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The Measurement of the Distribution Equilibrium Constant of Metallic Mercury for $Hg_{(aq)} \rightleftharpoons Hg_{(gas)}$

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Synopsis. The gas-aqueous distribution equilibrium constant of mercury(0) was determined in the temperature range from 5 to 45 °C. The experiment was made by volatilizing metallic mercury dissolved in water to the gas phase, which was connected with the absorption cell in a cold-vapor atomic absorption spectrophotometer, and by measuring the absorbance under gas-aqueous distribution equilibrium conditions. The distribution equilibrium constant, $[Hg]_{gas}/[Hg]_{aq}$, was found, *e.g.*, to be 0.40 ± 0.02 at 25 °C. The effect of the concentration of NaCl on the distribution equilibrium constant was measured at 25 °C. The salting-out effect was found to be expressed by the Setschenow equation, and the salting-out coefficient was found to be 0.105.

The behavior of mercury in an environment is interesting, although rather complicated and still not entirely explainable. The most distinct difference between mercury and the other metals is the high vapor pressure of mercury, so that the mercury volatilizes[1,2] from water surfaces, such as seas and rivers, to the atmosphere. The most important factor[3] in the mercury volatilization is the gas-aqueous distribution equilibrium constant of mercury, although the distribution equilibrium constant has not yet been measured, to our knowledge.

In this work, the distribution equilibrium constant was measured by volatilizing metallic mercury dissolved in water to the gas phase, which was connected with the absorption cell in a cold-vapor atomic absorption spectrophotometer.

Experimental

Doubly distilled water was used throughout this work. All the chemicals were of an analytical reagent grade. Analytical-grade metallic mercury was further purified in the usual manner.[4]

By shaking the distilled water containing a few drops of the purified metallic mercury and 0.001 mol dm^{-3} of phosphinic acid[5,6] as a reducing agent to prevent the mercury oxidation, the mercury was dissolved in the water. The solution with the dissolved free mercury was prepared in the vessel shown in Fig. 1, and stirred by means of a magnetic stirrer. The mercury in the solution was equilibrated with the gas phase,[7,8] which was connected with the absorption cell in a cold-vapor atomic absorption spectrophotometer (Hiranuma, HG-1). The absorbance became constant under the gas-aqueous distribution equilibrium conditions of mercury (first equilibrium conditions). The absorbance at equilibrium was measured, the stirring was stopped, and then the mercury vapor in the gas phase was swept by nitrogen gas into a $(KMnO_4+H_2SO_4)$ absorber without disturbing the aqueous phase. When the absorbance had returned to zero level (base line), the same procedure was repeated and a second absorbance was measured (second equilibrium conditions). The variation in the absorbance with the time is shown in Fig. 2. The experiment was made in the temperature range from 5 to 45 °C, the precision of the temperature in the aqueous and the gas phases being ±0.1 °C and ±0.5 °C respectively.

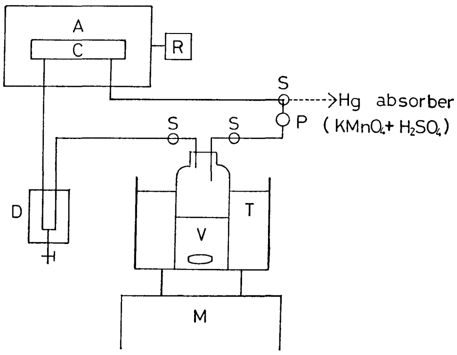

Fig. 1. Schematic diagram of apparatus.
A: Atomic absorption spectrophotometer, C: absorption cell, D: cold trap, M: magnetic stirrer, P: pump, R: recorder, S: stopcock, T: thermostat, V: mercury solution.

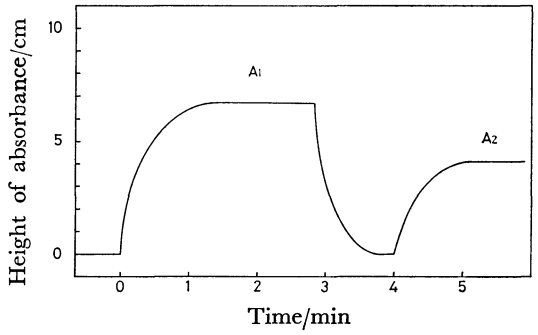

Fig. 2. Variation in absorbance with time at 25 °C. $[Hg]_0 = 1.32 \times 10^{-8}$ mol dm^{-3}, $V_L = 250$ cm^3, $V_G = 395$ cm^3.

