Sorption properties of zirconogels

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The effect of the pH of precipitation and the nature of the initial zirconium salt and the ionic medium on sorption properties (surface charge, kinetic parameters of sorption) of zirconogels formed due to alkaline hydrolysis of zirconium(IV) sulfate and zirconyl nitrate was studied. Zero point of charge methods, indicator reactions of heterogeneous hydrolysis, drop titration, and thermography were used in the study. The properties of the zirconogels are very close to those of ferro- and titanogels obtained under similar conditions. The composition of zirconogels, the activation energies of the indicator reactions of heterogeneous hydrolysis, and the dependences of the rate constants of these reactions on the nature and concentration of the ionic medium were determined.

Key words: sorption properties, zero point of charge, oxyhydroxide, zirconogel, indicator reaction rate.

The purpose of the comparative study of the sorption properties of hydrogels of metal oxyhydroxides in different ionic media is to create a theoretical model with which to predict the conditions for the extraction of complex-forming metals from complex-forming media by inorganic sorbents, oxyhydroxides.

Our previous studies of ferro- and titanogels[1–4] suggest that gels with specified sorption properties can virtually be obtained for almost any metal that forms weakly soluble gelatinous hydroxides, if the conditions favoring dehydration and (or) crystallization of gels are avoided.

The majority of works on the sorption properties of zirconium(IV) oxyhydroxides (see, *e.g.*, Refs. 5—9) examine dried or even calcined samples, in which the zero point of charge (ZPC) is in the range of pH < 6.5, which possess insignificant sorption capacity and selectivity, and which are characterized by diffusion sorption kinetics.[5–9] There is no published data on the sorption properties of gels of zirconium(IV) oxyhydroxides.

In this work, two series of zirconogels (based on $ZrO(NO_3)_2$ and $Zr(SO_4)_2$) were obtained, and their sorption properties were studied by the methods of ZPC and indicator reactions of the heterogeneous hydrolysis of complex anions ($IrCl_6^{2-}$).[2–4]

Experimental

For preparing the zirconogels, $ZrO(NO_3)_2 \cdot H_2O$ (analytical grade) and $Zr(SO_4)_2 \cdot H_2O$ (pure grade) were used. Zirconyl nitrate (2.19 g) or zirconium(IV) sulfate (2.86 g), which corresponds to 1.2 g of $Zr(OH)_4$, was dissolved in water (50 mL). The natural pH value was established at ~20 °C in the range of pH 0.8—1.1. No complete coagulation of the precipitate occurred up to a pH of precipitation equal to 4. A 2 *M* solution of NaOH (chemically pure grade) was added to the reaction mixture containing partially hydrolyzed zirconium(IV) with constant stirring and pH-metric control until a specified pH of the suspension (pH_s), which was stable for ~5 min, was established. The precipitate was separated by centrifugation, triply washed by decantation with H_2O, and centrifuged again. The samples of the precipitate obtained were suspended in water (100 mL) and used for the experiments to determine the pH_{ZPC} and rate constants of heterogeneous hydrolysis.

Composition of zirconogels. The compositions of the zirconogels obtained at different pH of precipitation (pH_1) were determined by drop titration of NaOH, as described in Ref. 4 (Fig. 1). The samples corresponding to 1.2 g of $Zr(OH)_4$

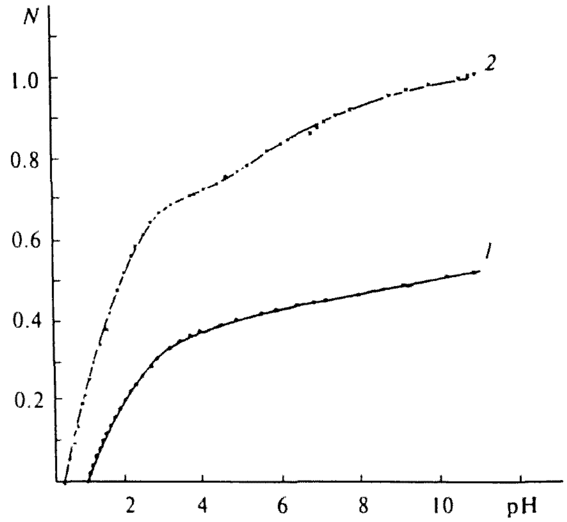

Fig. 1. Drop titration of $ZrO(NO_3)_2$ (*1*) and $Zr(SO_4)_2$ (*2*) with a solution of NaOH. *N* is the ratio of the added OH/0.25 Zr.

