Notes

Adsorption Behavior of Gold(III) on Hydrous Lead Dioxide from Dilute Sulfuric Acid Solution

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Hydrous lead dioxide (HLD), freshly prepared by hydrolysis of lead tetraacetate, has been investigated to elucidate its adsorption properties and explore its potential application as an adsorbent. The adsorption behavior of various metal ions such as Bi(III)^{1,2}, Cr(III), Cr(VI)³, Tl(I), and Tl(III)^{4,5} has been studied. HLD has characteristic properties associated with its strong adsorbing ability and strong oxidizing potential.

In a previous report, the adsorption behavior of Au(III) in hydrochloric acid solution was investigated.⁶ The hydrochloric acid concentration was low enough to prevent a decrease in HLD owing to reactions with Cl⁻. The adsorption increased with increasing pH, beginning at 0, reaching 100% at pH 2–7, and decreasing with increasing pH values above 8. These results show that the main species involved in the adsorption was an Au(III) chloride complex anion such as AuCl₄⁻.

In the present study, the adsorption behavior of Au(III) was studied using the sulfuric acid solution of Au(III). The results are compared with those of the adsorption behavior of Au(III) in dilute hydrochloric acid solution.

Experimental

Reagents

Sulfuric acid solution of Au(III): the stock solution was prepared by dissolving auric hydroxide in 10 M sulfuric acid to make Au(III) with a concentration of about 1.5×10^{-2} M. Auric hydroxide was precipitated from a concentrated tetrachloroauric acid solution by dropwise addition of sodium hydroxide solution.

Lead tetraacetate solution: the solution was prepared and standardized as described in a previous report.⁶

The other reagents were of analytical-reagent grade, and the water used was purified by distilling demineralized water containing small amounts of potassium permanganate and sodium hydroxide.

Apparatus

Atomic absorption spectrometry(AAS) measurements

were made with a Nippon Jarrell-Ash AA-855 flame atomic absorption spectrophotometer.

The other pieces of apparatus used were also described in a previous study.⁶

Procedure

HLD was prepared by hydrolyzing a given volume of tetraacetate solution, as described in a previous report.⁶ HLD (5×10^{-4} mol), a known amount of sulfuric acid solution of Au(III), and an appropriate buffer solution were added to a 200 ml Erlenmeyer flask with a rubber stopper and the mixture was diluted to 100 ml with distilled water. The pH or acidity of the suspension was adjusted with nitric acid or with 0.1 M CH₃COOH–0.1 M CH₃COONa buffer. The suspension was shaken for 1 h at 30°C. The HLD was then separated by filtration, using a membrane filter (Toyo Kagaku, Cellulose Nitrate Type, pore size 0.45 μm). Au(III) in the filtrate was determined by AAS, and the amount of Au(III) adsorbed was calculated from the difference in its concentration before and after adsorption.

Results and Discussion

Preparation of sulfuric acid solution of Au(III)

The solution was prepared by dissolving auric hydroxide in 10 M H₂SO₄ until it was saturated. The auric hydroxide was prepared as follows. Sodium hydroxide solution was added dropwise to saturated tetrachloroauric acid solution, and the resulting precipitate was washed thoroughly by adding water and then centrifuged to separate it from the water. The precipitate was then dissolved in warm 5 M NaOH, again precipitated by the addition of HNO₃, and washed with water as described above. The above operation was repeated four times.

The amount of Cl⁻ in the precipitate was examined. The precipitate was dissolved in 5 M NaOH, and Cl⁻ and Au(III) in the solution were determined by spectrophotometry with mercury thiocyanate⁷ and AAS, respectively. It was found that the Cl⁻ concentration

was less than 0.6% relative to the Au(III) concentration.

Adsorption behavior

The effect of pH on the adsorption of Au(III) on HLD from dilute H_2SO_4 solution is shown in Fig. 1, which also shows the effect of pH on the adsorption of Au(III) from dilute HCl solution, for purposes of comparison. Au(III) concentration was 1×10^{-5} M and the ratio of H_2SO_4 concentration to Au(III) concentration in the solution ($[\text{H}_2\text{SO}_4]/[\text{Au(III)}]$) was 700. The adsorption was almost 100% at pH 0–2; at higher acid concentrations, the adsorption decreased with the increase in acid concentration.