Results and Discussion

The distribution equilibrium constant, K, for $Hg_{(aq)} \rightleftharpoons Hg_{(gas)}$ is expressed as follows:

$$K = [Hg]_{gas}/[Hg]_{aq}, \tag{1}$$

where $[Hg]_{gas}$ and $[Hg]_{aq}$ are the mercury concentrations in the gas and aqueous phases respectively. Assuming that $[Hg]_0$ is an initial mercury concentration, V_G and V_L are the volumes in the gas and aqueous phases respectively under the first equilibrium conditions:

$$K = \frac{[Hg]_{gas\,1}\, V_L}{[Hg]_0\, V_L - [Hg]_{gas\,1}\, V_G} \tag{2}$$

and under the second equilibrium conditions:

$$K = \frac{[Hg]_{gas\,2}\, V_L}{[Hg]_0\, V_L - \{[Hg]_{gas\,1} + [Hg]_{gas\,2}\} V_G}, \tag{3}$$

where the subscript numbers 1 and 2 indicate the

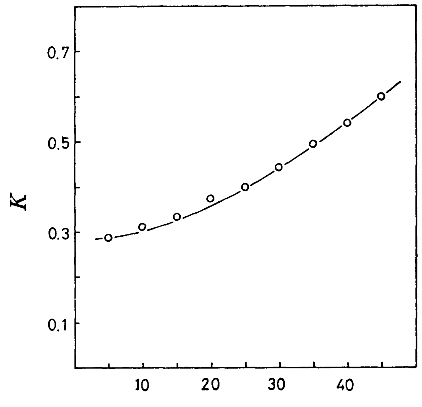

Fig. 3. Temperature dependence of K.

first and the second equilibrium conditions respectively. The relation between the mercury concentration in the gas phase and the absorbance is expressed as follows:

$$[\mathrm{Hg}]_{\mathrm{gas\,1}} = A_1 a$$
$$[\mathrm{Hg}]_{\mathrm{gas\,2}} = A_2 a, \tag{4}$$

where a is the mercury concentration in the gas phase per unit absorbance; it indicates a constant value if the temperature and the operating conditions of the spectrophotometer are fixed. Therefore, from Eqs. 2, 3, and 4, Eq. 5 is obtained:

$$K = \frac{A_1 - A_2}{A_2} \times \frac{V_L}{V_G}. \tag{5}$$

The distribution equilibrium constant, K, can be determined by measuring the absorbances, A_1 and A_2, under the gas-aqueous equilibrium conditions. In case of Fig. 2, $A_1=6.7$ cm** and $A_2=4.1$ cm** were measured. Therefore, the value of $K=0.40$ was calculated from Eq. 5. The value of K obtained at 25 °C is found to be 0.40±0.02 by measurements in the various cases of V_1 from 100 to 500 cm^3 and of $[\mathrm{Hg}]_0$ from $(0.35 \text{ to } 1.64)\times 10^{-8}$ mol dm^{-3}. The constant was found to be unaffected by the reducing-agent concentrations of phosphinic acid between 0.0005 and 0.02 mol dm^{-3}.

The standard Gibbs energies of the formation and the solution for the mercury element at 25 °C are 31.853[9] and 39 K J/mol[10] respectively. Using these values, $K=0.74$ is calculated. Compared with the K measured in this work, the calculated value is larger, though the ±2 K J/mol differences of $\Delta G°$ give about a 5-fold change of K in the calculating method of the free-energy change. The calculation of K by using the mercury solubility in water previously reported gives $K=0.79$ with Pariaud's data $(1.3\times10^{-7}$ mol dm$^{-3})$[11] and $K=0.34$ with Moser's data $(3.0\times 10^{-7}$ mol dm$^{-3})$.[5] According to recent solubility studies,[4,12,13] the latter value is preferable. The distribution equilibrium constant in this work is reasonable in view of the above discussion and the dilution of the mercury. The temperature dependence of K is shown in Fig. 3.

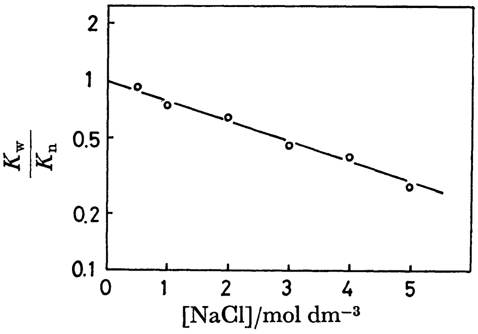

Fig. 4. Salting-out effect at 25 °C.
K_w: K for water (0.40), K_n: K for NaCl solution.

Instead of distilled water, sodium chloride solutions were used under the same distribution equilibrium experiments. The effect of the concentration of NaCl on the distribution equilibrium constant is shown in Fig. 4. A salting-out effect was observed; it could be explained by the Setshenow equation[14] for an aqueous electrolyte solution. The salting-out coefficient was found to be 0.105 at 25 °C.

Conclusion

The distribution equilibrium constant of metallic mercury between the aqueous and the gas phases was determined in the temperature range from 5 to 45 °C by using a cold-vapor atomic absorption spectrophotometer and the equation derived from the material balance of the mercury.

The effect of the concentration of NaCl on the distribution equilibrium constant was investigated at 25 °C, and the salting-out coefficient was determined in the concentration range from 0 to 5 mol dm^{-3}.

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** The absorbances, A_1 and A_2, were expressed by the height of the absorbance (cm) on the recorder chart in the cold-vapor atomic absorption spectrophotometer.