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Table. 1. Calculation of the OH/Zr ratio for drop titration of zirconium(IV) salts with a solution of NaOH

Initial salt	pH_1	pH_2	V_2 /mL	pH_s	pH_3	α	β	γ
$ZrO(NO_3)_2 \cdot 2H_2O$	4.10	3.41	246	4.25	4.35	1.492	0.0125 H^+	1.4795
	8.14	6.86	279	7.57	5.41	1.844	0.000126 H^+	1.8439
	11.05	11.36	278	10.7	7.85	2.042	0.0761 OH^-	1.9659
$Zr(SO_4)_2 \cdot 4H_2O$	3.98	3.76	307	3.00	3.02	2.830	0.00774 H^+	2.7991
	8.00	6.09	373	6.96	4.70	3.672	0	3.6724
	11.09	10.99	350	10.3	7.56	4.000	0.0107 OH^-	3.9560

Note: α is the sum of the added OH/Zr, equiv/g-atom; β is the sum of H/Zr added during washing or OH/Zr eliminated, equiv/g-atom; γ is OH/Zr in the precipitate, equiv/g-atom.

for three different pH of precipitation (Table 1) were washed off with water as described above and introduced into a 0.5 *M* solution of NaCl (200 mL). The precipitate was filtered off, and the pH values of the wash water (pH_2), the suspension in 0.5 *M* NaCl (pH_s), and the filtrate (pH_3) were measured. To calculate the OH/Zr ratio in the samples studied (Table 1), the amounts of the alkali washed off and displaced by an electrolyte were determined from the titration data.

After washing, the samples of gels were dried in a vacuum desiccator over concentrated sulfuric acid at ~20 °C for 6—7 days and were studied by DTA—TG methods (Fig. 2). The thermal analysis was carried out with a 0.1—0.2-g sample on an NTR-70 instrument combined with a PTR-1000 instrument and a Pt-PtRh-thermocouple, and on a PP-63 instrument combined with a VT-1000 torsion balance at a heating rate of 10 deg/min.

The compositions of the samples calculated from the DTA—TG curves are presented in Table 2, and the most typical thermograms are presented in Fig. 2.

The determinations of the pH of the zero points of charge of the zirconogels were performed by the Parks method[10] modified by us for gels[1] and by potentiometric titration of samples on a pH-121 pH-meter in a half-open type quartz cell in an argon flow with an ESL43-07 glass electrode and an EVL-1M1 accessory electrode immersed in a suspension of zirconogel (pH_s) or a reference solution (pH_0). Prior to titration, argon was bubbled for ~1.5 h through the suspension of zirconogel washed as described above and a solution of electrolyte to remove dissolved CO_2. Then the suspension (100 mL) was added to a solution of an electrolyte (100 mL) prepared in such a way that the concentration of the electrolyte was 1.0, 0.1, or 0.01 mol L^{-1} in the final volume of the suspension. To establish the initial pH or pH_0 value, a solution of carbonate-free alkali NaOH (0.123 mol L^{-1}, 5 mL) was added, and then the suspension was titrated by a solution of the acid (0.1 *M*, fixanal) whose anion corresponded to the anion of the electrolyte, at an interval of 0.4 mL min^{-1}. Recrystallized NaCl, Na_2SO_4, $NaClO_4$, and $NaNO_3$ were used as supporting electrolytes. The amount of excess $OH^-(H_3O^+)$ ions sorbed was determined by comparing pH_s and pH_0 during the blank experiment at a given volume of a titrant. Examples of the

