

Determination of the Mercury Solubility in Several Natural Gas Processing Fluids

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Abstract. The high concentration of mercury present in natural gas and the processing fluids can cause severe problems such as corrosion of installations, reduced catalyst life and environment pollution. The determination of mercury solubility in the processing fluids is required to determine the migration and distribution of mercury in various logistics during the production process and improve the efficiency of mercury removal. For this purpose, the solubility and the dissolving characteristics of mercury in several natural gas processing fluids (MEG, TEG and MDEA in particular) were studied at a temperature range from 253K to 373K. The dissolution experiments were carried out in the dissolving kettle and mercury concentration was analyzed by cold-vapor atomic absorption technique (CVAAS). The experimental results indicated that the solubility of mercury in these solvents showed an increasing trend with increased temperature and pressure. The results would be useful for the mercury pollution control and environmental risk management.

1. Introduction

With the increasing concern of mercury pollution, the mercury emission from the production and processing industries of natural gas has gradually been paid more attention from all over the world, and many countries are drawing up relevant measures and policies for the prevention and control of mercury [1-2]. Due to the high dispersion and volatility in the lithosphere, mercury is widely distributed in natural gas reservoirs [3]. Researches have shown that the limit of mercury concentration in natural gas is no higher than $30 \mu\text{g}/\text{m}^3$, which will not cause harm to equipment, personal safety and environment [4].

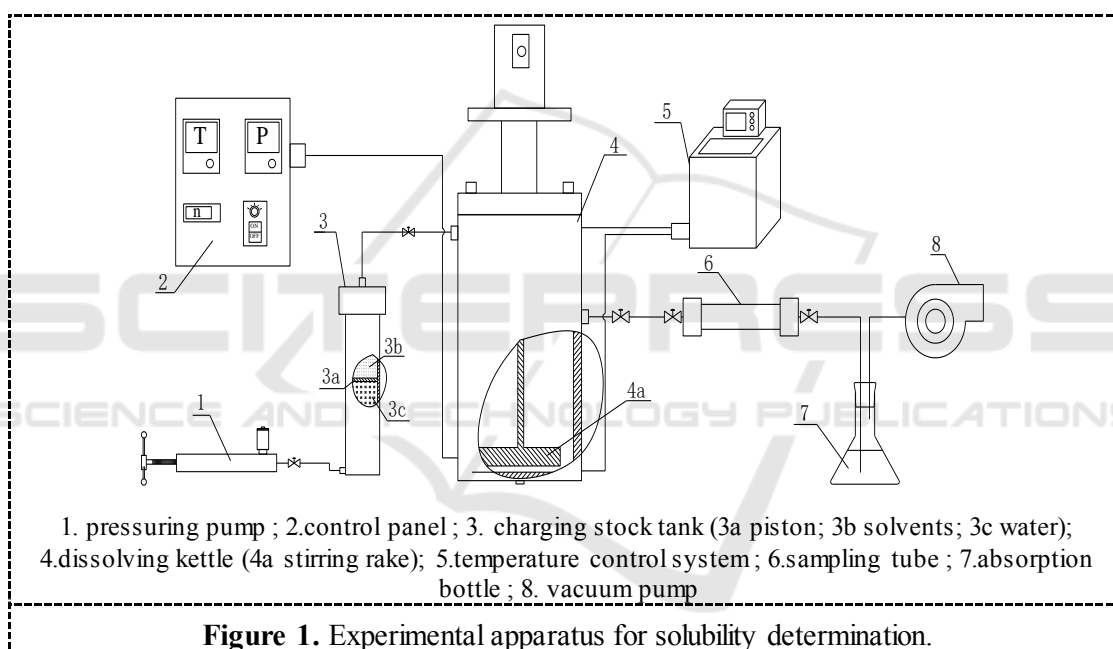
In the process of dehydration, de-hydrocarbon and de-acidification, mercury in the feed gas can be adsorbed by the pipe wall, discharged into the atmosphere with flash gas and regenerative gas, or drained into the sewage pool through sewage sludge, etc. Through on-site sampling and analysis, the concentration of mercury in this series of purification processes continuously decreases [5-6]. Therefore, it is of great interest to study the solubility and the dissolving characteristics of mercury in the natural gas processing fluids, especially in the MEG, TEG, and MDEA, which are widely used in the process of natural gas treatment.

