Reviews

The use of the pH at the point of zero charge for characterizing the properties of oxide hydroxides

S. I. Pechenyuk

I. V. Tananaev 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, Murmansk Region, Russian Federation.
Fax: +7 (477 8) 91 4131. E-mail: root@chemy.kolasc.net.ru

The modern theoretical views on the point of zero charge of the oxide hydroxide surface are considered. Methods for determination of the pH of the point of zero charge and the use of this value to characterize the properties of oxide hydroxides are described. Examples of using the pH of the point of zero charge in studies of oxide anodes and amorphous oxide hydroxide sorbents are presented.

Key words: point of zero charge, oxide hydroxide, sorption properties.

The values of pH at the isoelectric point and at the point of zero charge are characteristics that have been frequently used since the 80s in the foreign literature on electrosurface and sorption properties of solids including oxides and hydroxides.[1–13] However, in domestic publications these characteristics have not been employed,[23–25] except for the studies by the author of the present paper.[14–22]

In this review, we describe a simple and efficient method for the determination of this value and consider the relationship between this parameter and the surface properties of oxide hydroxides and the scope of its application.

The concept of the point of zero charge (PZC) and its definition, different from that given for the isoelectric point (IEP), were first formulated in the 60s.[26–28]

The term PZC is used to define a state of the surface of a dispersed solid phase at a "solid—electrolyte solution" interface such that the numbers of positive and negative potential-determining ions sorbed on the surface are the same and the total surface charge is equal to zero. In systems formed by aqueous solutions and oxides, hydroxides, or oxide hydroxides, the hydronium H_3O^+ and hydroxyl OH^- ions are the potential-determining species; therefore the surface charge depends on the pH of the solution. Meanwhile, the IEP characterizes a state of the surface such that the electric potential at the slip plane inside the double electric layer is equal to zero. A quantitative characteristic for both the PZC and IEP is the pH value of a solution at which the total charge of the surface contacting with this solution and the electric potential of the double electric layer are equal to zero.

In the absence of a specific interaction of the dispersed phase with electrolyte ions, $pH_{PZC} = pH_{IEP}$. Simple and effective procedures for determining the pH_{PZC} value by potentiometric titration[27] and by the method of static points[28] have been proposed. The difference between the PZC and IEP has been established and the known pH_{PZC} values have been summa-

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rized.[26] The author of the present communication has surveyed the data on the pH_{PZC} values reported in later studies.

The pH_{PZC} is a very important value for adsorption measurements and surface characterization.

This is due to several reasons. First, a crucial role in the sorption of protons and hydroxy groups is played by the acid—base properties of the surface. In a previous publication,[23] an equation was derived that relates the first and the second acid—base dissociation constants of the surface aqua and hydroxy groups to pH_{PZC}

$$pH_{PZC} = 0.5(pK_{a_1} + pK_{a_2}) - 0.5\log(1 + K_x a_x)/(1 + K_y a_y), \qquad (1)$$

where K_{a_1} and K_{a_2} are the acid—base equilibrium constants, K_x and K_y are the equilibrium constants for the association of the electrolyte cations and anions with the surface aqua and oxo groups, and a_x and a_y are the ion activities. A similar equation was reported previously.[3]

Second, the electrostatic sorption of electrolyte ions complicated by chemical interaction changes both the PZC and the IEP; however, these values change in opposite directions. Specific sorption of cations shifts the PZC toward lower pH values, whereas specific sorption of anions shifts it to higher pH. The IEP changes in the presence of specific sorption in the opposite directions. If the electrolyte cations and anions are sorbed equally ($K_x a_x = K_y a_y$) the sorption is nonspecific and $pH_{PZC} = pH_{IEP} = 0.5(pK_{a_1} + pK_{a_2})$. Thus, pH_{PZC} is related to the intrinsic properties of an oxide hydroxide to a greater degree than pH_{IEP}.

Finally, when there are no acidic or basic admixtures, the equilibrium of sorption of hydroxonium and hydroxyl ions is established very soon, namely, after 1 to 2 min at room temperature. This is very important for the study of nonequilibrium systems in which the states of one or several components rapidly change.

