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Sorption properties of freshly precipitated alumogels

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The influence of the pH of precipitation and the ionic medium nature on the composition, surface charge, and kinetic sorption characteristics of aluminum oxyhydroxides formed by alkaline hydrolysis of an aqueous solution of aluminum nitrate was studied. The methods of drop titration with alkali, argentometric titration, point of zero charge, and indicator reactions of heterogeneous hydrolysis were used. The composition of the freshly precipitated hydrogels of aluminum(III) oxyhydroxide, rate constants of heterogeneous hydrolysis of the $IrCl_6^{2-}$ ions as indicator reactions, and the pH of the point of zero charge were determined. The rate of indicator reactions (as for other oxyhydroxide hydrogels) depends strongly on the pH of precipitation. However, it is lower than the rates characteristics of iron(III) and chromium(III) oxyhydroxides obtained under similar conditions. The pH of the point of zero charge for the alumogels in a chloride medium is 8.3 and that in a sulfate medium is 9.5.

Key words: sorption properties, point of zero charge, oxyhydroxides, alumogels, indicator reaction rate.

The properties of metal oxyhydroxides (OHDs) strongly depend on the method of their preparation and composition of the starting salts.[1—6] For example, dispersity of the freshly prepared precipitates of Al^{III} OHD increases in the series $Al(NO_3)_3 < AlCl_3 < Al_2(SO_4)_3$.[7] When precipitated from sulfate solutions, Al^{III} OHDs are strongly contaminated with the sulfate ion[8] and, hence, to obtain products with an improved purity, solutions of Al^{III} chloride and nitrate are preferred. The nitrate ions, which have no remarkable complexation properties, can almost completely be removed from OHDs by washing.[9] When precipitated from concentrated solutions, the amorphous precipitates have a smaller volume and sorb less foreign ions.[8] Dispersion of the published[10—15] values for the pH of the point of zero charge (pH_{PZC}), surface charge, and acid-base dissociation constant is most likely accounted for by different conditions of OHDs formation.

Previously[1,2,4,16—19] we have studied the influence of the initial metal salt nature and pH of precipitation (pH_1) on the properties of the freshly prepared Fe^{III}, Cr^{III}, In^{III}, Sm^{III}, Ti^{IV}, and Zr^{IV} OHDs. In this work, we studied the properties of the freshly prepared Al^{III} OHDs (alumogels) obtained under similar conditions by the method of fast alkaline hydrolysis of a salt solution and examined how pH_1 values affect their composition, pH_{PZC}, and sorption power (activity) in the presence of chloride and sulfate background electrolytes.

Experimental

A solution of $Al(NO_3)_3$ obtained by the dissolution of a weighted sample of $Al(NO_3)_3 \cdot 9H_2O$ (reagent grade) in excess amounts of nitric acid (reagent grade) with the concentration of 1.807 *M* with respect to salt (48.75 g of Al L^{-1}) and 1 *M* with respect to HNO_3 was used to prepare alumogels. The samples were prepared as follows. The weight of the sample for experiments on determination of pH_{PZC} and sorption activity was 0.008 moles of hydrogel, which corresponded to 0.22 g of Al or 0.624 g of $Al(OH)_3$, *i.e.*, 4.4 mL of the initial solution taking into account some (~1—2%) loss on washing. This aliquot was poured into a small (25—30 mL) amount of distilled water and neutralized with a 2 *M* solution of NaOH (reagent grade) with continuous stirring and pH-metric monitoring until a desired pH of the suspension (pH_s) was established and remained unchanged for ~5 min. This process took ~0.5 h. Then the suspension sample was squeezed out on a centrifuge and thrice washed by decantation with distilled water. The washed-off and squeezed out sample was suspended in distilled water (100 mL) and used in experiments.

