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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Sol–Gel Synthesis of Carbonate-Containing Zirconium(IV) Hydroxide and Its Sorption Properties toward Alkaline-Earth Elements

L. M. Sharygin, M. L. Kalyagina, and O. L. Borovkova

Termoksid Production and Research Private Company, Zarechnyi, Sverdlovsk oblast, Russia

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Abstract—Carbonate-containing zirconium hydroxide with a CO_2 content of up to 0.5 mol per mole of ZrO_2 was prepared by the sol–gel procedure. The sorption power of the carbonate-containing zirconium(IV) hydroxide toward Sr^{2+}, Ca^{2+}, and Mg^{2+} ions was studied. The effect of pH and electrolyte concentration on the sorption power was examined.

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Zirconium(IV) hydroxide is used as ion-exchange material in fine purification of potable water to remove silicon, arsenic, and phosphorus compounds and other impurities, in radiochemistry for separation and purification of radionuclides, and in nuclear power engineering for treatment of aqueous media to remove radionuclides. The sorbent also shows much promise in medicine for removal of toxic compounds from biological fluids. It is known that sorption processes on oxyhydrates involve hydroxy groups which are capable of acid or base dissociation depending on pH. Hydroxy groups are nonuniform. Hydrated zirconium dioxide (HZD) contains [1, 2] two types of sorption centers with the dissociation constants pK_1 7.0 and pK_2 10.3. There is also the third group of weak acid centers with the dissociation constant close to that of water. The sorption capacity of HZD for alkaline-earth metals [1, 3] strongly depends on pH of solution. With an increase in pH, the capacity for alkaline-earth metals increases. With respect to the sorption capacity of HZD, alkaline-earth metal cations can be ranked in the following order: $Ba^{2+} > Ca^{2+} > Mg^{2+}$. Modification of HZD with multiple-charged oxygen-containing anions (CrO_4^{2-}, $Cr_2O_7^{2-}$, VO_3^{-}, AsO_4^{3-}, MoO_4^{2-}, CO_3^{2-}, etc.) significantly changes its sorption and selective properties [4, 5]. Of considerable interest as sorbents are carbonate-substituted forms of zirconium(IV) hydroxide, which is associated with properties of carbonate ions forming insoluble precipitates with some metals and water-soluble complexes with other metals.

The goal of this study was the development of a sol–gel procedure for preparing zirconium(IV) hydroxide modified with carbonate ions and examination of its ion-exchange properties.

The sol–gel synthesis of spherogranulated zirconium(IV) [6] hydroxide consists of the following main steps: preparation of zirconium(IV) hydroxide sol by electrolysis of a solution of zirconium chloride, gelation of sol drops into an ammonia solution to obtain zirconium hydroxide gel spheres, washing of these gel spheres, and their drying to a definite moisture content. It is the most appropriate to perform modification of zirconium hydroxide with carbonate ions in the step of treatment of gel spheres. To develop the modification process, we initially took the kinetic curves and isotherms of adsorption of hydrocarbonate ions on zirconium(IV) hydroxide gel spheres. In our experiments we used gel spheres prepared by the above-described procedure, with the grain size of 0.6–1.6 mm and moisture content of 77 wt %, determined from the weight loss on drying to constant weight at 100°C. The ZrO_2 content of the gel spheres, determined by calcination of the dried gel spheres at 950°C, was 1.2 mmol cm^{-3}. The gel spheres washed to remove ammonia were preliminarily neutralized with hydrochloric acid to pH 5–6 of the mother liquor, washed