Table 2. Composition of gels of zirconium(IV) oxyhydroxides

pH_1	Initial compound	
	$ZrO(NO_3)_2$	$Zr(SO_4)_2$
5	$[Zr(OH)_4] \cdot 1.9H_2O$	$[ZrO(OH)_2] \cdot 0.3H_2SO_4 \cdot 0.84H_2O$
6	$[Zr(OH)_4] \cdot 7.83H_2O$	$[ZrO(OH)_2] \cdot 0.18H_2SO_4 \cdot H_2O$
8	$ZrO_{1.33}(OH)_{1.33} \cdot 1.5H_2O$ $[Zr_3O_4(OH)_4] \cdot 4.5H_2O$	$ZrO_{1.5}OH \cdot 0.136H_2SO_4 \cdot 1.33H_2O$ $[Zr_4O_6(OH)_4) \cdot 0.54H_2SO_4 \cdot 5.3H_2O$
10	$ZrO_{1.5}OH \cdot 1.1H_2O$ $[Zr_4O_6(OH)_4] \cdot 4.4H_2O$	$ZrO_{1.5}OH \cdot 1.33H_2O$ $[Zr_4O_6(OH)_4)] \cdot 5.2H_2O$
12	$ZrO_{1.2}(OH)_{1.6} \cdot 3.9H_2O$ $[Zr_5O_6(OH)_8] \cdot 19.5H_2O$	$ZrO_{1.12}(OH)_{1.76} \cdot H_2O$ $[Zr_8O_9(OH)_{14}] \cdot 8H_2O$

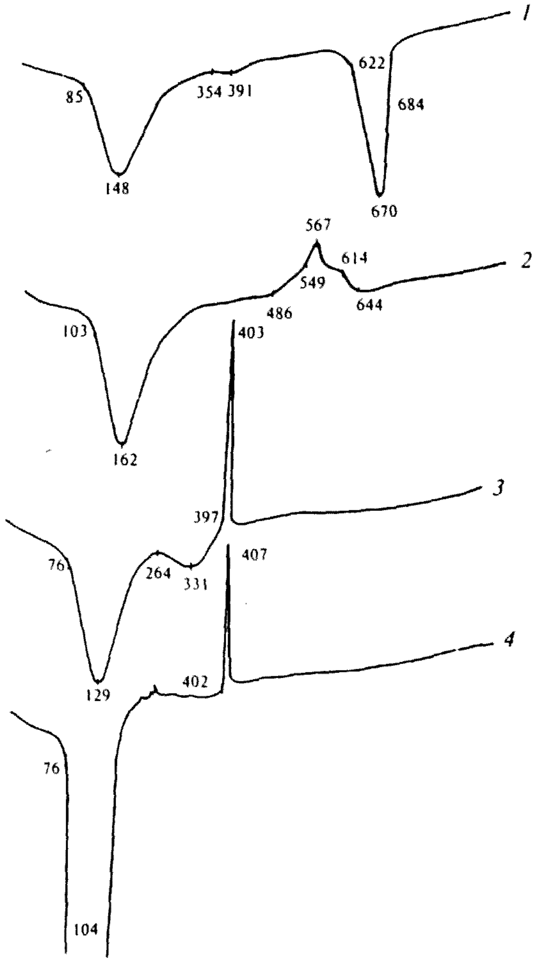

Fig. 2. Thermograms of xerozirconogels. Initial zirconium salt: *1* and *2*, sulfate; *3* and *4*, nitrate. pH_1: 5 (*1, 3*); 8 (*2*); and 6 (*4*). Heating rate: 10 K min^{-1}.

