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Reviews

Sorption properties of hydrogels of transition and p-metal oxide hydroxides

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The experimental data on the sorption properties of hydrogels of Fe^{III}, Ti^{IV}, Zr^{IV}, Sn^{IV}, In^{III}, Cr^{III}, Sm^{III}, Co^{II}, and Zn^{II} oxide hydroxides are summarized. The data were obtained by the point of zero-charge method and by measuring the rates of the indicator reaction, *viz.*, heterogeneous hydrolysis of the chloro complexes of platinum group metals. The compositions of the oxide hydroxides, the pH of the point of zero charge in various ionic media, and the rate constants of the indicator reactions were determined. The values obtained were analyzed in terms of their correlation with the charge, the radius, and the electronic structure of the central ion and with the composition and the preparation conditions of the oxide hydroxide. A data base that allows one to choose an appropriate oxide hydroxide sorbent for extraction of particular complex-forming metals from complexing media is presented. The data obtained confirm the model of the mechanism of heterogeneous hydrolysis and extend its predicting ability. The model was tested experimentally in relation to tin(IV) oxide hydroxide.

Key words: sorption properties, oxide hydroxide, point of zero charge, rate of indicator reaction, hydrogel, ionic media.

Introduction

Inorganic sorbents are used in industrial technologies and environment protection technology, in those cases where contamination of solutions with organic compounds should be avoided and/or radiation-resistant sorbents are required. Freshly prepared gel-like iron, zirconium and titanium oxide hydroxides used as sorbents possess substantial advantages over dry granulated oxides;[1] therefore, at present, wide use of crystalline or granulated inorganic sorbents is no longer justified.[2] Gel-like oxide hydroxide sorbents are highly efficient regarding both the sorption capacity and the rate of sorption; they even permit fairly selective and complete extraction of platinum metals, gold, mercury and copper from complexing media. Since iron and titanium are widespread in nature, gel-like sorbents based on them are cheap and environmentally clean. The synthesis of gel-

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like oxide hydroxides is simple, quick, and cheap. Similar sorbents based on zirconium, aluminum, and other metals are less versatile, but certainly, they can also find application in some cases.

As a result of numerous studies, we discovered and investigated a specific type of chemisorption, which applies to the sorption of complex ions; we called it "heterogeneous hydrolysis."[3–8]

Heterogeneous hydrolysis, which has been described in detail previously,[2,3] occurs as aquation* of the complex ions adsorbed on the surface of oxide hydroxides followed by the transformation of the resulting aqua complex into the hydroxide of the central ion of the complex, for example:[3]

$$[PtCl_4]_{aq}^{2-} + \{Ln_2O_3 \cdot nH_2O\}_{surf} + 2\,H_2O \longrightarrow \{Pt(OH)_2 \cdot Ln_2O_3 \cdot xH_2O \cdot 2H^+\}_{surf} + 4\,Cl^-_{aq}.$$

The new hydroxide phase is firmly bound to the surface of the oxide hydroxide sorbent. The rate of heterogeneous hydrolysis is determined by the basic properties of the surface (*i.e.*, the pH at the point of zero charge), by the supporting electrolyte, and the nature of the complex subjected to heterogeneous hydrolysis itself.[2,3]

In relation to ferrogels, we observed effects that had not been reported previously, namely, the change of the sorption properties of the gel induced by the short-term or prolonged interaction with an ionic medium.[3–9] In order to find out whether this type of behavior is typical of all hydrogels formed by poorly soluble metal oxide hydroxides or it is a specific feature of ferrogels, we studied the sorption properties of titanium and zirconium(IV) oxide hydroxides.[10,11] Since these oxide hydroxides were found to exhibit many specific features, the problem was formulated as follows. Based on investigation of a wider range of gels, a theoretical model suitable for predicting the sorption properties of oxide hydroxides in relation to extraction of complexing metals from complex-forming media (aqueous solutions of electrolytes) should be developed. As additional objects of investigation, we chose In^{III}, Cr^{III}, Co^{II}, Zn^{II}, and Sm^{III} oxide hydroxides.[12–15] For the latter compound, extensive investigations dealing with the crystalline oxide have been reported.[3,16]

We attempted to elucidate how the fundamental properties of the metal cation forming the oxide hydroxide sorbent, conditions of the oxide hydroxide synthesis, and its surface properties (the surface and volume charge, and the pH of the point of zero charge on its surface) affect the rate of heterogeneous hydrolysis in the presence of these oxide hydroxides. As the primary fundamental properties that apparently determine the properties of oxide hydroxides, we recognized the charge, the radius, and the electronic structure of the central atom (Table 1). Tentative analysis of some of the available data on the kinetics of heterogeneous hydrolysis from this viewpoint has been carried out in our previous study;[17] however, these characteristics seem to be inadequate to provide explanation of all the phenomena observed. A similar approach (except for the electronic structure) has also been used by other researchers.[18]

Table 1. Fundamental characteristics of the central atoms in oxide hydroxides

Metal	Goldschmidt radius /Å	Ionic potential, $I = z/r$	Electronic structure of the outer layer
Ti^{IV}	0.64	6.25	$3s^23p^6$
Zr^{IV}	0.87	4.60	$4s^24p^6$
Sn^{IV}	0.67	5.97	$4p^64d^{10}$
Cr^{III}	0.65	4.61	$3p^63d^3$
Sm^{III}	0.96*	3.12	$5s^25p^6$
Fe^{III}	0.67	4.48	$3p^63d^5$
In^{III}	0.92	3.26	$4p^64d^{10}$
Zn^{II}	0.83	2.41	$3p^63d^{10}$
Co^{II}	0.83	2.41	$3p^63d^7$

* Templeton and Dauben radius.[22]

The oxide hydroxide sorbents were prepared by alkaline hydrolysis of the corresponding metal salts in aqueous solutions at room temperature. The data on the composition of oxide hydroxides characterize the fast precipitation process. To prepare the sorbent samples, the alkaline hydrolysis was carried out for 5—10 min at a controlled pH of precipitation; then the samples were washed from the mother liquor by decanting and centrifugation for 40 min. The samples obtained in this way were gel-like; they contained the primary water that had not been removed during the gel preparation. These samples were used in the experiments on the determination of the surface charge and on the study of heterogeneous hydrolysis. The pH of precipitation (pH_1) served as the main independent parameter determining the properties of oxide hydroxides.

