Study on apparent absorption rate of H$_2$S in MDEA-PZ aqueous solutions at 313.2K

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Abstract: The apparent absorption rate of H$_2$S in piperazine (PZ) promoted N-methyldiethanol amine (MDEA) aqueous solution was determined at 313.2K. The mass fractions of PZ ranged from 0 to 0.1. The pressures of H$_2$S ranged from 300Pa to 500Pa. On the basis of experimental measurements, the influences of partial pressure and mass fractions of PZ on the apparent absorption rate of H$_2$S were demonstrated.

1. Introduction
The catalysts poisoning, human health and equipment corrosion in the coking industry caused by the emissions of hydrogen sulphide (H$_2$S) have attracted increasing attentions worldwide and the reduction of H$_2$S has become a global issue[1–3]. A wide range of approaches, including liquid absorption, solid adsorption, biological degradation, membrane separation [4-6], have been developed for H$_2$S removal. Among these technologies, amine-based absorption technologies are widely used in the gas separation for mixture gas containing H$_2$S[7]. Alkanolamines, such as N-methyldiethanolamine (MDEA), diisopropanolamine (DIPA), sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) and the chemical activators such as piperazine (PZ) have been widely applied to remove the acid gases in industrial processes [8-10]. However, the major disadvantages of traditional alkanolamine aqueous solutions are the high energy cost of regeneration and the corrosion. Due to the disadvantages of traditional alkanolamines, new absorbents with low corrosivity, low energy cost in regeneration, high absorption capacity and high reaction rate are urgently required [11].

As one of the tertiary amines, MDEA has the advantages of high resistance to thermal and chemical degradation, and low corrosivity [12]. Rinker et al. [13] shown that the density of aqueous MDEA increased with increasing H$_2$S loading while the viscosity decreases with increasing H$_2$S loading. MDEA is a tertiary amine that is widely used in the gas-processing industry and has proven to be an effective chemical solvent for selective absorption of H$_2$S [13]. And it has been well documented that adding activators such as PZ (piperazine) into alkanolamine aqueous solutions can improve absorption performance.

Mazloumi et al. [14] obtained that at acid gas loadings below the crossing point, and the H$_2$S solubility is enhanced with increasing PZ concentration. Haghtalab et al. [15] measured that at fixed partial pressure and constant mass percent of (AMP + PZ), with decreasing temperature the H$_2$S loading is enhanced. Speyer and Maurer [16] measured the solubility of H$_2$S in the aqueous of PZ at T = (313.5 and 392.2) K in the low loading region. However, the influences of concentration and partial pressure on apparent absorption rate of H$_2$S are still unknown.

The main purposes of this work are to experimentally determine the apparent absorption rate of H$_2$S in MDEA-PZ aqueous solution and demonstrate the effects of concentration and the partial
pressure of H\textsubscript{2}S.

2. Experimental Section

2.1. Materials
The MDEA was manufactured by Shanghai Aladdin Reagent, with a mass purity ≥ 99%. The PZ was purchased from Sinopharm chemical reagent, with mass purity ≥ 99%. They were used without further purification. Aqueous solutions of MDEA-PZ were prepared by adding the high purity water.

2.2. Apparatus and procedure
The apparent absorption rate was measured by the equipment composed of one high-pressure H\textsubscript{2}S tank, one mass flow controller (MFC), one mass flow meter (MFM), one absorption bottle, one constant temperature water bath, one desiccator and one H\textsubscript{2}S analyzer (manufactured by Germany Sensors Europe GmbH, the accuracy is ±2%).

During the experiment, H\textsubscript{2}S and N\textsubscript{2} from high-pressure tanks were respectively inlet into the mass flow controllers to maintain constant flow rates \(v_{H_2S}\) and \(v_{N_2}\), and then into the gas mixer. The gas mixture with certain volume fraction of H\textsubscript{2}S flowed into the absorption bottle and then was absorbed by the solution. The residual and unabsorbed gas firstly flowed into the desiccator, and then into the H\textsubscript{2}S analyser and finally into the mass MFM. The volume concentration of H\textsubscript{2}S (\(C_i\)) was measured by the H\textsubscript{2}S analyser, and the flow rate (\(v_i\)) was measured by the MFM. The \(C_i\) and the corresponding time (\(t_i\)) were simultaneously recorded by the computer (interval time \(Dt = 1s\)). We defined the absorption rate (R/g H\textsubscript{2}S 100g aqueous solution min\textsuperscript{-1}) as 0.5m/t 0.5 (\(t_{0.5}\) is the absorption time at which 50% of the absorption capacity is achieved).

3. Result and discussion
The experimental results for absorption rate of H\textsubscript{2}S in MDEA-PZ aqueous solutions are shown in Table 1.

| \(w_{MDEA}\) | \(w_{PZ}\) | 300 Pa | 400 Pa | 500 Pa |
|------------|-----------|--------|--------|--------|
| 0.3        | 0.00      | 0.397  | 0.411  | 0.422  |
|            | 0.05      | 0.519  | 0.528  | 0.544  |
|            | 0.075     | 0.630  | 0.654  | 0.667  |
|            | 0.4       | 0.05   | 0.400  | 0.523  | 0.645  |
|            | 0.00      | 0.396  | 0.511  | 0.624  |
| 0.4        | 0.075     | 0.405  | 0.535  | 0.647  |
Figure 1. Effect of $P_{H_2S}$ on the absorption rate of H$_2$S in 30%MDEA aqueous solution.
Symbols: experimental data; ● $w_{PZ}=0$; ◆ $w_{PZ}=0.05$; ▲ $w_{PZ}=0.075$. Lines: for guiding the eyes.

Figure 2. Effect of $w_{PZ}$ on the absorption rate of H$_2$S in 40%MDEA aqueous solution.
Symbols: experimental data; ● $P_{H_2S}=300$Pa; ◆ $P_{H_2S}=400$Pa; ▲ $P_{H_2S}=500$Pa. Lines: for guiding the eyes.

Figure 1 shows the effect of $P_{H_2S}$ on the absorption rate of H$_2$S in 30%MDEA aqueous solution, indicating that at given temperature the absorption rate increases with increasing partial pressure of H$_2$S.

Figure 2 shows the effect of $w_{PZ}$ on the absorption rate of H$_2$S in 40%MDEA aqueous solution, indicating that at given temperature the absorption rate increases with increasing $w_{PZ}$.

4. Conclusions
In this work, apparent absorption rate of H$_2$S in MDEA-PZ aqueous solution was determined. The effects of the mass fraction of PZ and different pressures of H$_2$S on apparent absorption rate were demonstrated. Our results show that:

(1) For MDEA-PZ aqueous solution, the absorption rate increases with the increase of $P_{H_2S}$ at given temperature and $w_{MDEA}$. The absorption rate of H$_2$S in MDEA aqueous solution is greatly affected by the partial pressure of H$_2$S.

(2) The absorption rate increases with the increase of the $w_{PZ}$ at given $w_{MDEA}$ and temperature.

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