Measurement of Elemental Mercury Solubility in Natural Gas Dehydrating Solvents

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Abstract. Mercury pollution and emission from natural gas processing industry has gradually received worldwide concern. Basic data and references are important for pollution control and environmental risk management. For this purpose, the solubility and the dissolving characteristics of mercury in the natural gas dehydrating solvents (methanol, mono-ethylene glycol and tri-ethylene glycol 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, whereas decreased with decreasing solvent concentration. The results would be useful for the research on the distribution of mercury in the natural gas processing and provide basis for the prevention and control of mercury pollution.

1. Introduction
Mercury (Hg) is one of the most toxic heavy metals commonly found in the global environment including the lithosphere, hydrosphere, atmosphere, and biosphere [1]. Due to the high toxicity and corrosiveness, the presence of mercury in natural gas can pose a potential threat to the health of operators, corrode pipeline equipment, cause poisoning of noble metal catalysts (e.g. platinum, palladium, silver, etc.) in the downstream industry and pollute the environment [2]. Glycol dehydration is widely used in gas processing operations, especially tri-ethylene glycol (TEG). Meanwhile, thermodynamic inhibitor (e.g. ethylene glycol (MEG) and methanol) is usually injected to prevent the formation of hydrates and then clog pipes and valves, to ensure dehydration and de-hydrocarbon processes successfully.

Carnell et al. [3] reported that the saturated concentration of mercury in tri-ethylene glycol can reach 2.90 ppm (the temperature and pressure is unknown). The solubility of Hg in water and methanol at room temperature were determined by Clever [4], which were 60 ppb and 722 ppb respectively. Sabri et al. [5] measured the solubility of Hg⁰ in ethylene glycol at room temperature using the Ontario method (OHM), which ranged from 0 to 60 ppb and can increase to 80 ppb when the pH dropped from 9 to 6. The solutions were analyzed using inductively coupled plasma mass spectroscopy (ICP-MS). In the recent work, Gallup et al. [6] determined elemental mercury’s
equilibrium concentration in several alcohols and glycols solvents under reducing condition, by adding a reducing agent such as stannous citrate in the solvents to inhibit the oxidation of mercury. Mercury concentrations were determined by cold vapor atomic fluorescence spectrometer (CVAFS).

Owing to different experimental conditions and analytical methods, there is still lacking of reliable experimental data of mercury solubility in alcohols and glycols. In this paper, the solubility of elemental mercury in water, methanol, ethylene glycol, tri-ethylene glycol and mixed solvents was determined by the equilibrium method. Meanwhile, the experimental data were correlated and fitted, which would be useful for the research on the distribution of mercury in the processing of natural gas and provide theoretical basis for the prevention and control of mercury pollution.

2. Experimental

2.1. Apparatus and procedure
The experiments were performed by placing 800ml of solvent spiked with 10g of liquid mercury (as Hg⁰) into the dissolving kettle. The diagram of the apparatus is shown in Fig.1. All the solvents were stirred together at a given temperature and pressure for a certain time (about 6h), then the upper solution was analysed after the stirring stopped for some time (about 2h), and the concentration of mercury was considered as the solubility at the temperature. The stirring and settlement time were determined by the exploratory experiments. The stirring and settlement time were determined by the exploratory experiments. 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.

![Figure 1. Experimental apparatus for solubility measurement](image)

1. Pressuring pump; 2. control panel; 3. charging stock tank (3a piston; 3b solvents; 3c water); 4. dissolving kettle (4a stirring rake); 5. temperature control system; 6. sampling tube; 7. absorption bottle; 8. vacuum pump

2.2. Analytical method
Because of the poor reproducibility of mercury detection, pretreatment is one of the main factors affecting the accurate determination of mercury content in samples. 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 HNO₃: H₂O₂= 5:1 through a number of preliminary experiments. After digestion, the sample was diluted with 5% HNO₃, and then analyzed 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 1 ng/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.