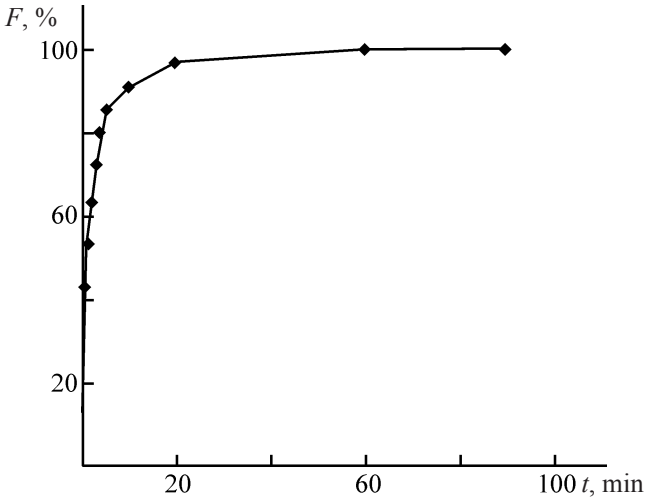

Fig. 1. Kinetic curve of sorption of hydrocarbonate ions on irconium dioxide gel spheres. (*F*) Degree of equilibrium attainment and (*t*) sorption time.

two times with water at S : L = 1 : 1, and pressed on a vacuum filter to remove the mother liquor. The kinetic curve of the sorption of HCO_3^- ions was taken by the limited volume method, providing the conditions of internal diffusion control. An adsorbent sample of weight 40.54 g, which corresponded to a volume of gel spheres of 50 cm^3, was poured over with 100 ml of a 0.2 M solu-tion of sodium hydrocarbonate, and the mixture was stirred. The concentration of hydrocarbonate ions in the solution was determined at regular intervals. To obtain the sorption isotherms, a 40.54-g sample of gel spheres was poured over with 100 ml of a sodium hydrocarbonate solution of various concentrations, and the mixture was stirred for 24 h. The concentration of hydrocarbonate ions in the initial and equilibrium solutions was determined by titration with hydrochloric acid using Methyl Orange indicator.

Figure 1 shows the kinetic curve of sorption of hydrocarbonate ions in the *F*–*t* coordinates, where $F = a_t/a_\infty$, a_t and a_∞ are the concentrations of HCO_3^- ions in the sorbent phase in time *t* and at equilibrium, respectively. As can be seen, the sorption is fast. Approximately equilibrium state in the sorption system is attained in 1.5–2.0 h. The half-exchange time on zirconium hydroxide gel spheres is $t_{1/2} = 60$ s. The coefficient of internal diffusion of hydrocarbonate ions into a sorbent particle, calculated by the formula

$$D = \frac{0.03 r_0^2}{t_{1/2}}.$$

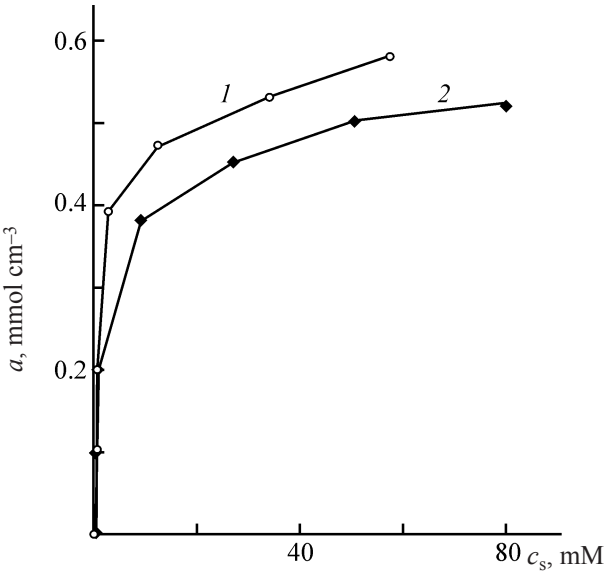

Fig. 2. Sorption isotherms of hydrocarbonate ions on zirconium dioxide gel spheres. (c_s) Sorbate concentration in solution and (*a*) sorption; the same for Fig. 3. Gel spheres: (*1*) freshly prepared and (*2*) aged; the same for Fig. 3.

where r_0 is the mean size of gel spheres, equal to 1.1 mm, was 5.8×10^{-10} m^2 s^{-1}.