Table 3. Values of pH_{ZPC} of zirconogels in solutions of electrolytes with different concentrations (*C*) prepared at different pH of precipitation (pH_1)

Electrolyte	*C* /mol L^{-1}	$ZrO(NO_3)_2$							$Zr(SO_4)_2$				
		pH_1											
		5.5	6	7	8	9	10	11	6	7	8	9	10
NaCl	1.0	5.5	6.2	7.3	8.2	9.0	9.4	10.3	—	5.4	6.7	8.4	9.7
	0.1	4.8	5.2	6.2	7.3	8.6	9.8	10.9	—	5.3	6.6	8.7	10.8
	0.01	4.1	4.1	5.1	6.7	7.7	10.3	11.2	—	5.3	6.4	8.9	11.4
Na_2SO_4	0.5	—	7.7	8.3	8.9	9.3	9.9	—	—	7.1	7.9	—	9.6
	0.05	—	7.2	8.1	8.6	9.5	10.0	—	5.5	6.7	7.2	9.0	10.0
	0.005	—	6.6	7.5	8.3	9.3	10.7	—	—	6.1	7.0	—	10.8
$NaClO_4$	1.0	—	—	6.1	—	—	—	—	—	5.6	—	8.6	9.1
	0.1	—	3.8	5.1	6.1	8.5	—	—	3.8	5.3	6.1	8.2	—
	0.01	—	—	3.9	—	—	—	—	—	4.1	—	8.0	—
$NaNO_3$	1.0	—	—	6.9	—	8.8	—	—	—	—	—	—	—
	0.1	—	—	—	—	8.9	—	—	—	5.2	—	7.9	—
	0.01	—	—	5.3	—	9.8	—	—	—	5.1	—	—	—

titration curves are presented in Fig. 3. The results of the determination of pH_{ZPC} are presented in Table 3.

Indicator reactions of heterogeneous hydrolysis. As in the other works,[2—4] the reaction rate of heterogeneous hydrolysis of the $IrCl_6^{2-}$ complex was used to characterize the surface properties of zirconogels. K_2IrCl_6 obtained by the procedure described in Ref. 11 and characterized by elemental and X-ray diffraction analyses was used. The initial concentration of Ir was ~$2.9 \cdot 10^{-4}$ mol L^{-1}, the volume of the reaction mixture was 200 mL, and the measurement and calculation procedures are described in Ref. 2. The results are presented in Tables 4 and 5.

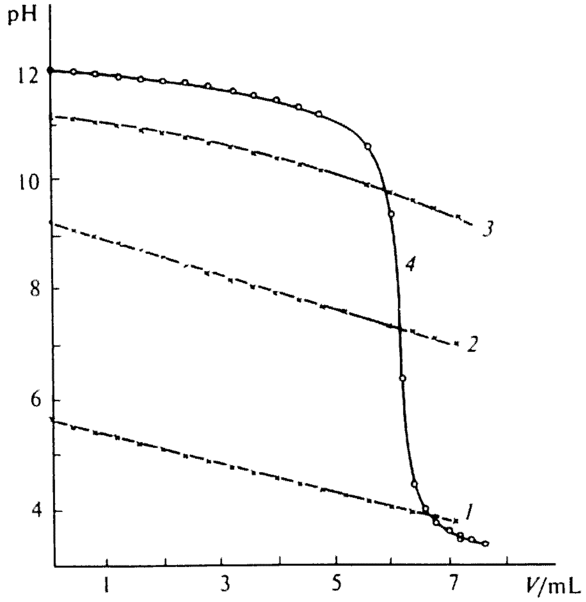

Fig. 3. Curves of the potentiometric titration of zirconogels in a 0.1 *M* solution of NaCl. Initial salt: $ZrO(NO_3)_2 \cdot 2H_2O$; *V* is the volume of the titrant (0.1 *M* HCl); pH_1: 5 (*1*); 8 (*2*); 10 (*3*); blank titration of the electrolyte (*4*).