To verify the reliability of the experimental apparatus, solubility of mercury in water was compared with literature data [6]. The result is shown in Fig. 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](image)

3. Results and discussion

3.1. Effect of temperature on mercury solubility

The measured solubility data of mercury in pure solvents at various temperatures (253K to 353K) are summarized in Table 1 and Figures 3. The results indicated that the solubility of liquid mercury in methanol, MEG and TEG increases in a temperature-dependent manner 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. In the same temperature range of 273-333K, the solubility of liquid mercury was the highest in methanol and the lowest in MEG. The maximum solubility of mercury was reported in methanol and was 4013.9 ppb at 333K followed by that in TEG (2014.1 ppb, at 333K) and MEG (1185 ppb, at 333K).

| T/K | 253 | 273 | 293 | 313 | 333 | 353 | 373 |
|-----|-----|-----|-----|-----|-----|-----|-----|
| MEG | 39.1 | 82.4 | 238 | 552 | 1185 | 2763 | 5280 |
| Methanol | 46.4 | 191.3 | 592.5 | 1814.8 | 4013.9 | - | - |
| TEG | - | - | 465.8 | 937.2 | 2024.1 | 4982 | 9610 |

Table 1. Solubility of mercury in pure solvents (ppb).
The growth trends of solubility were correspond with that reported by Gallup, however, the values measured in this study were slightly higher than those in the literature [6]. The reason may be that the addition of reductant in Gallup’s experiments inhibited the interaction between solute and solvent, which is an essential part of the dissolution process [7].

![Figure 3. Solubility of mercury in pure solvents](image)

In all three types of solvent, the measured solubility of mercury was an exponential function of temperature (Figure 3) and consequently $Hg^0$ solubility can be predicted using the equations listed in Table 2, which were fitted to the experimental data.

| Solvent | Mercury solubility | $R^2$ |
|---------|--------------------|-------|
| MEG     | $X_{Hg} = -105.584 + 0.0165e^{0.0397T}$ | 0.998 |
| Methanol| $X_{Hg} = -188.691 + 0.0088e^{0.0397T}$ | 0.997 |
| TEG     | $X_{Hg} = -333.411 + 0.0348e^{0.0397T}$ | 0.996 |

The comparison of mercury solubility in methanol and MEG shows that methanol used for gas dehydrating is much more likely to be contaminated by Hg than MEG [8]. The dissolution law of mercury indicates that the solubility will decreases when the temperature decreases. In industrial applications, mercury may precipitate and deposit on the bottom or surface of the equipment, causing corrosion to the low-temperature treatment equipment [9].

3.2. Effect of solvents concentration on mercury solubility
To determine the impact of the concentration of solvent, the pure glycols were diluted with water to simulate lean glycol and rich glycol. The experiment shows that the mercury solubility in the mixed solvent (MEG+ water) and (TEG + water) was lower than that in pure solvents. Therefore, as the concentration of glycols decreased, the solubility of mercury also decreased gradually, as expected.

| T/K | 253 | 273 | 293 | 313 | 333 |
|-----|-----|-----|-----|-----|-----|
| 99%MEG | 39.1 | 82.4 | 238 | 552 | 1185 |
| 82% MEG | 24.6 | 52.9 | 118.7 | 386 | 917 |
| 40% MEG | 12.3 | 27.6 | 70.2 | 166 | 463 |
Table 4. Mercury solubility in different concentrations of TEG (ppb).

| T/K | 293  | 313  | 333  | 353  | 373  |
|-----|------|------|------|------|------|
| 99% TEG | 465.8 | 937.2 | 2024.1 | 4982 | 9610 |
| 80% TEG  | 326  | 593.6 | 974  | 2461 | 5725 |
| 40% TEG  | 102.6 | 217.4 | 563.8 | 927  | 1930 |

Although the concentrations of mercury in these solvents are in ppb or ppm grade, they are still significant when considering that these Hg levels are much greater than drinking water (2ppb), or other standards for disposal of fluids to the environment. Due to high toxicity and corrosiveness, the presence of mercury in natural gas can pose a health threat to the workers, corrode pipeline equipment, cause poisoning of noble metal catalysts in the downstream industry and pollute the environment.

4. Conclusion
A set of solubility experimental apparatus for mercury determination was designed. The solubility of elemental mercury in several gas dehydrating solvents such as methanol, MEG and TEG was measured. Experimental results show that there are great differences in the solubility of mercury in different solvents. The solubility of mercury in the three solvents increased with temperature ranging from 253K-373K. In particular, mercury solubility in the solvents at range of 273 K -333K follows the general order: Methanol > TEG > MEG > Water. In addition, the effect of solvent concentration on mercury solubility was studied. The solubility decreased slight with the decrease of solvent concentration.

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