Figure 2 shows the sorption isotherms of hydrocarbonate ions on freshly prepared gel spheres and on those kept in the mother liquor (aged) for 6 months. The sorption isotherms have the shape typical of Langmuir isotherms, with the steeply ascending initial portion and the region of saturation. Aging of gel spheres leads to a decrease in their sorption power. A decrease in the sorption power with time can be attributed to the occurrence of oxolation processes with the transformation of diol bonds into an oxo bond [7]:

$$\begin{matrix} & OH & \\ Zr & & Zr \\ & OH & \end{matrix} = \begin{matrix} & & \\ -Zr-O-Zr- & & \\ & & \end{matrix} + H_2O,$$

which leads to a decrease in the amount of hydroxy groups. The data obtained indicate that aging occurs at room temperature relatively slowly.

Sorption of carbonates on zirconium hydroxide can be considered as acid–base interaction of carbonic acid and hydrocarbonate ions with hydroxy groups in accordance with the equations

$$\begin{matrix} \\ -Zr-OH \\ \end{matrix} + H_2CO_3 = \begin{matrix} \\ -Zr-CO_3H \\ \end{matrix} + H_2O, \quad (1)$$

$$\begin{matrix} \\ -Zr-OH \\ \end{matrix} + NaHCO_3 = \begin{matrix} \\ -Zr-CO_3Na \\ \end{matrix} + H_2O. \quad (2)$$

The process leads to the formation of a surface carbonate complex of Zr(IV), containing H^+ and Na^+ ions capable of ion exchange.

The reaction in the system mainly follows Eq. (2), because, in accordance with the acid–base equilibria of carbonic acid, at pH 7–8 the concentration of HCO_3^- ions will be considerably higher than that of H_2CO_3. In addition, in solutions the equilibrium of carbonic acid formation is attained considerably more slowly than the equilibrium of its ionization. The concentration constant of exchange by reaction (2) will be

$$K = \frac{a}{\bar{c}_{OH} c_s} . \quad (3)$$

where a and c_s are the carbonate concentrations in the gel spheres and in solution, respectively; $\bar{c}_{OH}$ is the concentration in the gel spheres of hydroxy groups capable of interaction under the given conditions,

$$\bar{c}_{OH} = a_m - a, \quad (4)$$

a_m is the capacity of the gel spheres for carbonate ions at constant temperature and pH.

It is known that the quantity a_m for weakly functional ion-exchange materials strongly depends on pH of the solution. Expression (3), taking into account (4), is transformed to the linear form of the Langmuir equation

$$\frac{1}{a} = \frac{1}{a_m} + \frac{1}{a_m K c_s} . \quad (5)$$

Experimental data on sorption of hydrocarbonate ions on gel spheres in the region of equilibrium concentrations of sodium hydrocarbonate from 5 to 80 mM (Fig. 3) are satisfactorily described by Eq. (5). The capacity of the aged gel spheres for CO_2 appeared to be equal to 0.54, and that of freshly prepared gel spheres, to 0.6 mmol cm^{-3}, i.e., to approximately 0.5 mol of CO_2 per mole of ZrO_2. Based on these data, the composition of the solid phase of carbonate-containing zirconium hydroxide is $Zr(OH)_{3.5}(NaCO_3)_{0.5}$. It is known [8] that addition of a solution of ammonium or alkali metal carbonate to solutions of zirconium salts leads to the formation of precipitates of variable composition, readily soluble in excess precipitant. As found by Limar' and Shatskaya [9], the reaction of zirconium(IV) oxochloride with ammonium carbonate at the initial molar ratio $(NH_4)_2CO_3 : ZrOCl_2 = 1 : 1$ yields a precipitate of zirconium hydroxocarbonate of the composition $Zr(OH)_2CO_3$, containing sorbed Cl^- anions and ammonium cations. The suggested procedure yields zirconium (IV) hydroxide modified with carbonate ions.