Table 4. Rate constants ($k_H \cdot 10^4/s^{-1}$) of the heterogeneous hydrolysis of $IrCl_6^{2-}$ on the surface of zirconogels in a 1 *M* solution of NaCl at different temperatures and pH of precipitation

pH_1	*T*/°C					E_a /kJ mol^{-1}
	50	60	70	80	90	
			Zirconyl nitrate			
6	—	—	3.4	7.7	26.5	110.0
7	—	1.4	4.4	11.3	30.7	103.5
8	0.9	2.7	7.4	33.4	—	110.1
9	1.8	4.7	17.8	—	—	107.6
10	3.5	15.0	34.6	—	—	110.0
11	5.5	13.7	28.6	—	—	81.9
12	4.2	15.3		—	—	—
7*	—	0.8	4.1	15.7	—	147.3
			Zirconium sulfate			
7	—	—	2.3	4.7	20.2	116.8
8	—	0.5	2.2	9.6	—	149.6
9	—	1.2	5.8	46.0	—	159.6
10	—	9.3	19.2	—	—	—
11	4.5	9.3	22.6	—	—	94.8
7*	—	—	1.8**	3.1	4.9	72.5

* The ionic background is 0.5 *M* Na_2SO_4. ** 75 °C.

Results and Discussion

Drop titration (Fig. 1, Table 1) and thermal analysis of washed samples (Table 2) showed that zirconogels obtained by treatment of a solution of zirconyl nitrate with NaOH followed by triple washing, unlike titanogels,[4] reach the composition of $Zr(OH)_4$ when the pH of precipitation is low. By contrast, when solutions of zirconium(IV) sulfate are treated with alkali, zirconyl derivatives are formed that fix some amount of H_2SO_4 in the range of low pH of precipitation. When the pH of

Table 5. Dependences of the rate constants of the heterogeneous hydrolysis of $IrCl_6^{2-}$ (k_H/s^{-1}) on the surface of zirconogels on the nature and concentration (C/N) of the ionic background

Initial Zr salt	T /°C	pH_I	Electrolyte	$k_H \cdot 10^4$ at C of the electrolyte			
				0.01	0.1	0.5	1.0
$ZrO(NO_3)_2$	70	8	Na_2SO_4	9.1	9.1	8.5	~10
	70	8	NaCl	—	25.0	8.4	7.4
	60	8	Na_2SO_4	2.2	2.4	~1.5	~1.2
	60	7	$NaClO_4$	*	—	*	8.9
$Zr(SO_4)_2$	70	8	NaCl	*	6.0	3.5	2.5
	80	9	Na_2SO_4	—	~6.6	~6.6	~6.5
	60	7	$NaClO_4$	—	—	~1.1	~0.8

* Very rapidly, so that k_H cannot be determined with sufficient accuracy.

precipitation is higher than 8, both initial products give partially dehydrated compounds, probably polymeric (Table 2), of composition $Zr_xO_y(OH)_z$, where x = 5—8, y = 6—10, and z = 4—14, as in the case of titanogels.[4] Comparing the results of thermal analysis and drop titration, one may conclude that the treatment of solutions of zirconyl nitrate and zirconium sulfate with alkali results in the addition and elimination of the water molecules coordinated at the central atom, respectively, although the amount of the alkali consumed in the titration reaches the stoichiometric value only at pH 11 (Fig. 1). It can be seen that anions of the initial salt can be easily removed from zirconogels, unlike ferrogels,[1,2] although even trace amounts of anions of the initial salt have a strong effect on the properties of the gel. SO_4^{2-} ions especially facilitate dehydration of gels, probably by enhancing the processes of oxolation and olation.*