It has been shown previously[15] that pH_{PZC} not merely characterizes the acid—base properties of oxide hydroxides but can also serve for comparison of the acid—base properties of oxides, hydroxides, oxide hydroxides, hydrolyzable salts in different crystal modifications, crystalline, amorphous, and supported materials, wet and dry, *etc.*

The surface properties of oxides of Ru^{IV}, Ir^{IV}, Mn^{IV}, Pb^{IV}, Ti^{IV}, Zr^{IV}, Sn^{IV}, Ce^{IV}, tantalum and spinels Co_3O_4 and $FeCo_2O_4$, which are used in electrochemical processes, have been reported.[1] The practical application of these oxides gives impetus to investigation of their acid—base properties, because their surfaces are pH-sensitive. However, when adsorbed ions are present on the surface, the surface potential does not always obey the Nernst equation. The intermediates of the redox processes on the oxide surfaces, which determine the state of ions sorbed on surface, have been poorly studied so far. The progress in surface chemistry is still not adequately used in the analysis of the electrochemical behavior of oxides, because the theoretical concepts do not match the experimental procedures used in surface chemistry. Nevertheless, it was suggested that the electrocatalytic activity of oxides is correlated with their pH_{PZC}, and a model for this correlation is being developed.

The electrocatalytic activity of various electrodes is usually estimated by comparing the rates of electrode reactions at a constant potential. The reaction rate depends not only on the chemical structure and the composition of the oxide surface (electronic factors) but also on the surface size (geometric factors). The influence of the specific surface area (S_{sp}) is usually very difficult to take into account, because there are no reliable methods for its determination. The pH_{PZC} value is an intensive property, which depends on the surface chemical and physical structure rather than on S_{sp}. If a particular oxide has been prepared by different methods, measurement of pH_{PZC} can demonstrate whether or not its electrocatalytic properties depend on the preparation procedure. In the case where the pH_{PZC} values of samples are equal, the difference in the electrocatalytic activity is normally attributed to the influence of S_{sp}.

The mechanism governing changes in the charge of an oxide surface depends on the pH of the solution to a greater degree than on the potential of the oxide electrode. This is yet another advantage of the PZC method for the study of oxides.

The pH_{PZC} value characterizes the acid—base properties of the surface and can be measured directly and accurately. Some researchers believe that this value depends on the strength of interaction of the central ion in an oxide hydroxide with the oxygen of the OH group attached to it. Correspondingly, the reaction intermediates formed in the transformations of oxygen, and, apparently, water are bound to the surface active sites and, therefore, the activation energies of these transformations also depend on the M—OH bond strength.[1] The active sites of an oxide hydroxide surface are Brønsted acids or bases.

The acid—base properties of oxide hydroxide sorbents are mostly studied by two methods. In the Parks potentiometric titration method,[27] a suspension of a hydrogel in a supporting electrolyte solution is placed in a half-open type quartz cell and purged with an inert gas for 1.5 h in order to remove dissolved carbon dioxide. Then the electrodes of a pH-meter are immersed into the suspension, and its initial pH value is determined by adding a definite amount of carbonate-free NaOH, equal for all experiments in a series. Then the suspension is titrated by a solution of an acid containing the same anion as the electrolyte. The corresponding volume of the supporting electrolyte is titrated as the reference experiment. The amount of the sorbed hydronium or hydroxyl ions is determined by comparing the two titration curves; the results are used to calculate the surface charge and the pH_{PZC}. This value is normally determined for at least three concentrations of the supporting electrolyte, which differ by an order of magnitude, for example, 0.01, 0.1, and 1.0 mol L^{-1} or 0.001, 0.01, and 0.1 mol L^{-1}.

According to the second (static points) method, solutions with different pH are prepared, and to equal volumes of these solutions, equal amounts of oxide hydroxides are added; after that, the pH value of the suspension is measured and the number of protons or hydroxyl groups sorbed by unit weight or unit oxide surface and the surface charge are calculated. By plotting the dependence of the surface charge on the solution pH, the pH value at which the surface charge is equal to zero is found (pH_{PZC}). The physical basis for both methods is the same; however, the method of static points suits better for dry samples but is not sufficiently convenient for gels because it is difficult to withdraw exactly equal gel portions from a suspension. In addition, during potentiometric titration, one can see whether the titration process is reversible. If the titration is reversible, then, for example, the gel-like oxide hydroxide retains its properties; if it is irreversible, the structure and composition of the sample rapidly change.

