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Abstract

Full Text

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SORPTION OF GERMANIUM ON ALUMINUM HYDROXIDE

Aluminum hydroxide is often used both in industry and in analytical chemistry [1] for the sorption of various substances. However, the literature contains no data on the sorption of microquantities of germanium by aluminum hydroxide. There is only a report by Schwarz [2] on the preparation of aluminum germanate by mixing solutions of aluminum chloride and sodium germanate at a molar ratio $GeO_2 : Al_2O_3 \geq 3$ and pH 7. He showed that under these conditions the compound $Al_2O_3 \cdot 2GeO_2 \cdot nH_2O$ is formed. The sorption of GeO_2 on aluminum hydroxide was also studied by Schwarz with a large excess of GeO_2 relative to aluminum hydroxide, the latter being used in the form of a dry powder; pH was not monitored. The maximum sorption (relative to the initial amount of germanium) reached 20%. Meanwhile, it is known that iron hydroxide gives practically 100% sorption of germanium [3,4], and iron germanates are insoluble [5].

In the present communication we give the results of studies on the sorption of germanium present in solution in the form of germanic acid and the anion $HGeO_3^-$ [6], as a function of the concentration of germanium, the pH of the suspension, temperature, and the time of contact of the precipitate with the solution. Working aqueous solutions of germanium dioxide and aluminum sulfate were prepared from chemically pure reagents.

Ammonia or alkali was added dropwise to the mixture of germanium and aluminum solutions. A precipitate of aluminum hydroxide then formed, sorbing germanium. The amount of coprecipitated germanium was calculated both from the germanium content in the residual solution and from its content in the hydroxide precipitate.

Analysis of the solution and of the hydroxide after dissolution in $4\,N$ HCl was carried out by the method of V. A. Nazarenko et al. [7]. For pH measurements a LP-5 potentiometer was used.

Preliminary experiments were performed to determine the influence of the contact time of a solution containing germanium (14 mg/liter GeO_2) with the precipitate and of the precipitation temperature at a weight ratio Al : Ge = 100 and pH 7. It was established that when the contact time was varied from 5 min to 48 h and the temperature from 20 to 80° (with 5-min contact), the sorption of

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Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

germanium amounted to 99% of the initial amount. In subsequent experiments all tests were carried out at room temperature and with a contact time of the precipitate with the solution of 24 h.

Figure 1 shows the effect of the pH of the suspension on the amount of germanium sorbed. As can be seen, maximum sorption is observed in the pH range from 6 to 9.6 (precipitation with ammonia), while complete precipitation of aluminum hydroxide is achieved at lower pH values than for germanium. With increasing alkalinity, aluminum hydroxide begins to dissolve first. Thus, at pH 9.6 about 20% of the aluminum dissolves, whereas germanium under these conditions practically does not pass into solution. At pH 11 (precipitation with sodium hydroxide), 70% of the aluminum dissolves and only about 20% of the germanium. The sorption isotherm of germanium on aluminum hydroxide in logarithmic coordinates is presented in Fig. 2, and the dependence of the equilibrium concentration of germanium dioxide in solution on the molecular ratio $Al_2O_3 : GeO_2$ is shown in Fig. 3.

The deviation of the sorption curve from rectilinearity (Fig. 2), the sharp bends, and its large magnitude (2.67 g Ge per 1 g Al) indicate the chemical nature of the sorption, i.e., sorption occurs as a result of the formation of insoluble aluminum germanates. The gradual rise of the curve up to the point of the first inflection (Fig. 2) and the increase in the equilibrium concentration of germanium (Fig. 3) with decreasing ratio $Al_2O_3 : GeO_2$ are explained by the fact that the precipitating aluminum germanates probably form solid solutions with aluminum hydroxide. Therefore, the equilibrium concentration of germanium in solution depends on the amount of germanium sorbed by aluminum hydroxide, i.e., on the concentration of germanate in aluminum hydroxide.