Composition of alumogels. The composition of the samples obtained at different pH_1 was determined by drop titration with NaOH to calculate the [OH] : [M] ratio (M is metal).[1] A solution of $Al(NO_3)_3$ (0.024 mol) was titrated with NaOH, and portions of the suspension with pH_s 5.5, 7, and 8.5 were sampled for analysis. At pH_s 5.5, 1/3 of the suspension volume was taken, the precipitate was separated as described above and washed with water, the washing waters (V_2 in volume) were collected, and their pH (pH_2) were measured. Then the washed-off and squeezed gel was introduced into 200 mL of a 0.5 *M* solution of

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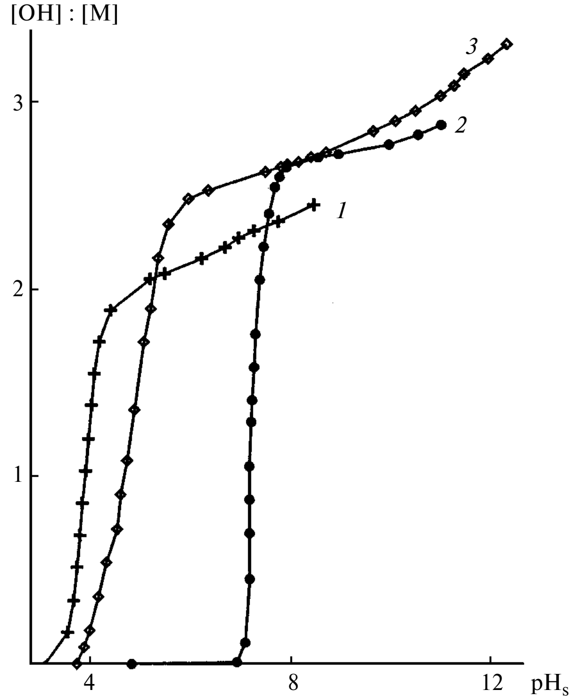

Fig. 1. Curves of drop titration of $Al(NO_3)_3$ (*1*), $Sm(NO_3)_3$ (*2*), and $CrCl_3$ (*3*) with a solution of NaOH.

KNO_3 (V_3), the precipitate was filtered off, and the pH of the filtrate (pH_3) were measured. When pH_s 7 was achieved, 1/2 volume of the remaining suspension was taken and treated as in the former case. The remaining suspension was titrated to pH_s 8.5 and treated similarly. Using these data, the amounts of bases washed-off and displaced by the electrolyte were calculated, and the [OH] : [Al] ratio was calculated in each titration point and in three reference points. The results of drop titration gave the composition of the hydrogel directly in the suspension (Fig. 1 and Table 1).

In addition to drop titration, the composition of the samples was determined using chemical analysis. The alumogels with pH_l 5.5, 6, 7, 8, and 9.2 were analyzed immediately after washing and centrifuging. The hydrogel weighted sample was calcined at 1000 °C, and the residue was weighted. Based on the thermal analysis data, the composition of the calcined residues was accepted as α-Al_2O_3. Using these data, the $Al_2O_3 : H_2O$ molar ratio was calculated[20—23] (Table 2). In addition, the samples were analyzed for the content of the residual nitrate ion (see Table 2).

Table 1. Calculation of the [OH] : [Al] ratio during drop titration of $Al(NO_3)_3$ with a solution of NaOH

pH_s	pH_2	V_2/мл	pH_3	OH^- * /equiv (g-at. Al)$^{-1}$
5.5	4.68	71.5	4.86	2.09
7	7.59	78.9	5.21	2.28
8.5	7.30	85.85	6.01	2.46

Note. For V_2, pH_s, pH_2, and pH_3, see remarks in Experimental.
* The amount of the introduced OH^- ions (washed-off OH^- ions or H^+ added during washing were not found); the content of the OH^- ions in the precipitate is equal to the amount of the introduced OH^- ions.

Table 2. Composition of freshly formed alumogels

pH_l	Al_2O_3* (wt.%)	$Al_2O_3 : H_2O$**	$Al_2O_3 : Na^+ : NO_3^-$**
5.5	2.40	1 : 231	1 : 0.12 : 0.15
6	2.27	1 : 245	1 : 0.12 : 0.22
7	2.21	1 : 251	1 : 0.13 : 0.17
8	2.12	1 : 262	1 : 0.16 : 0.10
9.2	2.28	1 : 244	1 : 0.28 : 0.17

* Residue after calcination.
** Molar ratio.

