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Changes in the acid-base properties of hydrogels of metal oxide hydroxides induced by aging in solutions of electrolytes

S. I. Pechenyuk and S. I. Matveenko*

Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials,
Kola Research Center of the Russian Academy of Sciences,
26a ul. Fersmana, 184200 Apatity, Russian Federation.
Fax: +7 (815 55) 7 6425. E-mail: root@chemy.kolasc.net.ru

Changes in the acid-base properties of titanium(IV), zirconium(IV), iron(III), chromium(III), and indium(III) hydrogels of oxide hydroxides induced by aging in sodium chloride and sulfate solutions were studied by the point of zero charge method. On aging in a solution of the sulfate electrolyte the hydrogels loose their basic properties much more rapidly than in the chloride solution. The most changes were observed in the region of high pH of the point of zero charge of the hydrogels. The changes in the acid-base properties can be explained by a decrease in the content of surface OH groups, which are displaced by the supporting electrolyte ions, and due to the oxolation of the hydrogels.

Key words: acid-base properties, oxide hydroxide, hydrogel, aging (of hydrogel), zero point of charge.

The nature of the ion background has a great effect on the rate and the extent of sorption of complexes on a hydrogel surface.[1-4] Works devoted to the stability of the amorphous state and stability of the sorption properties of hydrogels are as yet scarce.[5-7] It has been found for iron(III) oxide hydroxide that the aging of ferrogels in solutions of sodium chloride and sulfate during 1—2 h results in a substantial decrease in their basic properties, characterized by the pH of the point of zero charge (pH_{PZC}) and the capability of sorbing platinum metal complexes.[8-10] However, unlike the surface acid-base properties of freshly prepared hydrogels, changes in the pH_{PZC} of hydrogels[3,11-14] of metals due to aging in electrolyte solutions are poorly studied.

In this work, we used the point of zero charge method[9] to study the acid-base properties of titanium(IV), zirconium(IV), indium(III), chromium(III), and iron(III) oxide hydroxides aged in solutions of sodium chloride and sulfate. The corresponding data for freshly precipitated hydrogels are presented for comparison.

Experimental

The methods for preparation of samples of oxide hydroxide hydrogels have previously been published.[1,11-14] All compounds used were reagent or analytical purity grade. Titanogels were prepared by the hydrolysis of $TiCl_4$ followed by the neutralization of NaOH to adjust the pH to 4.5, 7, and 10; ferro-, indio-, and chromogels were prepared by the alkaline hydrolysis of

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$FeCl_3$ or $Fe(ClO_4)_3$, $In(NO_3)_3$, and $CrCl_3$, respectively, to adjust the pH to 7, 9, and 11, whereas zirconogels were hydrolyzed by $ZrO(NO_3)_2 \cdot H_2O$ to adjust the pH to 5.5, 7, and 10. The precipitation was performed at the permanent pH-metric controller until the desired pH of precipitation ($\mathrm{pH_I}$) was established in ~50 mL of the suspension, and this value was

Table 1. $\mathrm{pH_{PZC}}$ of hydrogels of titanium(IV), zirconium(IV), iron(III), chromium(III), and indium(III) oxide hydroxides

