Hg⁰(liq)–Hg⁰(solution) Equilibrium and Solubility of Elementary Mercury in Water

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Abstract—The solubility metallic mercury in water and its dominating forms were studied. The prevalence of the Hgₐq⁰ form in the high-temperature range was confirmed and the reaction constant \( \log K = \log m = -8.01 \) at 25°C with the predominance of oxidized forms of mercury for the 20–80°C area of low temperatures was found.

Keywords: metallic mercury solubility in water, dissolved mercury forms.
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INTRODUCTION

Many publications have been devoted to the solubility of elementary mercury in water. The data can be conditionally divided into two groups. At high temperatures, in the range of substantial vapor pressures of mercury, the dependence of the logarithm of the molarity of mercury vs. reverse temperature has a linear character. A large number of works in the range from 20 to 120°C along the line of the saturated vapor pressure of water with the apparent coincidence of the data and unity of the temperature-solubility dependence are in natural contradiction (figure). We studied the solubility of elementary mercury and its dominating forms upon variation of redox conditions for the first time.

The unusual nonlinearity of the \( \log(-m) - 1/T \) dependence for the simple reaction Hg⁰(liq)–Hg⁰(solution) at \( \Delta C_p = 0 \) forces one to suggest the substitution of the dominating form in solution in the low-temperature range. We propose that the Hg⁰(solution) form is completely predominant at high temperatures, where the solubility of elementary mercury is high, and oxidized forms of mercury are predominant at low temperatures. The value of solubility of Hg⁰, which corresponds to a concentration of 1.99 μg/l at a temperature of 20°C, was obtained according to the linear extrapolation of the published data to the low-temperature range.

ANALYTICAL SUPPLY

Analysis of mercury in aqueous samples was performed in the Laboratory of experimental geochemistry at MSU according to the “cold vapor” method with the detection of the vapors of the reduced metal by atomic absorption spectrometry (AAS) on a UKR-1MTs instrument with a PAR-3m adapter. Sodium borohydride NaBH₄ was chosen as the most optimal reagent; this coincides with the opinions of respected authors (Welz and Schubert-Jacobs, 1988). The concentration of zero-valent mercury Hg⁰ and net concentration of mercury Hgₜotal were determined in each sample; pH and Eh were controlled directly after their sampling.

MATERIALS AND METHODS

A series of experiments on the solubility of elementary mercury in water under various redox conditions was performed in the temperature range from 20 to 40°C. A small amount of metallic mercury was placed in three glass flasks with 2.5 l of double-distilled water. Barbotage of gases and sampling were performed through the inlets in the flasks. The first flask was kept in equilibrium with atmospheric air; argon was introduced through two others under pressure for 15 min. Sodium borohydride was initially added to the third flask, whose hydrolysis provided the generation of hydrogen and a reduction medium.

Samples with a volume of 25 ml were taken during the experiment several times with a 50 ml syringe. Initially, the experiment was performed at 20°C. After this, flask no. 3 was placed in a drying oven and saturation took place at a temperature of 33°C. NaBH₄ was then introduced in the flask with an oxygen atmosphere; the concentration of zero-valent mercury in the flask decreased and stabilized at a value of 2.75 μg/l.

Intense reduction obviously took place due to initially atomic hydrogen, which formed during the total
reaction of the hydrolysis of sodium borohydride NaBH₄:

\[ \text{NaBH}_4 + 4\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{BO}_3 + \text{NaOH} + 4\text{H}_2 \uparrow, \]
\[ \text{NaBH}_4 + 2\text{NaOH} + \text{H}_2\text{O} \rightleftharpoons \text{Na}_3\text{BO}_3 + 4\text{H}_2 \uparrow. \]

RESULTS AND DISCUSSION

The problem of the method for the individual determination of zero-valent mercury and the net content of its oxidized forms was solved. At low temperatures and oxygen and argon atmosphere, analytically dominant amounts of its oxidized forms are formed, whose concentrations increased continuously; this proved the oxidation of mercury by water. Concentration of both net and zero-valent mercury in the more oxidized medium increases; this may confirm the existence of an equilibrium between the oxidized and reduced forms, with its absence in the bottom phase and oxide film on metal. In the case of a strongly reducing environment at 20°C, the system reached equilibrium rapidly at a concentration of elemental mercury of 1.95 μg/l. Thus, the position of mercury in the standard galvanic series of metals is not a barrier to the formation of dominating concentrations of oxidized forms against the background of extremely low solubility of Hg⁰(solution) with the low vapor elasticity of mercury (volatility) in the range of standard temperatures. The experiments that were performed on the solubility of mercury in the low-temperature range in various redox conditions confirmed this suggestion. This is proven by the absolute coincidence of our data on the solubility of mercury in a reducing environment with the published data extrapolated to 20°C (Sorokin, Alekhin, and Dadze, 1988).

Thermodynamic calculations were performed using the HCG program (Shvarov, 2008) and the values of Gibbs free energy for Hg⁰(solution), which showed that Hg(OH)₃ is the predominant form at normal redox potential. Thus, the idea of the predominance of the Hg⁰(solution) form at high temperatures was confirmed and the Hg⁰(liq) ⇌ Hg⁰(solution) reaction constant at 20°C was determined (log \( K = -8.01 \)) under the complete predomination of oxidized forms of mercury in the low-temperature range.

CONCLUSIONS

1. The number of oxidized forms of mercury increased continuously with time in atmosphere air; this confirms the constant oxidation of elemental mercury by water.

2. The solubility value (1.95 μg/l) was experimentally obtained for the equilibrium Hg⁰(liq) ⇌

The solubility of mercury in water as an inverse temperature function. The initial experimental data of various authors are given from (Sorokin, Pokrovskii, and Dadze, 1988).