The methods of potentiometric titration[24] and static points[25] were used to determine pH_{PZC}. Potentiometric titration was performed using a half-open quartz cell and an EV-74 ionometer with an ESL-43-07 glass electrode and an EVL-1M1 auxiliary electrode immersed into the reaction mixture. Background electrolytes were NaCl and Na_2SO_4. The alumogel precipitate obtained as described above was suspended in distilled water (100 mL), argon was simultaneously bubbled for ~1.5 h through this suspension and electrolyte solutions (100 mL each) with a concentration of 0.02, 0.2, and 2.0 mol L^{-1} to remove dissolved CO_2. Then the gel suspension (100 mL) was introduced into each 100-mL electrolyte solution to obtain the electrolyte concentration in the final volumes of 1.0, 0.1, and 0.01 mol L^{-1}. To establish the primary pH_s value in titration, the exact and equal for this series amount of a solution of carbonate-free alkali (5 mL of 0.21 *M* NaOH) was added, and the suspension was titrated with 0.1 *N* HCl or H_2SO_4 in the chloride or sulfate medium, respectively, fixing the pH values for the initial point and after the addition of each portion of the titrant. The time needed to establish the acid-base gel—solution pseudo-equilibrium for each series of the samples did not exceed 3 min. The titration of an OHD suspension is reversible because the pH_s in the point of equivalence of the introduced alkali and acid is equal to pH_s until alkali is introduced into the system. Reversibility of titration of the gels indicates that the residual nitrate ions are not involved in the short-time interactions of the gel with alkali and acid, which satisfies the conditions of pH_{PZC} determination. For each entry on gel titration, the corresponding blank experiment on titration of the electrolyte under the same conditions was carried out. The amount of the excessively sorbed H_3O^+ and OH^- ions was determined comparing the pH_s and pH values of the electrolyte solution in the blank experiment (pH_{el}) at the given volume of the titrant (V_{titr}). The pH_{PZC} value was determined from the intersection point of the plots of pH_s *vs.* V_{titr} and pH_{el} *vs.* V_{titr} and by calculation.

To verify the data obtained by potentiometric titration, pH_{PZC} was also determined by the method of static points.[25] The formed and washed-off (as described above) alumogel (0.024 mol) was placed in a 500-mL volumetric flask, diluted with water to the mark, and thoroughly stirred. The same electrolytes in the same concentrations that in potentiometric titration were used for experiments.[24] For each concentration of the ionic background, eight solutions of the electrolyte (20 mL each) with the pH_{el} values from 4.5 to 8 were prepared. To establish the specified pH values, solutions of HCl and NaOH were used.

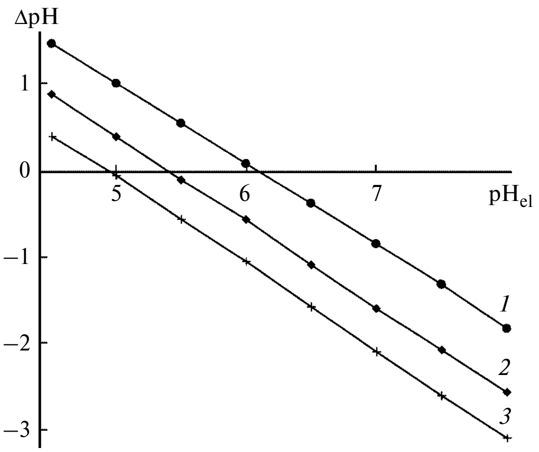

Fig. 2. Determination of pH$_{PZC}$ by the method of static points for alumogel with pH$_l$ 6 against the background of 1 (*1*), 0.1 (*2*), and 0.01 *M* (*3*) solutions of NaCl (ΔpH = pH$_s$ − pH$_{el}$).

The initial suspension (20 mL) was added to each prepared solution, the resulting mixtures were stirred for 3—5 min, and the pH$_s$ values were measured. The dependence of ΔpH = pH$_s$ − pH$_{el}$ on pH$_{el}$ was plotted (Fig. 2). These procedures were repeated for three concentrations of each electrolyte. The intersection point of each straight line with the abscissa is the pH$_{PZC}$ for this sample. The results of determination of the pH$_{PZC}$ by both methods are presented in Table 3.

Indicator reactions of heterogeneous hydrolysis. As in earlier works,[1,2,4,16—19] the heterogeneous hydrolysis rate for the platinum metal complexes was used as a characteristic of the sorption properties of alumogels. The experimental procedure named "kinetics under static conditions" in the isothermic regime was used.[1] Under these conditions, the $IrCl_6^{2-}$ ion is the most appropriate complex.