The composition of hydrogels was determined from the curves of drop titration** of solutions of metal salts, used to prepare the hydrogels of oxide hydroxides, with a base. The titration curves were recorded over a period of ~2 h. The samples prepared at specific precipitation pH values (three points, one located in the beginning, one in the middle, and one at the end of the titration curve, were normally chosen) were thoroughly washed, dried in a vacuum desiccator over strong sulfuric acid, and studied by thermal and X-ray diffraction analyses.

The pH value at the point of zero charge (pH_{PZC}) characterizes the pH of an electrolyte solution (in this particular case, an aqueous solution) such that a solid (gel) phase contacting with this solution adsorbs equal numbers of protons and hydroxyl groups. The pH_{PZC} was determined by potentiometric titration in a quartz

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* Replacement of the ligands in the complex by water molecules.

** A method of homogeneous titration,[19] which ensures instantaneous preparation of a solution or suspension, homogeneous regarding the composition and pH, is also known.

cell in a flow of an inert gas, according to the procedure reported by Parks.[20] The titration procedure has been described in detail previously.[3,5,10–16] It has been noted[2] that pH_{PZC} characterizes the acid-base properties of the oxide hydroxide surface in a given ionic medium and can be used in a comparative study of oxide hydroxides with different structural groups (different crystalline modifications; crystalline and amorphous; dry and "wet"), because pH_{ZCB} is an intensive property of the material, which does not depend on the specific surface area.[21] In addition, the Parks titration allows determination of the surface charge of oxide hydroxides at any pH of the medium; this, by itself, is an adsorption characteristic (pseudo-equilibrium adsorption of protons or hydroxyl groups).

In the study of heterogeneous hydrolysis, we were interested primarily in its kinetics. The procedure of the kinetic measurements has been described in detail.[3] Since hydrogels of oxide hydroxides are highly dispersed phases and their state is far from equilibrium, we believe that their sorption properties can be described most adequately in terms of kinetic parameters.

All the samples were characterized by the following values: (1) composition, (2) pH_{PZC}, and (3) rate constants for the indicator reactions of heterogeneous hydrolysis of platinum metal chloro complexes .

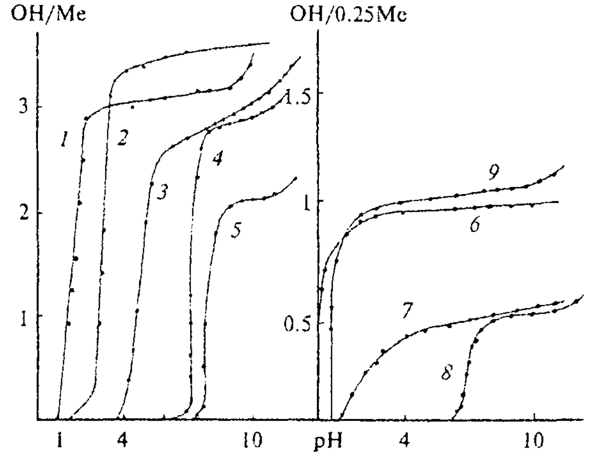

Fig. 1. Drop titration curves of solutions of metal salts (0.024 mol) with a solution of NaOH: *1*, $Fe(NO_3)_3$; *2*, $In(NO_3)_3$; *3*, $CrCl_3$; *4*, $Sm(NO_3)_3$; *5*, $CoCl_2$; *6*, $TiCl_4$; *7*, $ZrO(NO_3)_2$; *8*, $ZnCl_2$; *9*, $SnCl_4$.

Composition of oxide hydroxide hydrogels

All the cases of formation of metal oxide hydroxides upon the titration of a solution of a metal salt with

Table 2. Composition of hydrogels of metal oxide hydroxides, determined from the drop titration data

Metal	pH_1		
	4—6	7—9	10—13
Ti^{IV}	$TiO_{0.14}(OH)_{3.72}$	$TiO_{0.08}(OH)_{3.83}$	$TiO_{0.37}(OH)_{3.26}$
Zr^{IV}	$Zr(OH)_{2.96}(NO_3)_{1.04}$	$ZrO_{0.16}(OH)_{3.68}$	$ZrO_{0.03}(OH)_{3.94}$
Sn^{IV}	$Sn(OH)_4$	$Sn(OH)_4 \cdot 0.2NaOH$	$Sn(OH)_4 \cdot 0.4NaOH$
Cr^{III}	$CrO_{0.2}(OH)_{2.6}$	$CrO_{0.1}(OH)_{2.8}$	$CrO_{0.15}(OH)_{2.7}$
Sm^{III}	—	$Sm(OH)_{2.7}(NO_3)_{0.3}$	$Sm(OH)_{2.86}(NO_3)_{0.1}$
Fe^{III}	$Fe(OH)_{2.96}(NO_3)_{0.04}$	$Fe(OH)_3$	$Fe(OH)_3 \cdot 0.1NaOH$
In^{III}	$In(OH)_3 \cdot 0.2NaOH$	$In(OH)_3 \cdot 0.22NaOH$	$In(OH)_3 \cdot 0.25NaOH$
Zn^{II}	—	$ZnOHCl$	$Zn(OH)_{1.93}Cl_{0.07}$
Co^{II}	—	$Co(OH)_{1.76}Cl_{0.24}$	$Co(OH)_2$