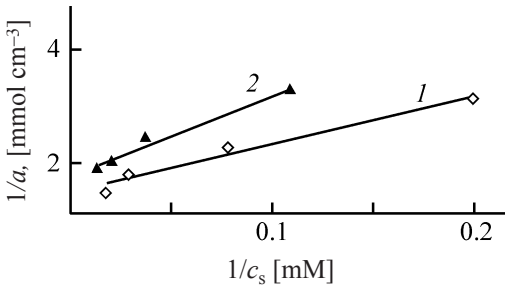

Fig. 3. Sorption isotherms of hydrocarbonate ions on zirconium(IV) hydroxide gel spheres, linearized in the coordinates of the Langmuir equation.

Thus, the modification procedure involves treatment of neutralized zirconium(IV) hydroxide gel spheres with a sodium hydrocarbonate solution to a carbonate content in gel spheres of 0.4–0.5 mmol cm^{-3}, followed by drying to a moisture content of 45–50 wt %.

By this procedure we prepared a batch of a carbonate-containing sorbent with the following characteristics: molar ratio $CO_2/ZrO_2 = 0.4$, moisture content 48 wt %, granule size 0.4–1.0 mm. The CO_2 content in the sorbent was additionally determined by the gasometric method [10], by treatment of a weighed portion of the material with hydrochloric acid, followed by determination of the volume of the released CO_2. The CO_2 content that we found was 5.0 wt %, which is in good agreement with the sorption data. For comparison, we determined by this procedure the amount of CO_2 in spherogranulated zirconium hydroxide prepared by the sol–gel procedure [7], with a moisture content of 48 wt %. The CO_2 content appeared to be equal to 1.3 wt %. This fact indicates that, in the course of the synthesis, the matrix was contaminated with CO_2, which should be taken into account when considering the ion-exchange properties of hydrated zirconium dioxide [11].

The sorption isotherms of alkaline-earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+}) on a sample of carbonate-containing zirconium(IV) hydroxide were taken under static condiions at S : L ~1 : 100 and keeping time of 48 h with intermittent stirring. The sorption was performed from a borate buffer solution (0.1 M H_3BO_3). The required concentration of hydrogen ions in solution was maintained by adding the calculated amounts of HCl and NaOH. The constant concentration of sodium ions

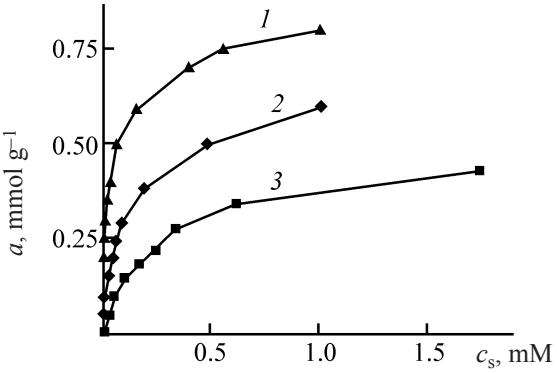

Fig. 4. Sorption isotherms of metal cations from borate buffer solution on carbonate-containing zirconium(IV) hydroxide in the presence of 0.02 M Na^+. (*a*) Sorption and (c_s) sorbate concentration in solution; the same for Figs. 5 and 6. Cations: (*1*) Sr^{2+}, (*2*) Ca^{2+}, and (*3*) Mg^{2+}.

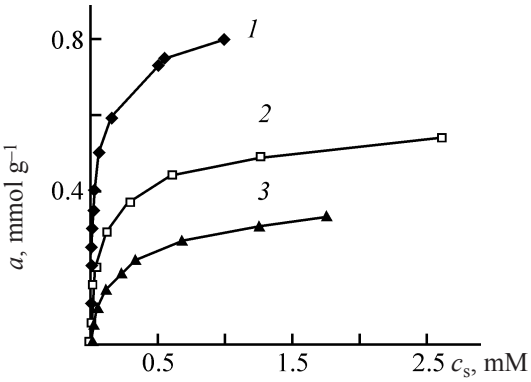

Fig. 5. Sorption isotherms of Sr^{2+} from borate buffer solution on carbonate-containing zirconium(IV) hydroxide in the presence of 0.02 M Na^+. pH: (*1*) 9.0, (*2*) 8.0, and (*3*) 7.5.

in solution was maintained by adding NaCl. The sorption isotherms were taken at low equilibrium concentrations of metal ions, mainly below 1 mM, because hydrolysis of the sorbent may lead to appearance of carbonate ions in solution, forming poorly soluble carbonates with metal cations. The concentration of alkaline-earth elements in the liquid phase was determined by volumetric EDTA titration [12].