Type of hydrogel	[NaCl] /mol L^{-1}	$\mathrm{pH_I}$	$\mathrm{pH_{PZC}}$					
			Ti^{IV}	Zr^{IV}	Fe^{III}		Cr^{III}	In^{III}
					From $Fe(ClO_4)_3$	From $FeCl_3$		
Freshly precipitated	0.01	4.5	4.80^{11}	—	—	—	—	—
		5.5	—	4.10^{12}	—	—	—	—
		7.0	8.70^{11}	5.10^{12}	5.60^{1}	—	5.55^{14}	5.10^{13}
		9.0	—	—	—	—	9.30^{14}	8.10^{13}
		10.0	11.10^{11}	10.30^{12}	—	—	—	—
		11.0	—	—	—	—	—	—
	0.1	4.5	4.75^{11}	—	—	—	—	—
		5.5	—	4.80^{12}	—	—	—	—
		7.0	8.17^{11}	6.20^{12}	6.90^{1}	—	6.40^{14}	5.90^{13}
		9.0	—	—	8.70^{1}	8.80	8.60^{14}	8.80^{13}
		10.0	10.85^{11}	9.80^{12}	—	—	—	—
		11.0	—	—	10.30^{1}	—	10.50^{14}	10.40^{13}
	1.0	4.5	4.70^{11}	—	—	—	—	—
		5.5	—	5.50^{12}	—	—	—	—
		7.0	7.65^{11}	7.30^{12}	7.15^{1}	—	6.90^{14}	6.70^{13}
		9.0	—	—	—	8.65	8.50^{14}	9.10^{13}
		10.0	10.10^{11}	9.40^{12}	—	—	—	—
		11.0	—	—	—	—	9.85^{14}	10.60^{13}
Aged in a 0.5 *M* solution of Na_2SO_4 (2 h, 80 °C)	0.01	4.5	—	—	—	—	—	—
		5.5	—	5.55	—	—	—	—
		7.0	7.67	6.30	6.00	—	7.55	5.75
		9.0	—	—	—	—	8.75	—
		10.0	—	9.90	—	—	—	—
		11.0	—	—	—	—	—	—
	0.1	4.5	3.05	—	—	—	—	—
		5.5	—	5.55	—	—	—	—
		7.0	6.90	6.37	6.30	—	7.67	5.60
		9.0	—	—	8.05	8.05	8.55	6.95
		10.0	9.60	9.30	—	—	—	—
		11.0	—	—	10.00	—	9.30	9.15
	1.0	4.5	—	—	—	—	—	—
		5.5	—	5.45	—	—	—	—
		7.0	6.70	6.40	7.15	—	7.45	6.10
		9.0	—	—	—	7.85	8.15	—
		10.0	—	8.90	—	—	—	—
		11.0	—	—	—	—	8.75	—
Aged in a 1 *M* solution of NaCl (2 h, 80 °C)	0.01	4.5	—	—	—	—	—	—
		5.5	—	2.75	—	—	—	—
		7.0	8.00	4.55	5.50	—	5.90	—
		9.0	—	—	—	—	8.75	—
		10.0	—	9.80	—	—	—	—
		11.0	—	—	—	—	—	—
	0.1	4.5	3.45	—	—	—	—	—
		5.5	—	3.80	—	—	—	—
		7.0	6.80	5.10	7.10	—	6.75	5.60
		9.0	—	—	8.50	8.30	8.15	7.30
		10.0	9.65	9.65	—	—	—	—
		11.0	—	—	10.00	—	9.55	9.50
	1.0	4.5	—	—	—	—	—	—
		5.5	—	4.60	—	—	—	—
		7.0	5.70	6.70	7.20	—	7.30	5.70
		9.0	—	—	—	8.05	8.20	—
		10.0	—	8.80	—	—	—	—
		11.0	—	—	—	—	8.60	—

maintained unchanged for ~5 min. The precipitates were separated from the mother liquor by centrifugation and triply washed by decanting with H_2O. After washing, the precipitates were centrifuged (2000 rpm) for 5 min. The precipitation and washing take from 1 to 1.5 h.

To study the aging effect, the samples of hydrogels were placed in 1 *N* solutions of NaCl and Na_2SO_4 with a ratio of the solid to liquid phases of 1 : 200 and stored with continuous stirring for 2 h at 80 °C. The precipitate was separated from the solution, washed, centrifuged as described above, and titrated to determine $\mathrm{pH_{PZC}}$ by the Parkes method.