Table 3. Composition of xerogels of metal oxide hydroxides

Metal	pH_1		
	4—6	7—9	10—13
Ti^{IV}	$TiO_{0.4}(OH)_{3.2}$	$TiO_{1.15}(OH)_{1.7}$	—
Zr^{IV}	$Zr(OH)_4$	$ZrO_{1.3}(OH)_{1.4}$	$ZrO_{1.5}OH$
Sn^{IV}	$SnO_{1.6}(OH)_{0.8}$	$SnO_{1.6}(OH)_{0.8}$	—
Cr^{III}	—	$CrO_{0.7}(OH)_{1.6}$	$CrO_{1.1}(OH)_{0.8}$
Sm^{III}	—	$Sm(OH)_{2.5}(NO_3)_{0.5}$	$Sm(OH)_{2.7}(NO_3)_{0.3}$
Co^{II}	—	—	$CoO_{0.5}OH$
Zn^{II}	—	$Zn(OH)_{1.6}Cl_{0.4}$	ZnO
Fe^{III}	$Fe(OH)_3$	$Fe(OH)_3$	$Fe(OH)_3 \cdot 0.1NaOH$
In^{III}	$In(OH)_3 \cdot 0.2NaOH$	$In(OH)_3 \cdot 0.2NaOH$	$In(OH)_3 \cdot 0.2NaOH$

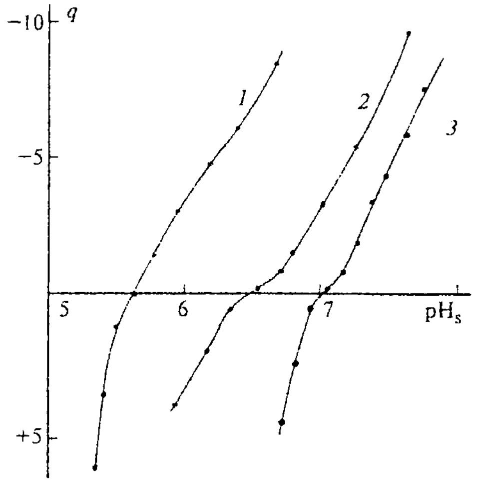

Fig. 2. Surface charge (q) of a chromogel with pH_i equal to 7 *vs* pH_s of the suspension with C_{NaCl}/mol L^{-1} = 0.01(*1*); 0.1 (*2*); 1.0 (*3*).

NaOH that we studied can be classified into two types. The first type is characterized by a more or less sharp break of the titration curve at an OH : Me ratio far from the equivalence point, followed by a slow increase in this ratio accompanied by a sharp increase in the pH of the suspension (Fig. 1). This type comprises Ti^{IV}, Zr^{IV}, and Cr^{III}. The second type is characterized by a sharper break of the titration curve at an OH : Me ratio close to the equivalence point followed by a very slow increase in the OH : Me ratio (see Fig. 1). This type includes Fe^{III}, Zn^{II}, and Co^{II}; the most typical representative is In^{III}. Sm^{III} occupies an intermediate position between these two types. The compositions of hydrogels, found from the titration curves, are presented in Table 2; the compositions of the samples prepared by careful drying of hydrogels (xerogels) are listed in Table 3.

It can be seen that the oxide hydroxides of the first type are highly susceptible to oxolation,* which occurs even directly during precipitation from the solution; this is defined most clearly in the case of Ti^{IV}. Upon drying, the effect becomes more pronounced. For the second type of oxide hydroxides and for Sm^{III}, the stoichiometric composition is retained even upon drying. Interestingly, numerous studies (see, for example, Refs. 22—27) have shown that Fe^{III} is extremely prone to hydrolytic polymerization, but it occurs only in solution and with time. Previously,[4] we reported that fast precipitation from acidic solutions affords $Fe(OH)_3$.

An X-ray diffraction study of the xerogels showed that, after the careful drying procedure, Ti^{IV}, Zr^{IV}, and Cr^{III} oxide hydroxides remain amorphous to X-rays and exhibit no signs of crystallization; Fe^{III} oxide hydroxides are low crystalline according to the pattern of cubic $Fe(OH)_3$ or akaganeite; the In^{III} oxide hydroxide is a low-crystalline $In(OH)_3$. Samarium oxide hydroxide is a low-crystalline product; its X-ray diffraction pattern could not be identified (apparently, it corresponds to $Sm(OH)_{2.5}(NO_3)_{0.5}$); Co^{II} oxide hydroxide is a low-crystalline material related to α- and β-$Co(OH)_2$. Zinc oxide hydroxide is the only compound that is completely converted into crystalline ZnO following drying.

Table 4. pH_{PZC} values of hydrogels for metal oxide hydroxides in NaCl

Initial salt	pH_i 6	7[a]	8	9	10	11
$FeCl_3$	4.48	6.32	—	9.73	—	—
	5.47	7.28	—	9.12	—	—
	6.27	7.72	8.10	8.76	9.00	9.35
$Fe(NO_3)_3$[b]	6.30	7.48	—	8.84	—	—
$TiCl_4$	7.49	—	—	10.64	—	—
	6.97	8.17	8.80	9.97	10.85	—
	6.62	—	—	9.46	—	—
$ZrO(NO_3)$	4.10	5.10	6.70	7.70	10.30	11.20
	5.20	6.20	7.30	8.60	9.80	10.90
	6.20	7.30	8.20	9.00	9.40	10.30
$In(NO_3)_3$	—	5.10	6.80	8.10	9.90	—
	—	5.90	7.60	8.80	10.20	10.40
	—	6.70	7.90	9.10	9.70	10.60
$CrCl_3$	—	5.55	7.00	9.30	10.60	—
	—	6.40	7.35	8.60	9.80	10.50
	—	6.90	7.80	8.50	9.30	9.85
$Sm(NO_3)_3$	—	7.60	7.89	7.80	8.20	—
	—	7.84	7.92	8.02	8.87	9.68
	—	7.78	8.25	8.58	9.47	—
$ZnCl_2$	—	7.68	7.35	7.70	7.80	7.73
	—	8.14	7.80	8.37	8.50	8.30
	—	8.67	8.50	9.20	9.35	9.98
$SnCl_4$	6.00[c]	8.70	—	—	—	—
	5.50	8.00	—	—	—	—
	4.75	7.10	—	—	—	—

Note. The values are given for electrolyte concentrations of 0.01, 0.1, and 1.0 mol L^{-1} and written in order of increasing concentration.