Figure 4 shows the adsorption isotherms of alkaline-earth metal cations from borate buffer solution on carbonate-containing zicronium(IV) hydroxide at pH 9 ± 0.1 and solution ionic strength of 0.02. With respect to the sorbability, the cations can be ranked in the following order: $Sr^{2+} > Ca^{2+} > Mg^{2+}$. This selectivity order for cation exchangers is usually attributed to a decrease in the cationic radius and correspondingly to an increase in the effect of cation hydration on the sorption interaction. The most

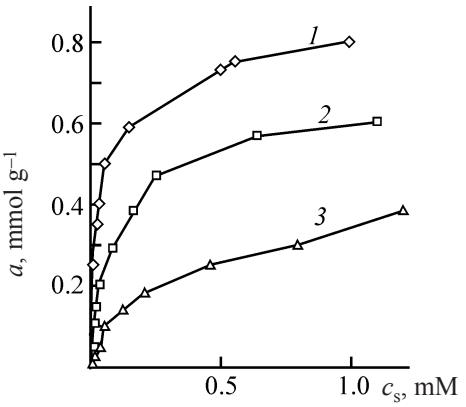

Fig. 6. Sorption isotherms of Sr^{2+} from borate buffer solution on carbonate-containing zirconium(IV) hydroxide at pH 9. Na^+ concentration, M: (*1*) 0.02, (*2*) 0.1, and (*3*) 0.52.

selective to zirconium hydroxide are strontium cations for which the distribution coefficient K_d is 10^4 even at sorbent filling of 0.5 mmol g^{-1}. For the Sr^{2+}–Mg^{2+} pair, the separation factor in the Henry region, calculated as $K_{Mg^{2+}}^{Sr^{2+}} = K_d^{Sr^{2+}}/K_d^{Mg^{2+}}$, was 10. For the Sr^{2+}–Ca^{2+} pair, the separation factor $1K_{Mg^{2+}}^{Sr^{2+}}$ under these conditions was 2.6. Presumably, the ion exchange on carbonate-containing zirconium(IV) hydroxide is accompanied by complexation of cations with surface carbonate groups. Therefore, the observed selectivity order can be correlated with the inverse order of solubility products of metal carbonates: $SP(SrCO_3) < SP(CaCO_3) < SP(MgCO_3)$.

With a decrease in pH (Fig. 5), the sorption capacity of the material for strontium cations decreases, that is typical of weakly acidic cation-exchange materials. The distribution coefficient of strontium ions, equal to 1.0×10^4 at an equilibrium Sr^{2+} concentration of 0.05 M and pH 9, decreases to 4.5×10^3 at pH 8 and to 1.5×10^3 at pH 7.5. The Na^+ ions exert a noticeable competing effect on the sorption of Sr^{2+} with carbonate-containing zirconium(IV) hydroxide (Fig. 6). With an increase in the Na^+ concentration, the sorption capacity of the material decreases. On the whole, the data we obtained allow carbonate-containing zirconium(IV) hydroxide to be recommended for recovery of strontium radionuclides from alkaline solutions with relatively low salt concentrations.

CONCLUSIONS

(1) An inorganic sorbent, carbonate-containing zirconium hydroxide with a CO_2 content of up to

0.5 mol per mole of ZrO_2, was prepared by the sol–gel procedure.

(2) With respect to the sorption capacity of carbonate-containing zirconium hydroxide, sorbate cations can be ranked in the following order: $Sr^{2+} > Ca^{2+} > Mg^{2+}$.

(3) With a decrease in pH and an increase in the concentration of sodium cations, the sorption capacity with respect to strontium cations decreases.

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