Since the pH_{PZC} value does not depend on the specific surface area of the sample, this method is exceptionally valuable for investigation of various metastable solid phases, gels, or amorphous structures, whose specific surface area and other surface characteristics undergo rapid changes.

We studied the interaction of anionic acido complexes of metals (mainly, platinum group metals, gold, chromium, copper, and mercury[14,17]) with oxide hydroxides of lanthanides,[14] oxides of Fe^{III}, Ti^{IV},[20] Zr^{IV},[16] Cr^{III},[20] *etc.*[18,21] at an "aqueous solution of the complex—oxide hydroxide surface" interface. Freshly precipitated gel-like oxide hydroxides, amorphous to X-rays, prepared by alkaline hydrolysis of solutions of the corresponding metal salts and containing primary water captured during precipitation were mostly used. A process called "heterogeneous hydrolysis" has been discovered and studied.[14] The essence of the phenomenon is as follows. When a solution of a complex contacts an oxide hydroxide, ions of the complex-forming metal gradually pass from the solution bulk on the oxide hydroxide surface; consequently, the complex is completely destroyed, the ligands remain in the solution, and a new phase of the hydroxide of the complex-forming metal is accumulated on the surface of the oxide hydroxide sorbent. The rate of this process depends on several factors; the major ones are the stability and the kinetic lability of the complex sorbate, temperature, acid—base properties of the oxide hydroxide sorbent, and the nature and concentration of the supporting ions.

A reliable model for this process was developed. The model assumes three consecutive steps: fast reversible sorption of the complex species predominating in the solution on the oxide hydroxide sorbent surface; slow reversible activation of the sorbed complex; fast irreversible acidic dissociation of the aqua complex of the metal, formed on the sorbent surface, due to interaction with the surface OH groups, which are basic, and formation of ol and oxo bridges between the new and old hydroxide phases. The occurrence of the third step makes the whole process irreversible.

Evidently, only highly basic OH groups on the surface can ensure the irreversible character of the process. It was found that the rate and the extent of heterogeneous hydrolysis depend to a large degree on the pH of precipitation of the oxide hydroxide gel. During heterogeneous hydrolysis, the amount of the acid or base in the system was kept constant; and only redistribution of the concentrations of the acid and base group took place during the process.

Characteristic features of heterogeneous hydrolysis were considered previously.[22] It was found that complex ions, which are gradually aquated in aqueous solutions, react with amorphous hydroxide phases, which also change with time. Hence, these systems are nonequilibrium with respect to all of the main components, and the PZC method gives good results in studies of the acid—base properties of the surface of hydrogel sorbents.

Using the Parks method,[27] we obtained a large number of data on the pH_{PZC} values for oxide hydroxides of some metals in solutions of sodium chloride and sulfate of various concentrations and demonstrated that in the case of hydrogels, unlike dry and crystalline samples, pH_{PZC} depends on the concentration of the supporting electrolyte and on the pH of precipitation. However, the curves for pH_{PZC} *versus* pH of precipitation (pH_I) plotted for various electrolyte concentrations and for a particular oxide hydroxide hydrogel intersect at one point (Fig. 1); we defined this point as a true PZC for a given combination of the initial metal salt and the supporting electrolyte.[18] Zinc oxide hydroxide is the only exception.

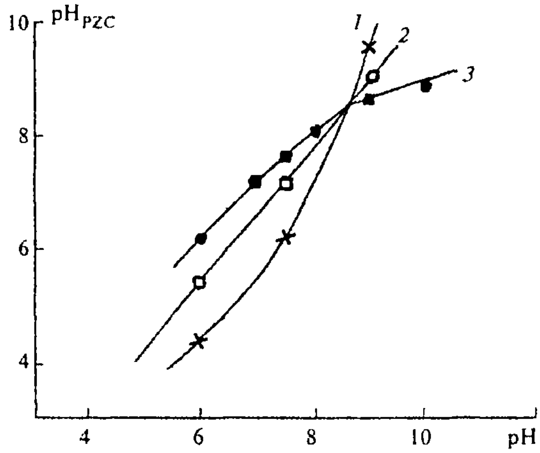

Fig. 1. pH_{PZC} *vs* the pH of precipitation (PH_I) for hydrogels of amorphous Fe^{III} oxide hydroxide in solutions of NaCl /mol L^{-1}: 0.01 (*1*); 0.1 (*2*); 1.0 (*3*).