The above result was compared with that obtained using dilute HCl solution. As shown in Fig. 1, the

Fig. 1 Effect of pH and acidity on the adsorption of Au(III) on hydrous lead dioxide (HLD). HLD, 5×10^{-4} mol; $[\text{Au(III)}]$, 1×10^{-5} M, solution volume, 100 ml; shaking time, 1 h; solutions: ○ dilute H_2SO_4 ($[\text{H}_2\text{SO}_4]/[\text{Au(III)}]=700$); ● dilute HCl ($[\text{Cl}^-]/[\text{Au(III)}]=10$).

Fig. 2 Relation between concentration of Au(III) added and the amount of Au(III) adsorbed on HLD. HLD, 5×10^{-4} mol; $[\text{H}_2\text{SO}_4]/[\text{Au(III)}]$, 700; $[\text{HNO}_3]$, 3 M; solution volume, 100 ml; shaking time, 1 h.

adsorption was still about 80% in 3 M HNO_3 with dilute H_2SO_4 solution. With dilute HCl solution, the adsorption decreased with decreasing pH values of 2 or below, and Au(III) was adsorbed very little in 3 M HNO_3 . The difference in the adsorption in the two cases is discussed in a later section.

No decrease in Au(III) concentration caused by hydrolysis was found during 1 h of shaking in the range of pH and acid concentration studied.

The relation between the concentration of Au(III) and the amount of Au(III) adsorbed on HLD was investigated at 3 M HNO_3 with 5×10^{-4} mol of HLD. The ratio of $[\text{H}_2\text{SO}_4]$ to $[\text{Au(III)}]$ was 700. The results are shown in Fig. 2, and a log-log plot of the equilibrium concentration of Au(III) vs. the amount of Au(III) adsorbed was linear.

Subsequent experiments were carried out to investigate the origin of the difference in the adsorption behavior exhibited in Fig. 1. From the H_2SO_4 stock solution of Au(III), 0.4, 1 and 5 M H_2SO_4 solutions containing 1 mM Au(III) were prepared, and the variation of the concentration of Au(III) with time was investigated for each solution using polarography. The results are shown in Fig. 3. The concentration of Au(III) decreased appreciably with time at low acid concentration, and a reddish-brown precipitate of auric hydroxide formed. Figure 3 also shows for comparison the result obtained using a 0.4 M H_2SO_4 solution of 1mM AuCl_4^- , which was prepared from the Au(III) standard solution as mentioned in a previous report.⁶ With dilute HCl solution the concentration of Au(III) did not change with time. The above results indicate that the interaction between the Au(III) ion and OH^- was stronger in dilute H_2SO_4 solution than in dilute HCl solution.

In addition, the variation in the spectrum of Au(III) in dilute H_2SO_4 solution was examined; the molar ratio of Cl^- to Au(III) was altered by adding KCl solution. The concentrations of Au(III) and H_2SO_4 in the solution are

Fig. 3 Effect of concentration of H_2SO_4 on the hydrolysis of Au(III). $[\text{Au(III)}]$: 1×10^{-3} M; temp., 25°C ; $[\text{H}_2\text{SO}_4]$: ○ 0.4 M; ● 1 M; △ 5 M. $\triangle$: 1×10^{-3} M AuCl_4^- in 0.4 M H_2SO_4 .

Fig. 4 Absorption spectral change of Au(III) in H_2SO_4 induced by addition of Cl^- . $[\text{Au(III)}]$, 2×10^{-5} M; $[\text{H}_2\text{SO}_4]$, 0.5 M; $[\text{Cl}^-]/[\text{Au(III)}]$, — 0; --- 2; 5; - - - 10.

2×10^{-5} M and 0.5 M, respectively. As shown in Fig. 4, the spectrum was in accord with that⁸ of AuCl_4^- when the molar ratio of Cl^- to Au(III) was 10 (In dilute HCl solution the molar ratio is approximately equal to 10.). The spectral change in Fig. 4 suggests that the replacement of ligands in a sulfate complex⁹ by Cl^- takes place readily to give finally AuCl_4^- . This result supports the above-mentioned results of the hydrolyzability of Au(III).

From these results we concluded as follows. In dilute HCl solution, neither the chloride exchange reaction of

AuCl_4^- nor the redox reaction between HLD and AuCl_4^- occurred during the process of adsorption and AuCl_4^- is the main species involved in the adsorption. On the other hand, in dilute H_2SO_4 solution, hydrolysis of Au(III) may occur on the surface of HLD, resulting in an increase in adsorption.

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