In this paper, a set of experimental device for determination of mercury solubility was established. The solubility and the dissolving characteristics of mercury in the MEG, TEG, MDEA and water were studied at a temperature range from 253K to 373K. In addition, pressure dissolution experiments were carried out. The experimental data will help to determine the migration and distribution of mercury in various logistics during the production process.

2. Methodology

2.1. Experimental apparatus and procedure

Due to the low dissolution rate and volatility of mercury, the solvents were very easy to evaporate when dissolving and sampling, especially in the high temperature experiments, which may cause mercury loss [7]. Therefore, a new method was developed and a set of solubility measurement devices was designed, which was mainly composed of temperature and pressure control system, magnetic stirring system, dissolving kettle and sampling system. The diagram of the apparatus is shown in Figure 1.



The experiments were performed by placing 800ml of solvent spiked with 10g of liquid mercury (as Hg^0) into the dissolving kettle. All the solvents were stirred together at a given temperature and pressure for about 6 h, then the upper solution was analyzed after the stirring stopped for about 2 h, and the concentration of mercury was considered as the solubility at the temperature. The sampling tube was vacuumed by means of the pump before the sampling operation to avoid mercury evaporation loss. In order to eliminate the influence of temperature fluctuation, the samples were quickly transferred into digestion tubes in water bath for further digestion and analysis.

2.2. Analytical method

The generally accepted procedure for the determination of trace amounts of mercury is the cold-vapor atomic absorption technique (CVAAS) because of its high sensitivity, which consists of stannous chloride reduction, nitrogen bubbling, and passing through a magnesium-perchlorate tube

for mercury-vapor drying [8]. The mercury concentration was determined from the area under the atomic absorption peak at 253.7 nm.

In this study, the sample digestion was carried out by the wet closed digestion combined with water bath and hydrogen peroxide mixed with nitric acid was used for digestion. The optimum ratio was determined as $\text{HNO}_3 : \text{H}_2\text{O}_2 = 5:1$ through a number of preliminary experiments. After digested and cooled to room temperature, the sample was diluted with 5% HNO_3 , and then analysed by automatic mercury measurement instrument Hydra AA (Leeman Labs Inc., USA). The analysis of all samples were done in triplicate, and the relative standard deviation (RSD) of the 3 replicates was controlled less than 3%. The minimum detection limit of the instrument was 1ng/L.

Calculation formula of solubility (equilibrium concentration) was described as follow:

$$X = \frac{c \times V}{m}$$

Where X was the solubility of mercury in the sample, c was the concentration of mercury in the sample after digestion, V was the total volume of the sample after digestion and m was the weight of sample. The unit of mercury solubility is ng/g and usually expressed as ppb.

To verify the reliability of the experimental apparatus, solubility of mercury in water was compared with literature data [9]. The result is shown in Figure 2. It can be seen that the experimental data reported in this study are in agreement with the data from the literature, and the biggest relative deviation calculated between the solubility of the literature and the measured solubility of this study is less than 5%.

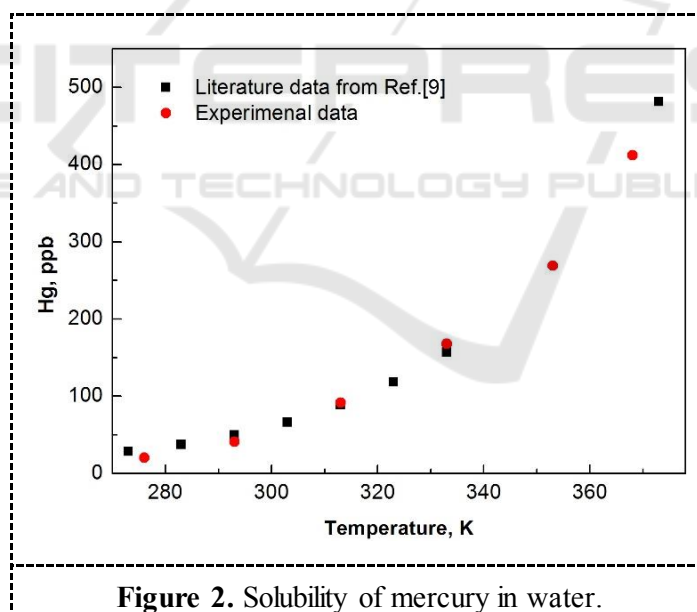


Figure 2. Solubility of mercury in water.