It seemed of interest to compare the true pH_{PZC} values that we obtained with those reported[1] for crystalline samples, the majority of which had been prepared by alkaline hydrolysis of solutions of salts followed by calcination of the resulting precipitates.

For hydrogels precipitated from solutions of nitrates and chlorides, the following "true" pH_{PZC} values were found for the NaCl medium:

Sample	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	3.8

According to a previous publication,[6] the pH_{PZC} values for powdered TiO_2 (anatase) vary from 5.5 to 6.5, those for rutile are from 5.0 to 5.6, for $Zr(OH)_4$, they range from 6.5 to 6.7, for zirconium dioxide,[1,6] from 4 to 8, and the values for tin dioxide[1] vary from 3.7 to 4.3. However, the pH_{PZC} value for zirconium oxide hydroxide obtained from the sulfate in the sulfate medium is equal to 8.5,[18] while that for Sn^{IV} oxide hydroxide in the sulfate medium is 4.1. The pH_{PZC} values for various oxide hydroxides determined recently are summarized in Table 1. It can be seen that for Ti^{IV}, Fe^{III}, Zr^{IV}, and Al^{III} oxide hydroxides, the pH_{PZC} values do not coincide even for the same crystal modification.

Table 1. pH_{PZC} values for various oxide hydroxides

Oxide hydroxide composition	Modification	pH_{PZC} (20—25 °C)	Ref.
$TiO_2 \cdot nH_2O$	Rutile	5.6	4
	Rutile	5.7	10
	Rutile	8.2	24
	Anatase	6.6	34
	Amorphous to X-rays	6.7	12
$Fe_2O_3 \cdot nH_2O$	Goethite	8.5	11
	Goethite	8.3	8
	Amorphous	7.1	9
	Akaganeite	7.25	9
$ZrO_2 \cdot nH_2O$	Monoclinic	6.5	4
	Amorphous to X-rays	6.6	6, 7
	Amorphous to X-rays	4.0	43
$Al_2O_3 \cdot nH_2O$	Amorphous to X-rays	7.7	35
	γ-Al_2O_3	6.45	5
	γ-Al_2O_3	7.3	36
	Boehmite	7.2	37
	γ-Al_2O_3	5.6	39
	Alumogel	6.8	41
$Cr_2O_3 \cdot nH_2O$	Amorphous to X-rays $Cr(OH)_3 \cdot 0.8H_2O$	7.9—8.4	13
$Ni(OH)_2$	Amorphous to X-rays	11.3	35
$Bi_2O_3 \cdot nH_2O$	—	9.4	35
RuO_2	—	5.5	2
$Ca(OH)_2$	—	12.7	35
$SiO_2 \cdot nH_2O$	Silica gel	2.0	38
$SnO_2 \cdot nH_2O$	—	3.0	40
$MnO_2 \cdot nH_2O$	Pyrolusite	6.8	42
CeO_2	Cerianite (cubic)	8.1	3
$In_2O_3 \cdot nH_2O$	Cubic	7.3 (in 1 *M* NaCl)	30

Thus, the nature of the ionic medium and the origin and preparation conditions of oxide hydroxides have a substantial effect on pH_{PZC}. Samples of the same purity, composition, crystal modification, and specific surface area in reality differ in their surface properties if their pH_{PZC} values are different. Hence, the PZC method reveals differences between samples that cannot be detected by other methods. In some cases, this method provides explanation for the nonreproducibility of the behavior of the samples in electrochemical and sorption processes, and it can be used to identify oxides employed in electrochemistry and sorption technology.

Thus, using this method, it was found that during washing and calcination of an oxide hydroxide, sulfuric acid is not completely removed and, therefore, pH_{PZC} cannot be determined. We observed this situation for titanium dioxide prepared by thermal decomposition of $(NH_4)_2TiO(SO_4)_2$[29] and for zirconium dioxide.[30] For both samples, the pH at each point of the titration curve does not reach an equilibrium value over a period of several hours, indicating that the solid grains contain impurities.