[a] For ferrogels, the pH_i was 7.5.

[b] The concentration of NaCl was 1.0 mol L^{-1}.

[c] For stannogels, pH_i was 5.0.

Acid-base properties of the oxide hydroxide surface

In the series of studies cited,[5,6,10—15] two significant facts were established, namely: (1) the pH of the point of zero charge determined by the Parks method depends on the supporting electrolyte concentration (Fig. 2) for all the hydrogels studied except for the cobalt hydrogels, and (2) the dependences of the experimental pH_{PZC} values on pH_i plotted for different electrolyte concentrations intersect at one point, which, as we have suggested,[17] is the true point of zero charge for an oxide hydroxide prepared from a particular salt in a particular ionic medium. An exception to this rule is zinc oxide hydroxide.

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* The formation of oxo (oxygen) bridges between the metal atoms in oxide hydroxide.

The pH_{PZC} value found for a hydrogel by the Parks method is the pH of an electrolyte solution occurring in pseudo-equilibrium with an unstable gel phase, and the change in the pH following the introduction of a hydrogel in an electrolyte solution is due to the fact that the gel tends to reach a composition corresponding to the point of zero charge.[5] Thus, the acid-base properties of a hydrogel should be characterized by its true point of zero-charge. The higher the true pH_{PZC} value, the stronger the intrinsic basic properties of the hydrogel surface, and *vice versa*. However, hydrogels show a unique ability to sorb excess hydroxyl groups during precipitation at relatively high pH values; these groups increase the surface basicity and can be consumed during heterogeneous hydrolysis. The excess OH groups are firmly bound and washed out with difficulty and incompletely. Therefore, the pH_{PZC} values found for hydrogels by the Parks method characterize the basicity of hydrogels obtained by precipitation at a particular pH and contacting with a particular electrolyte of a definite concentration (Table 4). Since these pH_{PZC} values depend linearly on the electrolyte concentration, they can be determined for any electrolyte concentration over a fairly broad range: at least, from 0.001 to 2—3 mol L^{-1}. All the objects that we studied including zinc oxide hydroxide are hydrogels of amorphous oxide hydroxides for at least 3—4 h after the onset of precipitation, as indicated by the dependence of pH_{PZC} on the supporting electrolyte concentration, which is typical of gels (see Table 4).

Table 5. pH_{PZC} values of hydrogels of metal oxide hydroxides in Na_2SO_4

Initial salt	pH_I 6	7	7.5	8	9	10
$FeCl_3$	6.70	—	7.82	—	9.87	—
	7.10	—	8.20	—	9.46	—
	7.52	—	8.35	—	9.13	—
$ZrO(NO_3)$	6.60	7.50	—	8.30	9.30	10.70
	7.20	8.10	—	8.60	9.50	10.00
	7.70	8.30	—	8.90	—	9.90
$CrCl_3$	—	7.25	—	7.95	9.00	10.55
	6.95	—	—	8.30	9.15	—
	—	7.55	—	8.45	9.15	9.50
$In(NO_3)_3$	—	—	—	7.70	8.60	10.10
	—	7.40	—	8.20	9.30	9.90
	—	—	—	8.40	9.30	10.00
$Sm(NO_3)_3$	—	—	—	—	7.97[a]	—
	—	—	—	—	10.75[b]	—
$SnCl_4$[c]	6.20	8.20	—	—	—	—
	5.50	7.85	—	—	—	—
	5.10	7.15	—	—	—	—

Note. The values are given for electrolyte concentrations of 0.005, 0.05, and 0.5 mol L^{-1} and written in order of increasing concentration.

[a] The electrolyte concentration was 0.005 mol L^{-1}.

[b] The electrolyte concentration was 0.5 mol L^{-1}.

[c] For stannogels, pH_I was 5 and 7.

The data presented in Tables 4—7 demonstrate that by varying the pH of precipitation, one can prepare sorbents highly active in heterogeneous hydrolysis even when the true pH_{PZC} value is relatively low, as for the Ti^{IV} oxide hydroxide.

We found the following true pH_{PZC} values for the metal oxide hydroxides studied in solutions of NaCl at the following pH_I:

	Fe^{III}	Ti^{IV}	Zr^{IV}	In^{III}	Cr^{III}	Sm^{III}	Sn^{IV}
pH_{PZC}	8.1	4.7	9.2	10.2	7.9	7.6	4.1
pH_I	8.1	4.5	9.4	10.0	8.4	7.0	4.0

On going to solutions of Na_2SO_4, the pH_{PZC} values for oxide hydroxides substantially change; this is true for both the values measured experimentally and the true pH_{PZC} value (see Table 5). The true pH_{PZC} in Na_2SO_4 solutions are the following:

	Fe^{III}	Zr^{IV}	In^{III}	Cr^{III}	Sn^{IV}
pH_{PZC}	8.6	9.3	10.0	9.1	4.1
pH_I	7.95	8.8	10.0	9.1	4.0

It can be seen that the true pH_{PZC} values in sulfate media are somewhat higher than those in chloride media.

It is of interest that (see Tables 3, 4) when pH_I is lower than the true pH_{PZC} value for the hydrogel, the

Table 6. Rate constants ($k_{obs} \cdot 10^4/s^{-1}$) of heterogeneous hydrolysis of $IrCl_6^{2-}$ (a 1 *M* solution of NaCl, 60 °C) as a function of pH_I of hydrogels

Metal	pH_I 6	7	8	9	10	11	12
Fe^{III}	1.6	2.3	4.1	8.9	13.0	13.0	13.0
Ti^{IV}	—	0.8	1.0	4.8	4.1	16.6	—
Zr^{IV}	—	1.4	2.7	4.7	15.0	13.7	15.3
In^{III} [a]	—	—	—	1.0	1.3	—	—
Sm^{III} [a]	—	2.9	3.2	4.3	6.0	8.5[b]	—
Zn^{II}	—	7.4	5.6	4.4	2.5	2.7	2.9

[a] Found by extrapolation from the E_a values and dependence of k_{obs} on the concentration of NaCl.