The experiment was carried out in a 200-mL reaction vessel with a hydroseal and a stirrer placed in a water thermostat. The OHD suspension (100 mL) and a solution of the sorbate (100 mL) (concentrations of the complex were $(1-4) \cdot 10^{-4}$ mol L^{-1}) were simultaneously maintained at a constant temperature, and then the suspension was poured into the reaction vessel with the sorbate solution. The time count started from this moment: the suspension samples were taken with a pipette at specified intervals. The duration of experiments ranged from 60 to 200 min. The samples were filtered through a paper filter, and the residual concentration of iridium (C_{Ir}) was determined in the filtrate using the "three acids" spectrophotometric method[26] on an SF-26 LOMO spectrophotometer.

Table 3. The pH$_{PZC}$ values of alumogels in solutions of electrolytes with different concentrations (*C*) at different pH of precipitation (pH$_l$)

Electrolyte	*C* /mol L^{-1}	pH$_l$				
		5.5	6	7	8	9.2
NaCl*	1.0	5.69	6	7.20	8	—
	0.1	5.04	5.20	6.50	7.60	—
	0.01	4.60	4.80	5.67	6.85	—
Na_2SO_4*	1.0	—	7.51	8.28	8.76	—
	0.1	—	7.05	8.10	8.57	—
	0.01	—	6.53	7.62	8.41	—
NaCl**	1.0	—	6.08	7.05	8.05	8.61
	0.1	—	5.40	6.40	7.59	8.55
	0.01	—	4.92	5.50	6.78	8.10

* The data were obtained by potentiometric titration.[24]

** The data were obtained by the method of static points.[25]

The results of kinetic experiments were processed by the graphical and calculation methods. With this purpose, the time dependence of C_{Ir} was plotted. The resulting plot was linear in all kinetic experiments, which is characteristics of first order reactions.[27] Hence, as the majority of earlier studied reactions of heterogeneous hydrolysis for other OHDs,[1,2,4,16—19] a similar reaction on alumogels can also be referred to a reaction of the first order with respect to the central ion concentration at the 20—80% conversions.[1] The obtained reaction rate constant k_{obs} was calculated for first order reactions[28] accepting the equilibrium concentration equal to zero because the process proceeds almost to completion. The k_{obs} value was determined as the average magnitude from 8—10 values, and the confidence interval for this value[29] with the confidence probability $\alpha = 0.95$ was calculated. The maximum deviation of the constant was 10—25%.

Heterogeneous hydrolysis results in the complete decomposition of the complex anion with elimination of all coordinated ligands, which transfer to an aqueous solution.[1] To be positive that the observed process involving alumogel actually proceeds as heterogeneous hydrolysis, we determined the number of the eliminated Cl^- ions in the presence of the $NaClO_4$ ionic background for 150 min at 80 °C. The degree of extraction of Ir with the precipitate is ~100%. The concentration of the Cl^- ions in the filtrate was determined using argentometric titration of the filtrate separated from the alumogel sorbent precipitate with the sorbate. For the initial amount of the Ir complex in experiment ($4.8 \cdot 10^{-5}$ mol), the amount of the eliminated Cl^- ions was found ($2.92 \cdot 10^{-4}$ g-ion), which is close to the calculated value ($2.86 \cdot 10^{-4}$ g-ion). Therefore, the observed process can be defined as heterogeneous hydrolysis.

Results and Discussion

The results of drop titration and determination of the composition (see Tables 1 and 2) show that the alumogels contain no excessive OH^- ions in the whole studied pH$_l$ region (5—9) but contain the residual NO_3^- anions. The curve of titration of the Al^{III} cation particularly resembles those for Cr^{III} and Sm^{III} (see Ref. 4 and Fig. 1). In the whole studied pH$_l$ region (5—11), the gel precipitates contain some amount of unsubstituted anions: $Al(OH)_{2.1-2.5}(NO_3)_{0.9-0.5}$ (data of this work), $Sm(OH)_{2.4-2.7}(NO_3)_{0.6-0.3}$,[16] and $Cr(OH)_{2.6-2.7}Cl_{0.4-0.3}$.[19]

According to the published data,[30] the region of existence of aluminum OHD ranges from pH 5.2 to pH 7.8, and other data give the pH region of 4.1—11.9.[31] Analysis for the content of free Al^{III} in the supernatant liquor after aluminum OHD was precipitated showed its insignificant amount (0.3—0.9 mg L^{-1}) at pH$_l$ 5.5—8. At pH 11.9 we obtained the $\mathrm{Al^{III}}$ concentration in the solution equal to 0.58 g $\mathrm{L^{-1}}$. Therefore, we did not use $\mathrm{pH_1} > 10$ and, hence, could not substantially increase the degree of substitution of the anions by the OH groups.