The question arises of how the pH_{PZC} value is related to other surface properties of oxide hydroxides. In the vast majority of works dealing with sorption equilibria at the "electrolyte solution—solid" interface, sorption is studied as a function of the solution pH, the sorbate concentration in the solution, the ionic strength of the solution, and the specific surface area of the sorbent.[4—13,34—43]

These works study the applicability of various double electric layer models for predicting the constants of surface complexation for sorbates, which are normally represented by metal cations. Since these constants characterize the strength of binding of the sorbate to the sorbent surface, they can be used to evaluate the efficiency of a sorbent for the extraction of sorbates. Analysis of the resulting binding constants (Table 2) in combination with the pH_{PZC} values (see Table 1) shows that the higher pH_{PZC}, the greater the binding constants. Thus despite the fact that the pH_{PZC} values for sorbents with the same composition differ markedly, the sorbents can be arranged in a sequence which coincides with the order of increasing pH_{PZC}: silica gel < tin(IV) oxide hydroxide < titanium(IV) oxide hydroxide < zirconium(IV) oxide hydroxide < aluminum oxide hydroxide, pyrolusite, indium(III) oxide < iron(III) oxide hydroxide, chromogel < $Ni(OH)_2$ < $Ca(OH)_2$.

The strength of retention of the same cation by various sorbents changes in the following way:

Pb^{2+}: titanium(IV) oxide hydroxide < aluminum oxide hydroxide < goethite

Cd^{2+}: titanium(IV) oxide hydroxide < aluminum oxide hydroxide

Zn^{2+}: titanium(IV) oxide hydroxide < iron(III) oxide hydroxide

Calculations of the surface complexation constants listed in Table 2[12] were based on the following reactions:

$$=S{-}O^- + nH_2O \leftrightarrow =S{-}OH_n^{(n-1)+} + nOH^-; \quad (1)$$
$$K_H = \{=S{-}OH_n^{(n-1)+}\}/[OH^-]^n\{=S{-}O^-\};$$

$$=S{-}O^- + M^{2+} + nH_2O \leftrightarrow$$
$$\leftrightarrow =S{-}O{-}M(OH)_n^{(1-n)+} + nH^+; \quad (2)$$
$$K_M = \{=S{-}O{-}M(OH)_n^{(1-n)+}\}[H^+]^n/[M^{2+}]\{=S{-}O^-\},$$

where =S is a surface atom. For the process,

$$=S{-}OH + M^{2+} \leftrightarrow =S{-}O{-}M^+ + H^+; \quad (3)$$
$$K_{int} = \{=S{-}O{-}M^+\}[H^+]/\{=S{-}OH\}[M^{2+}].$$

Since, as a rule the first steps of reactions (1) and (2) take place, the expressions for K_H and K_M can be simplified:

$$K_H = \{=S{-}OH\}[OH^-]/\{=S{-}O^-\},$$

and

$$K_M = \{=S{-}O{-}M^+\}[H^+]/[M^{2+}]\{=S{-}O^-\};$$

then

$$K_H/K_M = \{=S{-}OH\}[OH^-][M^{2+}]/\{=S{-}O{-}M^+\}[H^+] =$$
$$= K_W/K_{int}[H^+]^2;$$

hence,

$$K_{int} = K_W K_M/K_H[H^+]^2,$$

and

$$\log K_{int} = -14 + \log K_M - \log K_H \text{ (here 9.23)} - 2\log [H^+].$$

For Zn^{2+} at pH = 3 and $K_M = 1.5 \cdot 10^8$,

$$\log K_{int} = -14 + 8.17 - 9.23 + 6 =$$
$$= -14 + 11.12 = -9.06,$$

while the results of calculations for other ions at pH = 3 are listed in Table 2.

Although the number of data being compared is limited, it can be concluded that the strength of binding of metal cations is correlated with the surface basicity, *i.e.*, with the pH_{PZC} value. Evidently, the process of precipitation of metal cations on an oxide hydroxide surface largely resembles precipitation of a hydroxide from a solution by an alkali.

Most of the published data on the pH_{PZC} and the surface complexation constants for ions were obtained for sorbents synthesized under arbitrarily chosen conditions and usually subjected to more or less prolonged aging. These samples are similar but, as can be seen from Table 1, they are not identical.

Surface complexation constants are thermodynamic characteristics of the sorption process; they do not reflect the role of time scaling; meanwhile in reality, nonequilibrium sorption systems can be encountered more frequently than equilibrium systems.