The acid-base titration curves of zirconogels (Fig. 3) are typical of amphoteric oxyhydroxides, which possess weak acid-base properties.[2] As in the case of ferro- and titanogels,[2—4] the titration is reversible. The results of the determination of pH_{ZPC} (Table 3, Fig. 4) show that the curves of the dependence of pH_{ZPC} on pH_I for different concentrations of electrolytes intersect at one point, and this point is different for different electrolytes and different initial zirconium salts. For example, in solutions of NaCl, the pH_I of the intersection point for nitrate gels is equal to 9.3 and for sulfate gels is 8.3, and the pH_{ZPC} values corresponding to the intersection points are equal to 9.2 and 7.0, respectively. In solutions of Na_2SO_4, analogous points are observed at pH 8.8 and 8.8 (pH_I), 9.3 and 8.5 (pH_{ZPC}). This means that zirconogels obtained at pH_I under and above the intersection point of the curves differ as follows: for the first of them in the range of low electrolyte concentrations, $pH_{ZPC} < pH_I$, while for the second type of zirconogels, $pH_{ZPC} > pH_I$. However, in all cases, the dependence of pH_{ZPC} on the electrolyte concentration is very strong. As previously, we explain this fact by the redistribution of H_3O^+ and OH^- between the charged surface of the gel and the solution of the electrolyte. It can also be assumed that true neutral states (true pH_{ZPC} values) correspond to the intersection points indicated (Fig. 4) and a lower value is observed for sulfate gel, which is more disposed to polymerization and dehydration.

When other conditions are equivalent, pH_{ZPC} of zirconogels in sulfate media are higher than in chloride media, and those in chloride media are higher than those in nitrate and perchlorate media. In 1 N solutions of the electrolyte for nitrate gels, the pH_{ZPC} values in the medium of NaCl and $NaNO_3$ are close to pH_I (for example, 6.2 and 6.0, 8.2 and 8.0), those in the medium of Na_2SO_4 are 1—1.5 units higher than pH_I (*e.g.*, 7.7 and 6.0, 8.9 and 8.0), and in the medium of $NaClO_4$, they are ~1 unit lower than pH_I (*e.g.*, 6.1 and 7.0). For sulfate gels, correspondingly, in the media of NaCl and $NaNO_3$ pH_{ZPC} are 0.5—1.5 units lower than pH_I, in the medium of Na_2SO_4 the values are close, and in the medium of $NaClO_4$ they are 0.5—1 units lower than pH_I.

Zirconogels are similar to ferrogels in many respects, not only qualitatively, but in their quantitative parameters as well: at the same pH_I they have very close pH_{ZPC} values and, as will be seen, even very close values of the observed rate constants k_H of heterogeneous

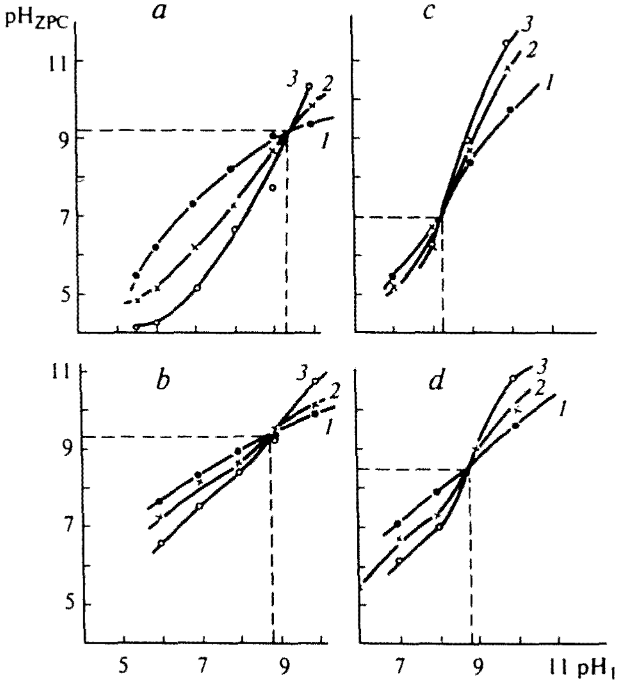

Fig. 4. Dependences of pH_{ZPC} on pH_I. Gels: nitrate (*a*, *b*), sulfate (*c*, *d*); supporting electrolyte: NaCl (*a*, *c*), Na_2SO_4 (*b*, *d*); concentration of the supporting electrolyte, mol L^{-1}: 1.0 or 0.5 (*1*); 0.1 or 0.05 (*2*); 0.01 or 0.005 (*3*).

