Solubility of low partial pressure H$_2$S in MDEA-PZ aqueous solution

C Li$^1$, Y X Chu and D Fu

School of Environmental Science and Engineering, North China Electric Power University, Baoding, HB 071003, China

E-mail addresses: 1434854669@qq.com

Abstract: The solubility of hydrogen sulfide (H$_2$S) in piperazine (PZ) promoted N-methyldiethanolamine (MDEA) aqueous solution was investigated. The temperature ranged from 303.2K to 323.2k. The mass fraction of MDEA and PZ respectively ranged from 0.3 to 0.4 and 0 to 0.075. On the basis of experimental measurement, the effects of mass fraction and temperature on the solubility of H$_2$S in PZ-MDEA aqueous solution are illustrated.

1. Introduction

The pipe corrosion and catalyst poisoning caused by H$_2$S have attracted increasing attentions worldwide and the removal of H$_2$S has become a hot issue [1-3]. The amine-based chemical absorption technologies are considered to be the most robust and promising methods for removing H$_2$S [4-6]. Alkanolamines, including monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), piperazine (PZ) and 2-amino-2-methyl-1-propanol (AMP) have been widely used to remove H$_2$S from a variety of industrial processes [7-10].

Recently, the using of blended amine absorbents has attracted more and more attention. For example, application of the blends of MDEA with primary, secondary or sterically hindered amines in H$_2$S removal process attracted great attentions. It is well known that MDEA takes the advantages of high resistance to thermal and chemical degradation, low enthalpy of absorption, low solution vapor pressure and low corrosion [11-13]. Many studies have been focused on the absorption capacity of H$_2$S in the MDEA-based mixed alkanolamine solutions. Shokouhi M et al. [14] studied the absorption performance of H$_2$S in AMP promoted MDEA aqueous solution. Their results showed that with the increasing of [AMP]/[MDEA] ratio, the H$_2$S loading increased. Rebolledo-Libereros M. E. et al. [15] investigated the solubility of H$_2$S in MDEA-DEA aqueous solution at pressures ranging from 2.5 to 1036 kPa. Zoghi A T et al. [4] measured the equilibrium solubility of H$_2$S in MDEA-AEEA-H$_2$O systems.

Apart from this, PZ is considered to be a promising activator. Previous work shows that adding small amount of PZ into alkanolamine aqueous solutions can significantly enhance the absorption capacity [16,7,8]. It provides very useful information and important guidance for the follow up studies. Due to the advantages of PZ and MDEA, it is reasonable to expect that MDEA-PZ aqueous solution may be an attractive solvent for the removal of H$_2$S. However, experimental work concerning the solubility of H$_2$S in MDEA-PZ aqueous solutions is relatively rare.

The main purpose of this work is to experimentally determine the effects of temperature and solution concentration on the absorption capacity of H$_2$S in PZ promoted MDEA aqueous solution. To
this end, the solubility of H$_2$S in MDEA-PZ aqueous solution was measured under different temperatures and solution compositions.

2. **Experiment**

2.1. **Materials**

Chemicals used in this work are detailed in Table 1. They were used without further purification. Aqueous solutions of MDEA-PZ were prepared by adding deionized water (Electrical resistivity >15 MΩ•cm at 298 K) obtained from the Heal Force ROE-100 apparatus. An analytical balance (Jingtian FA1604A) with an accuracy of 0.1 mg was used to weigh all required chemicals.

| Chemical name | CAS No. | Purity (mole fraction, as stated by the supplier) | source |
|---------------|---------|-----------------------------------------------|--------|
| MDEA          | 105-59-9| ≥98%                                          | Aladdin Reagent |
| PZ            | 110-85-0| ≥99%                                          | Sinopharm Chemical Reagent |

2.2. **Apparatus and Procedure**

The experimental system to measure the absorption capacity is composed of one high-pressure H$_2$S tank, one high-pressure N$_2$ tank, two mass flow controllers (MFCs), one absorption bottle, one constant temperature water bath, one desiccator and one H$_2$S analyzer (manufactured by Germany Sensors Europe GmbH). The absorption bottle (250 mL) was immersed into the thermostatic bath and the temperature of the solution can be regulated within 0.1 K. The equipment was designed to operate at atmospheric pressure (±5 kPa) and the total pressure of the (H$_2$S + N$_2$) mixture is 100 kPa.