Fig. 1. Effect of pH on the sorption of germanium by aluminum hydroxide. Concentration GeO_2 14 mg/l; Al : Ge = 100.
1 –percentage of germanium sorption (precipitation with NH_4OH), 2 –percentage of germanium sorption (precipitation with NaOH), 3 –percentage of aluminum precipitation

Fig. 2. Sorption isotherm of germanium on aluminum hydroxide

At a molar ratio $Al_2O_3 : GeO_2$ 40 (or 1 g Ge per 30 g Al), a saturated solid solution of germanate in aluminum hydroxide is formed, and with a further decrease in the ratio $Al_2O_3 : GeO_2$ a separate solid phase of aluminum germanate appears. From this point on, the equilibrium concentration of germanium in solution no longer depends on the ratio $Al_2O_3 : GeO_2$, i.e., on the amount of germanate precipitated, and is determined only by the solubility of the latter, amounting to ~0.32 mg/l GeO_2 (Figs. 2 and 3). This continues as long as there is enough aluminum to form the sparingly soluble germanate. The second bend

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Fig. 3. Dependence of the equilibrium concentration of germanium in solution on the initial molar ratio $Al_2O_3 : GeO_2$

Figure 2: Fig. 3. Dependence of the equilibrium concentration of germanium in solution on the initial molar ratio $Al_2O_3 : GeO_2$

of the curve in Fig. 2 and the bend of the curve in Fig. 3 indicate a deficiency of aluminum relative to its stoichiometric amount in the germanate. As a result, the amount of germanium in solution begins to increase sharply as the ratio $Al_2O_3 : GeO_2$ decreases.

Thus, the ratio $Al_2O_3 : GeO_2$ at the point of inflection corresponds to their ratio in the most readily formed germanate. From Fig. 3 it is evident that this ratio is 1.5. Further sorption of germanium at $Al_2O_3 : GeO_2 < 1.5$ is probably explained by the formation of a more soluble germanate with a higher germanium content ([2]).

It seems to us that the reaction proceeds according to the following equation:

$$1.5\,Al_2O_3 \cdot GeO_2 \cdot nH_2O + 2H_2GeO_3 \rightarrow 1.5\,Al_2O_3 \cdot 3GeO_2 \cdot mH_2O + qH_2O$$

and goes to completion only with a large excess of GeO_2 in solution ($GeO_2 : Al_2O_3 > 3$, see Fig. 4).

Thus, in order to sorb germanium present in solution at concentrations below 0.3 mg/l, large ···

ratios of $Al_2O_3 : GeO_2$ at which solid solutions with a small concentration of germanate in aluminum hydroxide are formed.

Weight ratio Al : Ge	1	5	100	200	2000	5000	10 000
Ge concentration, mg/l	100	30	10	1	0.1	0.02	0.01
Ge precipitation, %	99	99	99	99	96	97	96

The data presented show that it is possible practically completely to precipitate germanium on aluminum hydroxide (pH 7-8; 2% $(NH_4)_2SO_4$) even if

Fig. 3. Dependence of the equilibrium concentration of germanium in solution on the initial molar ratio $Al_2O_3 : GeO_2$

the concentration of the former is 0.01 mg/l. For this, weight ratios $Al : Ge = 10\,000$ should be taken (or $M\,Al_2O_3 : M\,GeO_2 \geq 13\,000$). For better coagulation of the hydroxide, an electrolyte should be added to the solution. Numerous experiments have established that the addition as electrolytes of such salts as NH_4Cl, $(NH_4)_2SO_4$, and NaCl has practically no effect on sorption.

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Fig. 4. Molar ratios $GeO_2 : Al_2O_3$ in the precipitate as a function of the initial ratios of these components in solution

Figure 3: Fig. 4. Molar ratios $GeO_2 : Al_2O_3$ in the precipitate as a function of the initial ratios of these components in solution

Fig. 4. Molar ratios $GeO_2 : Al_2O_3$ in the precipitate as a function of the initial ratios of these components in solution

The conditions we found for the quantitative sorption of germanium by aluminum hydroxide, together with its high sorption capacity, made it possible to propose a new gravimetric method for determining semimicroquantities of Ge ($\geq$ 100 mg/l) in solution. The determination can be carried out by precipitating with ammonia (pH $\sim$ 7–8) a known amount of aluminum from a pure solution and from a solution containing germanium. In both cases the precipitate is filtered, washed, ignited, and weighed. The increase in the weight of the precipitate in the second case corresponds to the germanium content in the tested sample of solution.

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