CO}_2$  is more than  $\text{H}_2\text{S}$ . Moreover, the simultaneous data of the  $\text{CO}_2 + \text{H}_2\text{S}$  solubility is needed for design an acid gas removal unit. Several works have been carried out for measurement of the solubility of the mixture of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  in the aqueous alkanolamines. Ho and Eguren [13] measured the solubility of the  $\text{H}_2\text{S} + \text{CO}_2$  in the aqueous MDEA and DEA solutions at 313 and 373 K. Jou et al. [14] measured the solubility  $\text{H}_2\text{S} + \text{CO}_2$  in the aqueous MDEA solutions at 313 and 373 K. Savage et al. [15] obtained data on the simultaneous absorption of  $\text{CO}_2 + \text{H}_2\text{S}$  in the MDEA solution. They illustrated that MDEA is selective toward  $\text{H}_2\text{S}$  and the  $\text{CO}_2$  absorption is controlled kinetically. Huttenhuis et al. [16] obtained the experimental data of the solubility of the  $\text{H}_2\text{S} + \text{CO}_2$  simultaneously in MDEA with methane and nitrogen as the makeup gases so that it was concluded that type of the inert gas presents an influence on the  $\text{H}_2\text{S}$  solubility. However, the partial pressure of the  $\text{CO}_2$  was not affected by type of the inert gas and the partial pressure of the  $\text{H}_2\text{S}$  enhances greatly with increasing the  $\text{CO}_2$  loading. Lawson and Garst [17] measured the simultaneous absorption of  $\text{CO}_2 + \text{H}_2\text{S}$  in MEA and DEA over wide range of acid gas composition and temperature. They compared their data with the others so that they made some assumptions in their calculations such as keeping water/amine ratio the same at the equilibrium condition. Mandal and Bandyopadhyay obtained the experimental data on the simultaneous solubility of  $\text{H}_2\text{S} + \text{CO}_2$  in the aqueous solution of AMP + DEA [18] and MDEA + DEA [19]. They illustrated that the aqueous solution of AMP + DEA presents an efficient solvent for simultaneous absorption of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  [18]. Also, they suggested that for absorption of  $\text{CO}_2 + \text{H}_2\text{S}$  simultaneously, it will be favorable to use the aqueous AMP with low composition of DEA. Moreover, they observed [19] that for the aqueous MDEA + AMP, the rate of absorption of  $\text{CO}_2$  increases quickly with increasing DEA concentration in the blends, while that of  $\text{H}_2\text{S}$  increases to a much lesser extent. Thus, there is an expected decrease in the selectivity factor with increasing concentration of DEA. Blanchon Le Bouhelec-Tribouillois et al. [20] used a semi-synthetic apparatus to measure the solubility of the mixture of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  in the diethanolamine aqueous solution. They observed that at a fixed  $\text{H}_2\text{S}$  loading, injecting of  $\text{CO}_2$  to the gas stream enhances the partial pressure of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  and vice versa. Lee et al. [21] and Jane et al. [8] obtained data on the solubility of mixture of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  in the aqueous DEA solution at 323 and 373 K and the aqueous DEA + AMP solution at 313 and 353 K, respectively. Yih and Sun [22] measured solubility of the  $\text{CO}_2 + \text{H}_2\text{S}$  mixture in the aqueous DIPA solution. They studied the effect of the liquid and gas flow rates, temperature and liquid concentration on the absorption rate and selectivity factor. They concluded that the operation at low liquid and high gas flow rates, low temperature and low DIPA concentrations leads to selective removal of  $\text{H}_2\text{S}$  from the acid gas mixtures. Li and Chang [23] measured the simultaneous absorption of  $\text{CO}_2 + \text{H}_2\text{S}$  in the aqueous MEA + AMP mixture so that it was observed this amine mixture presents the higher  $\text{H}_2\text{S}$  and lower  $\text{CO}_2$  loading capacities. Mandal et al. [24] investigated the selective absorption of  $\text{H}_2\text{S}$  from the  $\text{N}_2$  streams containing  $\text{H}_2\text{S}$  and  $\text{CO}_2$  into the aqueous solutions of AMP as well as MDEA. They found that the effect of gas-phase resistance on the absorption of  $\text{H}_2\text{S}$  was significant. Also they observed

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