During the experiment, H$_2$S and N$_2$ from high-pressure tanks were respectively inlet into the mass flow controllers to maintain constant flow rate, and then into the gas mixer. The gas mixture with certain volume fraction of H$_2$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$_2$S analyzer. The H$_2$S concentration was measured by the H$_2$S analyzer. The data was recorded by a computer.

3. **Results and discussion**

The experimental results for the solubility of H$_2$S are shown in Table 2.

| $w_{\text{MDEA}}$ | $w_{\text{PZ}}$ | 303.2K | 313.2K | 323.2K |
|-------------------|-----------------|--------|--------|--------|
| 0                 | 0               | 0.575  | 0.402  | 0.340  |
| 0.30              | 0.050           | 0.986  | 0.798  | 0.651  |
| 0.075             | 0.050           | 1.257  | 0.917  | 0.731  |
| 0.40              | 0.050           | 0.687  | 0.455  | 0.361  |
| 0.075             | 0.050           | 0.897  | 0.747  | 0.534  |
| 0.40              | 0.075           | 1.065  | 0.817  | 0.612  |
Figure 1 shows the influence of $w_{PZ}$ on the absorption capacity of H$_2$S in MDEA-PZ aqueous solutions. From this figure, one may find that at given temperature and given $w_{MDEA}$, the absorption capacity increases with the increasing $w_{PZ}$.

Figure 2 shows the influence of temperature on the absorption capacity of H$_2$S in MDEA-PZ aqueous solutions. From this figure, one may find that at given $w_{MDEA}$ and given $w_{PZ}$, the absorption capacity decreases with the increasing temperature.

4. Conclusions
In this work, the absorption capacity of H$_2$S in PZ promoted MDEA aqueous solutions was investigated. The effects of $w_{PZ}$ and temperature on the absorption capacity were demonstrated. Our results show that:

1) At given temperature and given $w_{MDEA}$, the increase of $w_{PZ}$ tends to increase the absorption capacity of H$_2$S in MDEA-PZ aqueous solution.

2) The absorption capacity of H$_2$S decreases with the increase of temperature at given $w_{MDEA}$ and given $w_{PZ}$ in MDEA-PZ aqueous solution.

References
[1] Sadegh N, Stenby E H and Thomsen K 2015 Fluid. Phase. Equilibr 392 24-32
[2] Mochizuki Y and Tsubouchi N 2017 Energy. Fuel 31 8087-94
[3] Ma Y, Chen Z and Gong H 2016 Renew. Energy 96 1119-26
[4] Zoghi A T and Shokouhi M 2016 J. Chem. Thermodyn 100 106-15
[5] Sidi-Boumedine R, Horstmann S, Fischer K, Provost E, Fürst W and Gmehling J 2004 Fluid. Phase. Equilibr 218 149-55
[6] Uusi-Kyyny P, Dell’Era C, Penttilä A, Pakkanen M and Alopaeus V 2013 Fluid. Phase. Equilibr 338 164-71
[7] Mazloumi S H, Haghtalab A, Jalili A H and Shokouhi M 2012 J. Chem. Eng. Data 57 2625-31
[8] Haghtalab A and Izadi A 2015 J. Chem. Thermodyn. 90 106-15
[9] Dicko M, Coquelet C, Jarne C, Northrop S and Richon D 2010 Fluid Phase. Equilibr 289 99-109
[10] Sadegh N, Thomsen K, Solbraa E, Johannessen E, Rudolfsen G I and Berg O J 2015 Fluid Phase. Equilibr 393 33-9
[11] Fu D, Feng X and Zhang P 2017 J. Chem. Thermodyn 113 250-6
[12] Fu D, Zhang P and Mi C L 2016 Energy 101 288-95
[13] Jou F Y, Carroll J J, Mather A E and Otto F D 1993 Can. J. Chem. Eng 71 264-8
[14] Shokouhi M, Bozorgzade H and Sattari P 2015 J. Chem. Eng. Data 60 2119-27
[15] Rebolledo-Libreros M E and Trejo A 2004 Fluid. Phase. Equilibr 224 83-8
[16] Fu D, Wang L M, Mi C L and Zhang P 2016 J. Chem. Thermodyn 101 123-9