3. Results and discussion

3.1. Mercury solubility determination

The measured solubility data of mercury in the studied solvents within their respective operating temperature ranges are shown in Figure 3. The results indicated that the solubility of liquid mercury in MDEA, MEG and TEG shows a temperature dependence and is much higher than that in water, which may result from the hydroxyl groups in these solvent molecules and interaction between mercury and solvent molecules. The maximum solubility of mercury was reported in TEG (99%) and

was 9610 ppb at 373K followed by that in MEG (99%, 1185 ppb, at 333K) and MDEA (45%, 614 ppb, at 353K). The solubility of mercury in TEG is only about one-tenth of the solubility in an alkane, but it is almost 30 times more soluble than in water [10].

In addition, dielectric constant of the solvents is in the following order: Water > Glycols > Amine [11]. Comparison of solubility data as a function of dielectric constant of solvents suggests that the solubility of mercury increases with a decrease in the dielectric constant of amine and glycols. The measured solubility values of pure glycols in this study were found in a good agreement with the literature values [9].

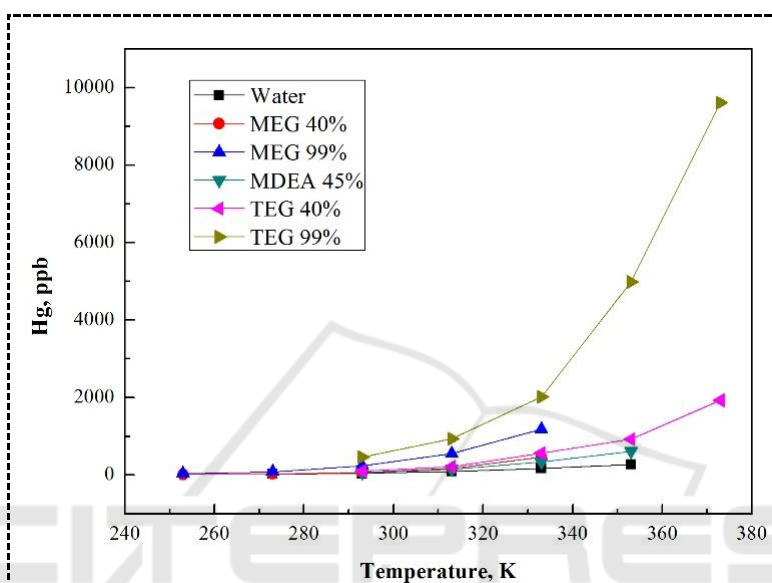


Figure 3. Solubility of mercury in the studied solvents.

The main potential source of error in the experimental method employed in this work is the loss of mercury due to adsorption of Hg on the walls of the sampling container. This error is considered to be negligible, because the measured concentration of mercury in repeated experiments was reproducible to 98%.

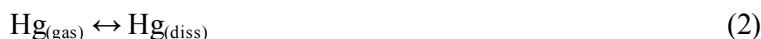
The discrepancy of solubility data in the literature available may be due to the different digestion methods and the different detection instruments. Because the mercury concentration in these solvents were at ppb grade, and the experimental conditions and analytical methods have a great impact on the experiment results. In this study, the dissolution process occurs in a closed reactor to ensure that the dissolution process does not contact with the atmosphere, thus avoiding the interference of environmental oxidation.

3.2. The effect of pressure on mercury solubility

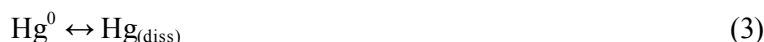
Through pressure dissolution experiments, it was found that with the increase of pressure, the equilibrium concentration of mercury in MEG and TEG increased slightly at the same temperature, but the effect of pressure on the solubility of mercury was not obvious compared with the temperature. The variation of solubility in MEG and TEG with pressure is shown in Figure 4 and Figure 5.