Titration was carried out on a pH-121 pH-meter in an atmosphere of argon in a half-open-type glass cell with an ESL-43-07 glassy electrode and an EVL-1M1 auxiliary electrode immersed in the suspension. Prior to titration, argon was passed through the gel suspension and a solution of the supporting electrolyte (NaCl) for 1.5 h to remove dissolved CO_2, after which 50 mL of the suspension were introduced into 150 mL of an electrolyte solution prepared to produce a final volume of the suspension with a concentration of NaOH equal to 1.0, 0.1, or 0.01 mol L^{-1}. The initial pH value was established by a carbonate-free solution of NaOH, and the suspension was titrated by a 0.1 *M* solution of HCl. In the comparison experiment, the corresponding volume of the supporting electrolyte was titrated similarly. The number of sorbed hydroxonium or hydroxide ions was determined by comparison of these titration curves; based on these results, the surface charge was calculated and $\mathrm{pH_{PZC}}$ was found (Table 1).

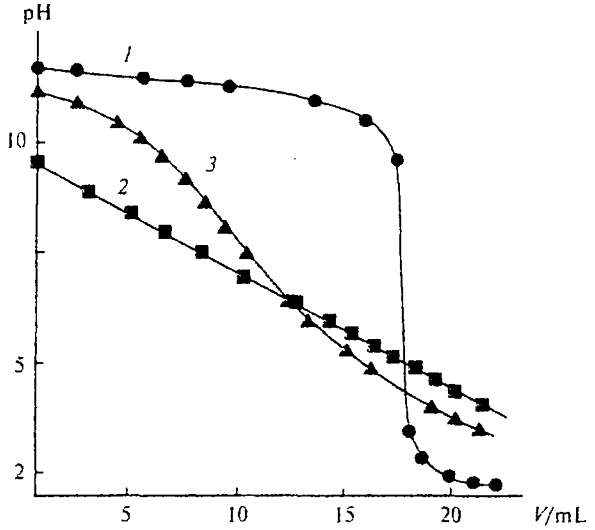

Fig. 1. Results of potentiometric titration of zirconium(IV) oxide hydroxides in a 0.1 *M* solution of NaCl: *1*, blank experiment; *2*, freshly precipitated zirconogel with $\mathrm{pH_i} = 7$; and *3*, zirconogel with $\mathrm{pH_i} = 7$ aged in a 1 *M* solution of NaCl. *V* is the volume of the titrant (0.1 *M* HCl). The pH values of the suspension measured by a pH-meter are plotted on the ordinate.

Results and Discussion

The experimental results serve to compare the effect of aging on the behavior of hydrogels of oxide hydroxides the central ions of which are either full electron analogs (titanium (IV) or zirconium (IV), ions with the same charges and radii but with different electronic structures (iron (III) and chromium(III), or ions bearing the same charges but differing in radii and electronic charges (iron(III), chromium(III), and indium(III)).

On aging in electrolyte solutions hydrogels lose their basic properties characterized by the $\mathrm{pH_{PZC}}$ value (see Table 1). Comparison of the $\mathrm{pH_{PZC}}$ values of hydrogels aged in chloride and sulfate solutions shows that the effect of sulfate ions is usually somewhat stronger than that of chloride ions. In addition, the dependence of the $\mathrm{pH_{PZC}}$ on the electrolyte concentration becomes weaker (see the results for the samples aged in a sulfate solution at $\mathrm{pH_i} = 5.5$, 7, and 10 in Table 1). Comparison of titration curve *2* in Fig. 1 corresponding to the freshly precipitated sample with curve *3* obtained for the aged gel shows that the slope of the curve with respect to the abscissa increases with aging. The curves become similar in shape to the titration curves of crystalline samples of oxides, for example, REE oxides.[4] This agrees with the decrease in the water content in the hydrogel samples after aging in solutions of electrolytes.[15]

Two processes are known[1,5–8] to play the main role during aging of oxide hydroxides: the formation of olic (hydroxyl) bridges between the metal ions and the formation of oxo (oxygen) bridges (olation and oxolation). These processes increase the degree of polymerization and molecular weight of hydrolytic polymers of oxide hydroxides. The observed situation (see Fig. 1) indicates a decrease in the sorption capacity of the gel with respect to OH^- ions: the pH of the suspension with the same amount of added alkali for the aged sample is 1.8 pH units higher than that for the freshly prepared sample. Therefore, much less OH groups were sorbed from the solution in the case of the aged sample (curve *3*). This can be explained by the reduction of its specific surface due to the growth of the oxide hydroxide particles by oxolation.