The results of chemical analysis collected in Table 2 show that the $\mathrm{Al_2O_3 : H_2O}$ molar ratio in the squeezed alumogel at all $\mathrm{pH_1}$ is approximately the same. The alumogel can be compared in water content to indiogel,[22] which also was prepared from the corresponding nitrate. The results of analysis of the squashed alumogels for the content of the $\mathrm{NO_3^-}$ and $\mathrm{Na^+}$ ions show that washing probably entrains additional hydrolysis because the number of the nitrate ions at all $\mathrm{pH_1}$ is much smaller than it follows from the calculation of the [OH] : [Al] ratio in drop titration (see Table 1). However, all samples contain an admixture of the $\mathrm{Na^+}$ cations, whose concentration is not evidently related to the content of the nitrate ions. It can be assumed that the admixture of the $\mathrm{Na^+}$ cation is caused partly by the impurities of $\mathrm{NaNO_3}$ that could not be removed by washing and partly by NaOH sorbed on the alumogel surface at $\mathrm{pH > pH_{PZC}}$.

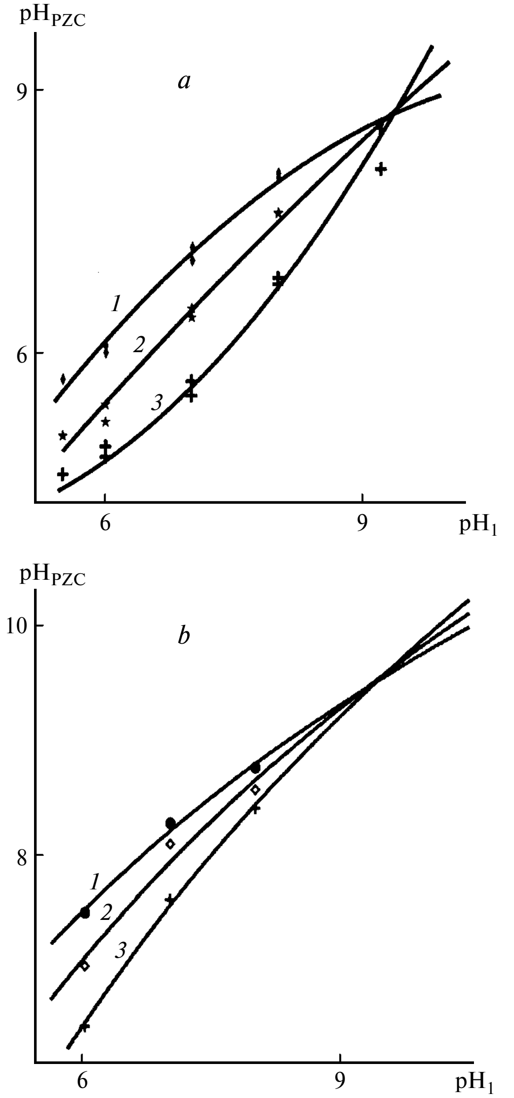

Fig. 3. Plot of the $\mathrm{pH_{PZC}}$ of alumogels *vs.* $\mathrm{pH_1}$ against the background of solutions of NaCl (*a*) and $\mathrm{Na_2SO_4}$ (*b*) with concentrations 1 (*1*), 0.1 (*2*), and 0.01 *N* (*3*).