According to M M Miedaner et al. [12], the dissolution of metallic mercury into the polar solvent can be expressed by the following reactions:





which can be simplified to an overall reaction:



The effect of pressure on the dissolution of liquid is quite complex. Volatile liquids have the properties similar to the gas, and their solubility may be greatly influenced by pressure [13]. Therefore, it may be speculated that the phenomenon that the solubility of mercury increases with the increase of pressure may be due to the volatility of the mercury that makes it similar to the solubility of gas. According to the law of gas dissolution, the pressure increases and the solubility of gas increases.

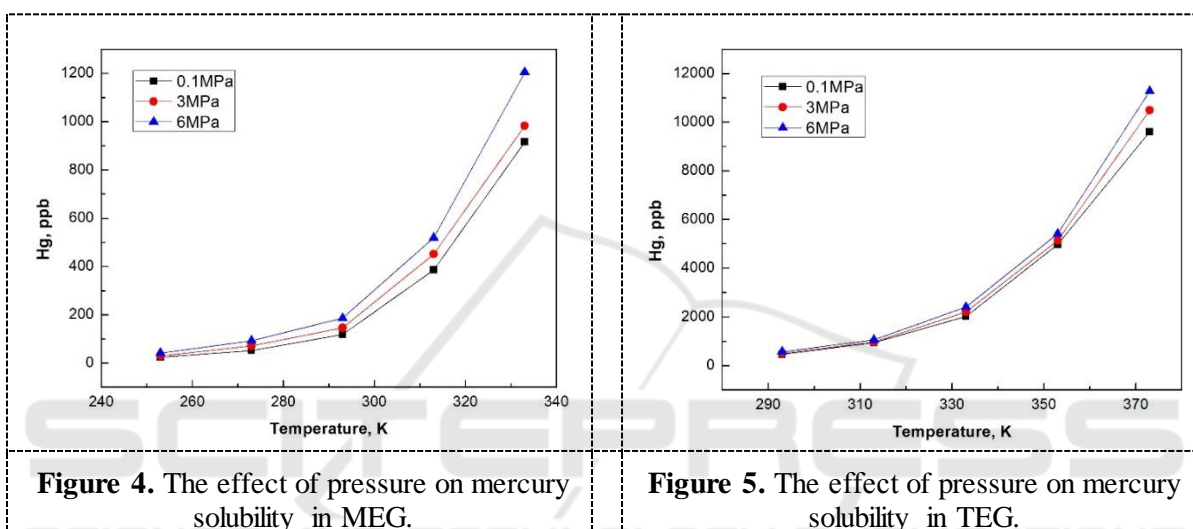


Figure 4. The effect of pressure on mercury solubility in MEG.

Figure 5. The effect of pressure on mercury solubility in TEG.

3.3. Application of the solubility data

According to the experimental data of mercury solubility in this study, a large amount of mercury in natural gas may enter the rich gas processing solvents. Although there is no limit of the mercury concentration in the glycol and amine quality index, sewage discharge from the regeneration process of gas processing solvents should be carried out by GB8978-1996 Integrated Wastewater Discharge Standard of the state, and the maximum permitted discharge concentration of total mercury is 0.05mg/L. The government of Thailand requires that the total mercury concentration of the treated sewage is less than 0.005 mg/L, and the mercury emission limits of the United States are as low as 0.079 $\mu\text{g/L}$ [14].

The enrichment of mercury in natural gas treatment equipment may be harmful to the health of operators and maintenance personnel. In particular, when mercury-contaminated facilities are repaired during maintenance, the staff will be exposed to high concentration of mercury vapor above the valve limit and maximum allowable concentration if no special precautions are taken.

4. Conclusions

The solubility of liquid elemental mercury in the natural gas processing solvents (MEG, TEG and MDEA) was determined within their respective operating temperature ranges. Experimental results show that there are great differences in the solubility of mercury in different solvents. The solubility of mercury in these solvents increased with temperature ranging from 253K-373K. In particular, mercury solubility in the solvents at range of 273K-353K follows the general order: Glycols (TEG,

MEG) > MDEA > Water. In addition, the pressure dissolving experiment indicated that mercury solubility in MEG and TEG increased slightly with the increased pressure.

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