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* Formation of oxygen and hydroxo bridges between metal atoms to form oxyhydroxide.

hydrolysis of $IrCl_6^{2-}$, although the dependences of pH_{ZPC} and k_H on pH_l reach the plateau at $pH_l > 9$ less distinctly.

The results of studies of zirconogels by the method of indicator reactions of the heterogeneous hydrolysis of $IrCl_6^{2-}$ show that the rate of decrease in the concentration of iridium(IV) in the solution contacting the zirconogel obeys the first-order law, as for heterogeneous hydrolysis on the surface of REE oxyhydroxides, ferro- and titanogels.[2,4] The k_H values for zirconogels are somewhat lower than for ferrogels and considerably higher than for titanogels at the same temperatures, pH_l, and parameters of the ionic medium. The temperature dependences of the rate and activation energy E_a of the indicator reactions on zirconogels are also characteristic of the heterogeneous hydrolysis of $IrCl_6^{2-}$ (Table 4). The dependences of k_H on pH_l and concentration and on the nature of the gel and electrolyte are of the same type for ferro-, titano-, and zirconogels. The E_a values in 1 M solutions of NaCl are very close (within 100—120 kJ mol^{-1}) for ferro-, titano-, and zirconogels obtained from the initial chloride and nitrate salts.[2,4] However, a sharp deviation from this value is observed for the sulfate-sulfate system (see Table 4): E_a decreases to 72.6 kJ mol^{-1} (the same phenomenon is observed for ferrogels: there is a decrease to 68 kJ mol^{-1}).[2] Similarly to ferrogels, E_a increases to 140—150 kJ mol^{-1} for sulfate zirconogels against a background of 1 M NaCl and for nitrate gel against a background of 0.5 M Na_2SO_4.

The fact that the rate of heterogeneous hydrolysis is related to the concentration of surface OH groups is especially clearly demonstrated by the following experiment: sulfate zirconogels with $pH_l = 10$ and 11 were repeatedly washed until constant pH 10.3 of wash water was established, and the kinetics of the indicator reaction was studied at 70° C in 1 M NaCl. This procedure removes 0.017 and 0.078 g-ion/g-atom Zr, respectively. The coinciding kinetic curves were obtained, which corresponded to $k_H = 1.53 \cdot 10^{-3}$ s^{-1}. Based on the dependence of k_H on pH_l, we can say that the samples obtained by triple washing correspond to $pH_l = 9.5$. This result can be explained as both the hydrolytic elimination of OH groups by washing and gradual polymerization of gels over time due to olation.

The determination of the composition of the precipitated form of iridium shows that the situation observed corresponds to the scheme of heterogeneous hydrolysis.[4]

The effect of the nature and concentration of the ionic background (Table 5) on the rate of heterogeneous hydrolysis of $IrCl_6^{2-}$ on the surface of zirconogels coincides on a whole with the situation observed[2] in the case of ferrogels: an increase in the concentration of NaCl in solution results in a decrease in the reaction rate according to the equation: $\log k_H = a - b\log C_{Cl}$, which is similar to that obtained for heterogeneous hydrolysis on ferrogel, and a and b for the data presented in Table 5 are equal to 1.4 and 0.6 for nitrate and 0.86 and 0.4 for sulfate zirconogels. The electrolyte Na_2SO_4 somewhat suppresses the process, but a change in the concentration of this electrolyte has a weak effect on the rate. The rate of the process on the surface of chloride gels is higher than that on the surface of sulfate gels, which is explained by the lower basicity of the latter.

Thus, gels with specified sorption properties (kinetic and capacity parameters, surface charge) can be obtained for zirconium(IV), and their behavior in reactions of sorption from solutions should be quite similar to that of ferro- and titanogels. Apparently, the assertion that the conditions of the preparation of zirconium oxyhydroxide exert no effect on its sorption properties[5] is not correct.

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