[b] For pH_I of 10.5.

Table 7. Rate constants ($k_{obs} \cdot 10^4/s^{-1}$) of heterogeneous hydrolysis of $PtCl_4^{2-}$ (a 1 *M* solution of NaCl, 60 °C) as a function of pH_I of hydrogels

Metal	pH_I 6	7	8	9	10	11
Zr^{IV}	—	—	4.8	8.5	12.0	11.5
Cr^{III}	2.2	2.6	3.2	2.9	2.6	2.7
In^{III} [a]	—	~7	4.5	4.0	3.0	3.8
Sm^{III} [a]	—	—	—	—	6.6	8.6
Ti^{IV} [b]	—	—	0.8	3.9	13.6	—

[a] Found by extrapolation from dependence of k_{obs} on the concentration of NaCl.

[b] At 80 °C.

experimental pH_{PZC} values for different electrolyte concentrations (g-equiv L^{-1}) vary as follows: 0.01 < 0.1 < 1.0, and *vice versa*. This is observed for all oxide hydroxides capable of binding excess OH groups; for the Sm^{III} oxide hydroxide, which contains unsubstituted nitrate ions, the opposite situation is observed. It can be assumed that the point of intersection of the curves $pH_{PZC} = f(pH_i)$ that we found corresponds to a basic salt, while a pure hydroxide should possess one more intersection point at $pH_i > 12$.

The rate of heterogeneous hydrolysis in the presence of oxide hydroxides

Previously[5,6,10–15] we studied the indicator reactions of octahedral Ir^{IV} and Rh^{III} complexes and a square-planar Pt^{II} complex. The rates of these indicator reactions on the surface of almost all the oxide hydroxides studied follow pseudo-first order kinetics with respect to the complex concentration. The indicator reaction with a rhodium complex is less suitable for measurements because its rate is too high; therefore, the sorption properties of the oxide hydroxides were mainly characterized by the reaction rate constants for the indicator reactions with Ir^{IV} and Pt^{II} complexes (see Tables 6, 7), except for the Cr^{III} oxide hydroxide. Since the latter compound possesses reductive properties, we did not use Ir^{IV}, which is an oxidant, in order to avoid superposition of hydrolysis and redox reactions. It follows from Table 6 that as the pH_i increases, the rate of the sorption-hydrolytic precipitation of iridium from solutions increases in the presence of any oxide hydroxide, except for zinc oxide hydroxide.

We have noted that the behavior of square-planar Pd^{II} and Pt^{II} complexes is very specific and that characteristic features of heterogeneous hydrolysis on the surface of ferrogels found for these compounds differ substantially from those found for octahedral complexes.[3] This is also true for other hydrogels. The data on the kinetics of heterogeneous hydrolysis of $PtCl_4^{2-}$ on the surface of oxide hydroxides (see Table 7) indicate that the dependence of the rate constants on pH_i found for the reaction on the surface of Zr^{IV}, Ti^{IV}, and Sm^{III} oxide hydroxides differs from the dependence, or, more precisely, from the absence of any dependence observed for the Cr^{III} and In^{III} compounds. It should also be noted that the variation of the rate of precipitation of Pt^{II} as a function of pH_i in the presence of Zr^{IV}, Ti^{IV}, and Sm^{III} oxide hydroxides is similar to that found for octahedral complexes, whereas in the case of Cr^{III} or In^{III}, no similarity is observed.

It can be seen from Figs. 3 and 4 that the samples of hydrogels with pH_{PZC} values close to the true pH_{PZC} value show the maximum rate of sorption among octahedral complexes. The sorption activity toward $IrCl_6^{2-}$ in this region depends on the nature of the central cation in the oxide hydroxide: $Zr^{IV} \geq Fe^{III}$, $Sm^{III} > Ti^{IV}$, $Zn^{II} > In^{III}$. Since the iridium complex is among the most stable and, simultaneously, most inert complexes,

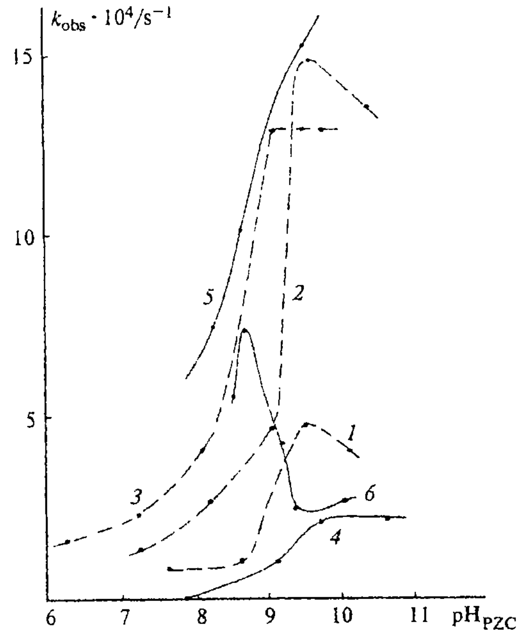

Fig. 3. Rate constants for heterogeneous hydrolysis of $IrCl_6^{2-}$ (60 °C, a 1 *M* solution of NaCl) *vs* their pH_{PZC} in the presence of hydrogels of Ti^{IV} (*1*); Zr^{IV} (*2*); Fe^{III} (*3*); In^{III} (*4*); Sm^{III} (in 2 *M* NaCl) (*5*); and Zn^{II} (in 0.5 *M* NaCl) (*6*) oxide hydroxides.

