

## PA8 Absorption of Methyl Mercaptan into Aqueous Diethanolamine

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### 1. INTRODUCTION

Methyl mercaptan as known as methanethiol is an invisible gas with typical sulfur odor. It is the sulfur analog to methanol. The gas is toxic and very corrosive and may form explosive mixtures with air.

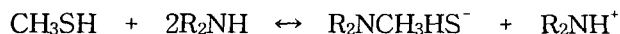
The objective of the work presented here is to measure the total solubility of Methyl mercaptan in DEA solutions over a wide range in temperature and Methyl mercaptan partial pressure and to measure the physical solubility of N<sub>2</sub>O in these solutions as a function of the CO<sub>2</sub>-loading.

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Thiols do not develop any hydrogen bonds therefore they have a high vapor pressure. The removal of sulfur gases relies on the physical solubility which is low in water and aqueous solutions. Methyl mercaptan is a weak acid and forms salts with aqueous bases. The reactivity in alkaline solutions is low. Only strong hydroxide solutions will act as appropriate chemical solvents. Often organic solvents are more effective than hydroxide for absorption of sulfur gas impurities. The pK<sub>a</sub>-value is between 10 and 12. The molecular weight is 48.11 g/mole. Because of its structure it is assumed to have a non-ideal gas behavior. The used methyl mercaptan has been delivered from Aldrich Chemical Company, Milwaukee. The gas has a purity of at least 99.5%.

Diethanolamine DEA is a common solvent in acid gas treating processes. Amines are able to accept protons easily because they have a couple of free electrons at the nitrogen atom. Therefore amines have a strong alkaline character in aqueous solutions. The molecular weight M<sub>DEA</sub> = 105.14 g/mole.

The reaction between DEA and methyl mercaptan is thought to be



It is expected a second-order kinetics.

## 2. EXPERIMENTAL

Figure 1 shows a schematic drawing of the modified Zipperclave reactor used in this work. The reactor consists of a one liter stainless steel cylindrical tank with an air-driven magnetically coupled stirrer on the top. There are valves for inlet of gas and liquid, and a connection to a vacuum pump. A thermocouple inserted in the cell measures the temperature to an accuracy of  $\pm 0.1^\circ\text{C}$ . The pressure is measured by a pressure transducer with an accuracy of  $\pm 0.02$  psi.

Initially a weighed sample of approximately 500g liquid is sucked into the reactor. The temperature is then adjusted to the desired value through use of the external heating jackets. A vacuum is then pulled on the reactor so that the liquid exists under its own vapor pressure. This solution vapor pressure,  $P_v$ , is measured.

## 3. RESULTS AND DISCUSSION

This equilibrium pressure  $P_{\text{CO}_2}$  ( $= P_{\text{T1}} - P_v$ ) is measured and the moles of  $\text{CO}_2$  remaining in the gas phase is determined from

$$N^g_{\text{CO}_2} = P_{\text{T}_2} - P_{\text{CO}_2} - P_v$$

The moles of  $\text{CO}_2$  in the liquid is then determined from

$$N^l_{\text{CO}_2} = N_{\text{CO}_2} - N^g_{\text{CO}_2}$$

The  $\text{CO}_2$ -loading in the liquid phase is defined as

$$L_{\text{CO}_2} = \frac{N^l_{\text{CO}_2}}{N_{\text{Am}}}$$

The moles of  $\text{N}_2\text{O}$  in the gas phase are determined from  $P_{\text{N}_2\text{O}}$  by

$$N^g_{\text{N}_2\text{O}} = \frac{z_{\text{N}_2\text{O}} P_{\text{N}_2\text{O}} V_g}{RT}$$

## 4. CONCLUSION

The nitrous oxide analogy method may be used with the  $H_{\text{N}_2\text{O}}$  data presented here to estimate the physical solubility of  $\text{CO}_2$  as a function of temperature and  $\text{CO}_2$ -loading. The physical solubility of  $\text{CO}_2$  is the key physicochemical property needed to calculate  $\text{CO}_2$  mass transfer rates.

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