The dependence of $\mathrm{pH_{PZC}}$ on the electrolyte concentration presented in Table 3 has repeatedly been observed previously for gel-like OHDs of other metals.[1–4,16–19] Therefore, this dependence can be considered typical of gels and confirms, in this case, the gel-like nature of aluminum OHD. Coincidence of the results of $\mathrm{pH_{PZC}}$ determination obtained by two independent methods[24,25] indicates that the data are reliable (see Table 3). The curves of $\mathrm{pH_{PZC}}$ *vs.* $\mathrm{pH_1}$ in a NaCl medium intersect at $\mathrm{pH_1}$ 9.4 and $\mathrm{pH_{PZC}}$ 8.3, and those for the $\mathrm{Na_2SO_4}$ medium intersect in the $\mathrm{pH_1}$ interval from 9.1 to 9.4 and $\mathrm{pH_{PZC}}$ 9.4—9.6 (see Fig. 3, *a*, *b*). Therefore, the $\mathrm{pH_{PZC}}$ of the alumogel depends on the ionic background nature in the same way as for other OHDs.[1,4] Based on these values, the surface of the freshly formed alumogels is much more basic than the surface of the $\mathrm{Sm^{III}}$ OHD gel,[4,16] for which $\mathrm{pH_{PZC}}$ in the NaCl medium is 7.6. The $\mathrm{pH_{PZC}}$ value of the alumogel is close to those obtained for the $\mathrm{Zr^{IV}}$ [2,4] and $\mathrm{In^{III}}$ [4,17] OHD gels at the corresponding $\mathrm{pH_1}$.

The results of studying the $\mathrm{pH_1}$ and temperature plots of the rate constants of heterogeneous hydrolysis of $\mathrm{IrCl_6^{2-}}$ (Table 4) shows that k_{obs} increase regularly, as was reported earlier,[1,2,4,16–19] with an increase in $\mathrm{pH_1}$ and temperature. The activation energy (E_a) of indicator reactions on the alumogels (70—90 kJ $\mathrm{mol^{-1}}$) yet lies within E_a characteristic of the chemical reaction of heterogeneous hydrolysis (50—140 kJ $\mathrm{mol^{-1}}$), but for the $\mathrm{IrCl_6^{2-}}$ ion (see Table 4) it is lower than for all other OHDs (100—130 kJ $\mathrm{mol^{-1}}$).[4]

The character of changes in the heterogeneous hydrolysis rate at 60 °C with changes in the sorbate and sorbent concentrations reflects the competition of the reacting particles for the reaction sites on the surface[1] (Table 5).

We failed to measure the specific surface area of the alumogels by the method developed for estimation of the specific OHD surface from the amounts adsorbed by the

Table 4. Rate constants of heterogeneous hydrolysis (k_{obs}) of the $\mathrm{IrCl_6^{2-}}$ ion on the surface of alumogels (concentration of the sorbent is 3 g $\mathrm{L^{-1}}$) in a 1 *M* solution of NaCl at different temperatures and different pH of precipitation ($\mathrm{pH_1}$)

$\mathrm{pH_1}$	$k_{\mathrm{obs}} \cdot 10^4/\mathrm{s^{-1}}$			E_a /kJ $\mathrm{mol^{-1}}$
	60 °C	70 °C	80 °C	
6	—	—	0.86	—
7	0.56	1.04	2.22	67.6
8	0.95	2.34	6.45	93.5
9.2	1.86	5.89	10.49	84

Table 5. Rate constants of heterogeneous hydrolysis (k_{obs}) of the $IrCl_6^{2-}$ ion on the surface of alumogels at different concentrations of the sorbent and sorbate in a 1 *M* solution of NaCl at 60 °C and pH_1 9.2

$C_{IrCl_6^{2-}} \cdot 10^{-4}$ /mol L^{-1}	C_{gel} /g L^{-1}	$k_{obs} \cdot 10^4$ /s^{-1}
2.5	1.5	1.23
2.5	6	3.22
2.5	12	3.14
0.5	3	2.23
5	3	1.58

OH groups[32] because at pH > 11 onset of dissolution of alumogel is observed.

The obtained results suggest that the sorption and surface properties of the freshly precipitated alumogels in the pH_1 region, which provides their stable existence in the gel phase, resemble the corresponding properties of OHD hydrogels of other high-valence metals (Fe^{III}, Sm^{III}, In^{III}, Cr^{III}, Ti^{IV}, Zr^{IV}). However, the sorption activity of the alumogels is somewhat lower than that of OHDs of the listed metals. Nevertheless, the regularities observed for OHDs[4] are valid for alumogels: the heterogeneous hydrolysis rate increases with pH_1 and the maximal value of the sorption rate for the $IrCl_6^{2-}$ ion is achieved for the alumogel samples with the pH_{PZC} corresponding to the true point of zero charge. Therefore, alumogels can be considered as analogs of ferro-, chromio-, indio-, titanio-, and zirconiogels.

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