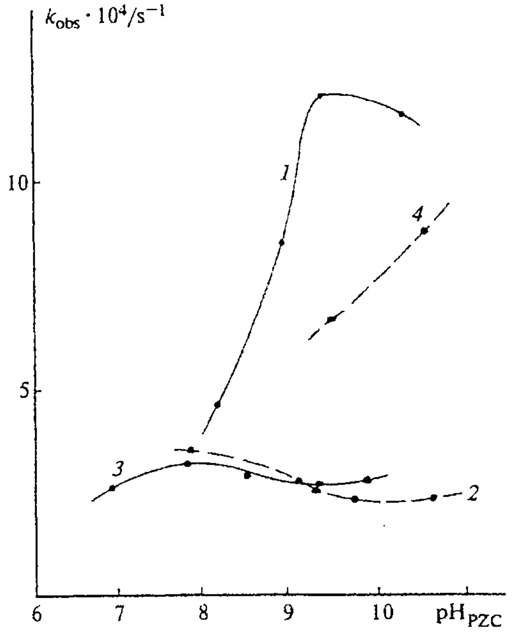

Fig. 4. Rate constants for heterogeneous hydrolysis of $PtCl_4^{2-}$ (60 °C, a 1 *M* solution of NaCl) *vs* their pH_{PZC} in the presence of hydrogels of Zr^{IV} (*1*); In^{III} (in 0.1 *M* NaCl) (*2*); Cr^{III} (*3*); and Sm^{III} (*4*) oxide hydroxides.

these data are very illustrative from the viewpoint of predicting the possibility of extracting complex-forming metals from complexing media.

For the square-planar Pt^{II} complex, the sorption activity of Zr^{IV} oxide hydroxide markedly exceeds that of any other oxide hydroxide studied; this is followed by Fe^{III} and Sm^{III} oxide hydroxides, whereas the Cr^{III} compound is the least reactive toward $PtCl_4{}^{2-}$. It follows from Table 8 that the activation energies for the sorption-hydrolytic precipitation of iridium on all of the oxide hydroxides studied, except for zinc oxide hydroxide, are close to (110±10) kJ mol^{-1}; those for the precipitation of Pt^{II} are (80±10) kJ mol^{-1} (except for Cr^{III} oxide hydroxide). The magnitude of the rate constant points to an effect of the properties of the sorbent surface. A large deviation of the activation energy from the above-mentioned average values can imply a different mechanism of the process, for example, an increased contribution of physical (electrostatic) sorption or participation of water molecules and surface OH groups in addition to the complex (this has been noted in sulfate media[3,11]).

The relationship between the nature of the central ion of oxide hydroxide and its sorption properties

The central ions in the oxide hydroxides are similar regarding the following parameters. The Ti^{4+}, Cr^{3+}, and Fe^{3+}; Zr^{4+}, Zn^{2+}, and Co^{2+}; and Sm^{3+} and In^{3+} ions have close radii. The Zr^{4+}, Cr^{3+}, and Fe^{3+}; Sm^{3+} and In^{3+}; and Zn^{2+} and Co^{2+} ions possess close ion potentials. The Ti^{4+} and Zr^{4+} and Sn^{4+}, In^{3+}, and Zn^{2+} ions are electronic analogs. The Cr^{3+}, Fe^{3+}, and Co^{2+} ions have no electronic analogs. Sm^{3+} can be considered to be an analog of Ti^{4+} and Zr^{4+}, because 4f electrons are located at a substantially lower electronic level than 5s and 5p electrons.

In terms of the ion radius, the central ions can be arranged in the following sequence: Sm^{3+} > In^{3+} > Zr^{4+} > Zn^{2+}, Co^{2+} > Sn^{4+} > Fe^{3+}, Cr^{3+}, Ti^{4+}; the ionic potential varies in the order Ti^{4+} > Sn^{4+} > Zr^{4+}, Cr^{3+}, Fe^{3+} > In^{3+} > Sm^{3+} > Zn^{2+}, Co^{2+} (see Table 1).

Table 8. Average activation energies (E_a) of indicator reactions of heterogeneous hydrolysis in the presence of oxide hydroxide hydrogels in chloride solutions

The central cation of the oxide hydroxide	E_a/kJ mol^{-1}		
	$IrCl_6{}^{2-}/IrCl_6{}^{3-}$	$PtCl_4{}^{2-}$	$RhCl_6{}^{3-}$
Fe^{III}	119.5±8.6	76.8±16.9	112.8±10.8
Ln^{III}(REE*)	110.2±10.8	87.8±11.8	94.0±6.4
Ti^{IV}	112.7±11.9	~46*	—
Zr^{IV}	103.8±7.5	78.0±11.0	—
In^{III}	109.8±7.6	87.0±4.4	—
Cr^{III}	—	55.7±5.2	96.6±17.7
Zn^{II}	63.9±10.1	—	—

Note. The average absolute errors, $\Delta a = \Sigma\Delta a/n$, are given.

* For pH$_1$ of 10.

The sorption activity of the oxide hydroxides formed by cations, which are electronic analogs, is correlated with their basic properties (true PZC) and with the ionic potential of the cation.[17] Thus for the cations with the s^{2}p^6 electronic structure, the sorption activity of the oxide hydroxides varies in the order Sm^{III} ≥ Zr^{IV} > Ti^{IV}. Similarly, for sorption activity of cations with the p^{6}d^{10} electronic structure, we have Zn^{II} > In^{III}. The Fe^{3+}, Cr^{3+}, and Co^{2+} cations have no electronic analogs among the other cations that we studied, but each of them contains a partially occupied 3d level. The sorption activity of Cr^{III} oxide hydroxides is the least among these three compounds. Ti^{IV} and Cr^{III} oxide hydroxides possess high tendency to oxolation. According to the model of the mechanism of heterogeneous hydrolysis developed previously,[3] hydroxyl groups act as the sorption sites on the hydrogel surface and the rate of the process is proportional to the concentration of surface OH groups in unit weight of the hydrogel.

We determined the pseudo-equilibrium sorption capacity (Q) of oxide hydroxide samples with pH$_1$ 9 in relation to $RhCl_6{}^{3-}$ at 50 °C.

Central ion	Fe^{III}	Ti^{IV}	Zr^{IV}	Cr^{III}	In^{III}
Q/mol 10^4 g^{-1} of M(OH)$_z$	4.2	3.6	6.0	5.4	4.2

Since three OH groups are needed to bind the Rh^{III} aqua complex, we found the concentrations of the OH groups in oxide hydroxides to be 1.26, 1.08, 1.8, 1.62, and 1.26 (g-ion 10^3) g^{-1}, respectively, *i.e.*, these values are of the same order of magnitude.