No basic difference due to different electronic structures and different radii or charges of the central ion is observed in the behavior of the oxide hydroxides: the general tendency to a decrease in the $\mathrm{pH_{PZC}}$ remains unchanged. It has been established[15] that the water content in the samples of the hydrogels under study strongly depends on the nature of their central ions: it decreases for the $\mathrm{Fe^{III}}$ and $\mathrm{In^{III}}$ oxide hydroxides, increases for the $\mathrm{Cr^{III}}$ oxide hydroxide, and remains unchanged for the $\mathrm{Ti^{IV}}$ and $\mathrm{Zr^{IV}}$ oxide hydroxides. It is seen from our data that the tendency of decreasing the basic properties of the hydrogels during aging is independent of the difference in the water content in the gel.

The general tendency of decreasing the basic properties is retained, whereas the results for particular hydrogels substantially differ, especially for zircono- and chromogels. For example, the dependence of the $\mathrm{pH_{PZC}}$ on the concentration of the titrated electrolyte almost disappears for chromogels with $\mathrm{pH_i} = 7$ and 9 and zirconogels with $\mathrm{pH_i} = 5.5$ and 7 aged in a sulfate solution. This dependence is characteristic of hydrogels of oxide hydroxides.[1,3] At the same time, the prepared samples remain amorphous to X-rays rather than crystalline.[16] This confirms our assumption on the formation of stable noncrystalline aggregates of the type of nonstereoregular organic polymers in media of chromo- and zirconogels.

The published data[7] also confirm this assumption. At room temperature, the average rate constants of olation are $6.4 \cdot 10^{-2}$ L mol^{-1} s^{-1} and those of oxolation amount to $5.0 \cdot 10^{-5}$ s^{-1}. Based on these values and on the rate constants of the first- and second-order reactions, we calculated that the half-lives of zirconium oxide hydroxide during olation and oxolation at room temperature are equal to 0.5 min and 1.7 h, respectively. Therefore, the olation goes nearly to completion within the time of precipitation and washing of the zirconium(IV) oxide hydroxide, whereas the extent of oxolation reaches 70—75% within the time of precipitation, washing, and treatment of the hydrogel with an electrolyte solution (3—3.5 h). Since in our experiments the treatment with an electrolyte solution is performed at 80 °C, the process rate should increase by at least 2—2.5 times even if the olation is diffusion-controlled. Partially hydrolyzed cations are very rapidly polymerized in solutions of chromium(III) salts with increased alkalinity.[17] The rate constants of protonation—deprotonation for chromium(III) aquahydroxo compounds are close to 10^5 s^{-1}.

Evidently, the aging of ferro- and indiogels is much slower. The half-life of a variety of ferrogel at room temperature has been estimated[6] as 2—3 years. Increasing the temperature to 80 °C, a 10—60-fold acceleration of the oxolation of the ferro- and indiogels can be expected, *i.e.*, reduction of the half-life to 0.5—2 months.

The aging of the chromo- and zirconogels in a chloride medium is much slower than that in a sulfate medium. It is most likely that the sulfate ions accelerate the oxolation itself.

Thus, the obtained data imply that the exposure of oxide hydroxide hydrogels to solutions of electrolytes accelerates their aging and in this way weakens the basic properties of their surface. The oxolation rate determines the observed sequence of events. When the oxolation of oxide hydroxides is fast, metastable noncrystalline structures are formed and the basic properties decrease during aging due to the displacement of the OH groups by the anions of the electrolyte. In this case, sulfate ions with a charge of −2 are much more reactive than chloride ions with a charge of −1, which is confirmed by a stronger effect of the sulfate electrolyte on the basic properties of the oxide hydroxide (see Table 1). When the oxolation is slow, the state of the gel remains unchanged and the pattern of dependences of the acid-base properties on pH_i and electrolyte concentration remains unaltered.

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