Two extreme cases are possible, namely, highly developed surface with a low concentration of OH groups and a poorly developed surface with a high concentration of OH groups; this would have the same influence on the rate of the process. The fact that the sorption properties of ferro- and chromogels are substantially different, although not only the radii and charges of the central cations but the concentrations of the OH groups are equal, requires special consideration. The hydrogels discussed here seem to differ only in the tendency to oxolation. It can be suggested that the basicity of the OH groups in oxide hydroxides decreases upon oxolation; this might be the reason for the observed differences. However, the reason for the different tendencies of Cr^{III} and Fe^{III} oxide hydroxides to oxolation is unknown. Some role might be played by the reductive properties of Cr^{III}; *i.e.*, by the relatively high energy of the 3d^3 electrons and the asymmetry of this electronic level.

The model of the mechanism of heterogeneous hydrolysis on oxide hydroxides and its predicting ability

The model of the mechanism of sorption-hydrolytic precipitation of some metals from solutions of their complexes on the surface of poorly soluble oxide hydroxides of other metals[2,3] (heterogeneous hydrolysis), proposed previously, represents this process as consisting of three successive steps (1) fast reversible sorption of the complex species predominating in the solution on the surface of the gel phase of the oxide hydroxide sorbent; (2) slow reversible aquation of the sorbed complex; and (3) fast irreversible acid dissociation of the aqua complex of the metal being precipitated, formed on the sorbent surface, as a result of interaction with the surface basic OH groups and the formation of "ol" (hydroxyl) and oxo bridges between the new (sorbate) and old (sorbent) hydroxide phases.

According to this model, activity in heterogeneous hydrolysis should be exhibited by poorly soluble amorphous oxide hydroxides aquated during the preparation (primary water) and formed by metal cations for which the ratio between the charge and the radius (the so-called ionic potential) ranges from 2.5 to 5.0. Moreover, the oxide hydroxide sorbents should be relatively resistant to crystallization and oxolation and capable of sorbing and retaining excess OH groups for some period

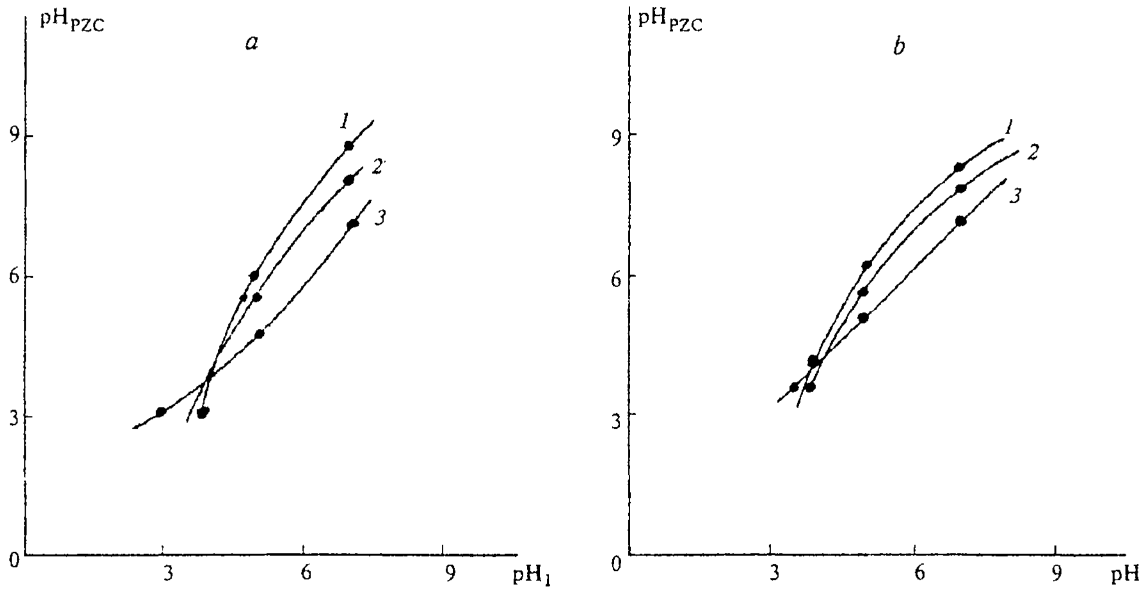

Fig. 5. Determination of the "true pH_{PZC}" of stannogels in NaCl (*a*) and Na_2SO_4 (*b*) at the electrolyte C/g-equiv. L^{-1} = 1.0 (*1*); 0.1 (*2*); 0.01 (*3*).

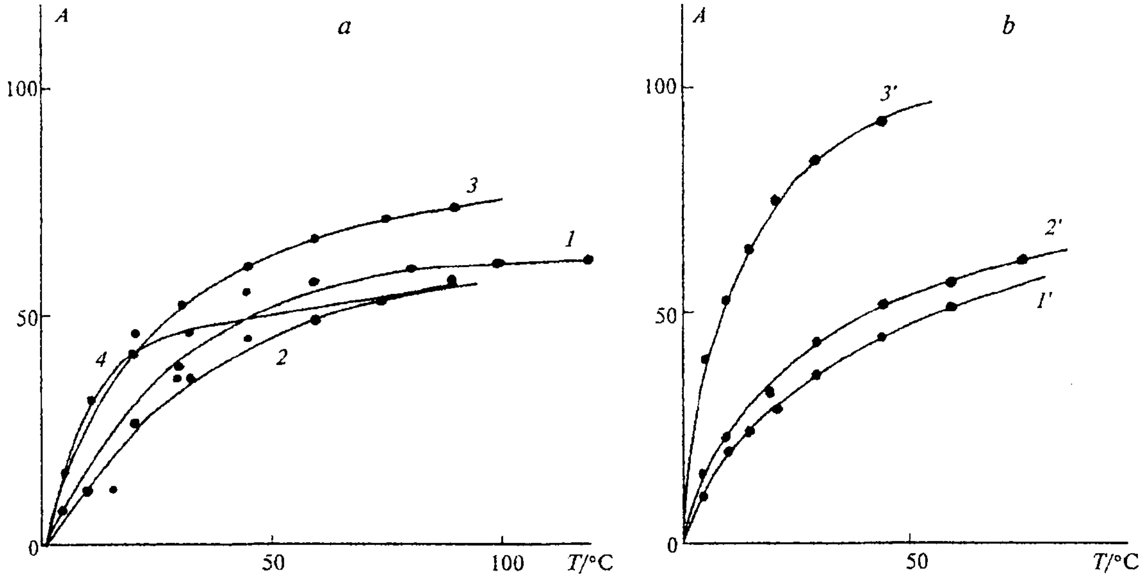

Fig. 6. Kinetic curves of sorption of $IrCl_6^{2-}$ (*a*) and $PtCl_4^{2-}$ (*b*) on stannogels at T/°C = 80 (*1*, *1'*, *2'*), 70 (*2—4*), 50 (*3'*) and pH_i 7 (*1—3*, *1'*), 9 (*4*, *2'*); A (%) is the degree of extraction; ionic medium is 0.5 M NaCl; for *3*, 1 M $NaClO_4$. For comparison: *3'* is a typical kinetic curve for heterogeneous hydrolysis of $PtCl_4^{2-}$ in the presence of an Sm gel with pH_i 11.

of time, which would extend the scope of their application. Heterogeneous hydrolysis occurs for acido complexes with stability constants of $K_{st} < 10^{40}$; in addition, this process is more efficient for octahedral complexes and less efficient for square-planar and tetrahedral complexes.[3] If the above conditions are not fulfilled, sorption occurs by a different mechanism, which requires lesser changes in the initial composition of the sorbate and, hence, provides a lower selectivity and extent of the sorption extraction.

To test the predicting power of this model, we estimated tentatively the sorption behavior of Sn^{IV} oxide hydroxide and then verified the prediction experimentally.

The electronic structure of Sn^{4+} is p^6d^{10}; it is an electronic analog of In^{3+} and Zn^{2+}. Its ionic potential is close to that of Ti^{4+} (see Table 1). Taking into account analogies, the data obtained suggest that Sn^{IV} oxide hydroxide should show low tendency to oxolation, and, like In^{III} oxide hydroxide, it should be relatively inactive in heterogeneous hydrolysis; its true PZC should lie in the pH range 3—4.

The results of the experimental investigation of Sn^{IV} oxide hydroxide are presented in Tables 2—5 and in Figs. 1, 5, and 6. Samples prepared by alkaline hydrolysis of $SnCl_4$ according to the above-described procedure were studied by the method of the point of zero-charge and by measuring the kinetics of indicator reactions; the curve for the drop titration of $SnCl_4$ and thermograms of xerogels were recorded. It was found that during alkaline hydrolysis, the hydroxide does not undergo oxolation, but it loses almost all the structural water when dried; like indium hydroxide, Sn^{IV} hydroxide strongly binds excess alkali, whose content reaches 0.4 g-equiv. mol^{-1} of the hydroxide. In the pH range 3—9, tin completely precipitates (the residual tin concentration is below the limit of detection attainable by the atomic-absorption method); the dependence of the pH_{PZC} on pH_l for stannogels is normal for gels; the true pH_{PZC} is 3.8 in a chloride solution at pH_l 4.0; in a sulfate solution, this value is 4.1 at pH_l 4.0 (see Fig. 5). The shape of the kinetic curves for sorption of $IrCl_6^{2-}$ and $PtCl_4^{2-}$ is not typical of heterogeneous hydrolysis (see Fig. 6); they rather resemble the kinetic curves for physical sorption by a sorbent with a very low sorption capacity. The rate of sorption barely depends on temperature. Special experiments on the determination of the degree of ligand elimination during sorption on a stannogel with pH_l 7 (in a solution of $NaClO_4$) demonstrated that when sorption is complete, the degree of elimination of chloride ions from $PtCl_4^{2-}$ is not higher than 40%, and that from $IrCl_6^{2-}$ does not exceed 70%.

Thus, the obtained experimental characteristics and the assumptions regarding the mechanism of sorption on stannogel are in good agreement with the predicted parameters and, hence, our prediction has been confirmed.

It remains unknown why sorption on stannogel differs so crucially from sorption on titanogel with the same pH_l value, although all the other characteristics of both materials are very close. Presumably, the electronic structure of the central cation is more significant than the ionic potential. Perhaps, at higher pH_l the behavior of stannogels would be more similar to the hydrogels of other metals, but it is impossible to carry out this comparison, because stannogels with $pH_l > 9$ are peptized to complete dissolution during washing.

Conclusion

The results of studies[10—15,17] considered in this review made it possible to confirm the model of the mechanism of heterogeneous hydrolysis, to obtain more detailed information on this process, and to supplement the data base composed previously. This data base allows one to predict with confidence what sorbent and what conditions are needed for extracting a particular complex-forming metal from a particular complexing medium.

The utility of the concept considered here and the composed data base can be illustrated by a work[28] in which an attempt was made to design an inorganic ion exchanger based on Sn^{IV} oxide hydroxide for separation of the nuclear fission products (Cs, Ba, Ru, Ce^{III}, Nd, La, Y, Pm, Zr, Nb). If data on the dependence of the sorption properties of oxide hydroxides on their nature and preparation conditions had been available, a more efficient sorbent could have been chosen. The same is true for another work[29] in which zirconium and manganese oxide hydroxides were used without allowance for the data on the pH_{PZC} values.

Whereas the properties of Fe^{III} oxide hydroxides have been the subject of numerous publications, the majority of which, including voluminous reviews,[25—27] deal with amorphous gel-like modifications, published data on the amorphous modifications of Ti^{IV}, Zr^{IV}, Cr^{III}, In^{III}, Zn^{II}, and lanthanide oxide hydroxides are rather scarce; moreover, this tendency does not change with passing years. Our studies[10—15,17] extend the information available in this field.

The data that we obtained confirm the previously stated[1,2] principles of the extraction of complex-forming metals from complexing media.

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