In some works, the kinetics of sorption have been studied. Thus the rate of sorption of chromate ions on titanium(IV) dioxide, represented by reactive rutile with S_{sp} = 4.3 m^2 g^{-1}, was investigated as a function of the medium pH and the temperature.[33] Kinetic curves show that the equilibrium sorption of chromate depends crucially on the sorbent and sorbate concentrations and that the maximum degree of sorption capacity (70—80%) is

Table 2. Surface complexation constants of some metal ions

Ion being sorbed	Sorbent	$\log K_{int}$	Ion medium	Reference
Hg^{2+}	Amorphous iron (III) hydroxide	6.9	Cl^-	32
	α-SiO_2	$K_{int} \to 0$	Cl^-	32
	Goethite	4.97	—	31
Cu^{2+}	Anatase	4.76	NO_3^-	34
	Goethite	1.92	—	31
	Ferrogel	0.065	NO_3^-	44
Pb^{2+}	Goethite	1.16	—	31
	γ-Al_2O_3	0.77	ClO_4^-	5
	$TiO_2 \cdot nH_2O$	−6.11	HNO_3	12
	Ferrogel	0.013	NO_3^-	44
Zn^{2+}	Goethite	0.34	—	31
	$TiO_2 \cdot nH_2O$	−9.06	HNO_3	12
	Amorphous FeOOH	−1.7	NaCl	9
	FeOOH	−3.2	Salt water	46
	Ferrogel	0.072	NO_3^-	44
Cd^{2+}	γ-Al_2O_3	3.96	ClO_4^-	5
	$TiO_2 \cdot nH_2O$	−8.79	HNO_3	12
Ni^{2+}	Amorphous FeOOH	−2.73	NaCl	9
	FeOOH	−3.45	Salt water	46
Mn^{2+}	Amorphous FeOOH	−2.29	NaCl	9
	FeOOH	−4.4	Salt water	46
Mg^{2+}	$ZrO_2 \cdot H_2O$	−8.6	Cl^-	7
Ca^{2+}	$ZrO_2 \cdot H_2O$	−8.6	Cl^-	7
Sr^{2+}	$ZrO_2 \cdot H_2O$	−8.8	Cl^-	7
Ba^{2+}	$ZrO_2 \cdot H_2O$	−9.0	Cl^-	7
UO_2^{2+}	$TiO_2 \cdot nH_2O$	−5.48	HNO_3	12
Co^{2+}	Amorphous FeOOH	−2.54	NaCl	9
	FeOOH	−3.93	Salt water	46
Li^+	Amorphous $ZrO_2 \cdot nH_2O$	−5.9	NaCl	43
Na^+	Amorphous $ZrO_2 \cdot nH_2O$	−5.8	NaCl	43
K^+	Amorphous $ZrO_2 \cdot nH_2O$	−5.8	NaCl	43
NO_3^-	Alumogel	−5.6	K^+	41
Cl^-	Alumogel	−5.4	K^+	41
Br^-	Alumogel	−5.5	K^+	41
I^-	Alumogel	−5.5	K^+	41

Note. K_{int} is the first surface complexation constant corresponding to the formation of the surface complex $=S{-}O{-}Me^{(z-1)+}$.

achieved during the first minute of contact of the phases at pH 6; the time needed for equilibration does not depend on the temperature and does not exceed 30 min. This contradicts the opinion[33] that rutile is a good sorbent for the extraction of chromate ions from solutions. The kinetics of sorption of Co^{2+} and Cs^+ cations as a function of the pH of the medium were studied.[42] It was found that the maximum amount sorbed and the maximum rate of sorption of Co^{2+} ions are observed near the pH_{PZC} of the sorbent, *i.e.*, on a neutral surface (as was reported in Ref. 33). The higher the pH of the medium and the greater the difference between the pH of the medium and pH_{PZC}, the higher the rate of sorption and the sorbed amount of Cs^+. This implies that Co^{2+} is adsorbed according to the sorption-hydrolytic mechanism, while adsorption of Cs^+ follows an electrostatic mechanism on the negatively charged surface. The kinetics of sorption of long-lived $^{137}Cs^+$, $^{90}Sr^{2+}$, and $^{60}Co^{2+}$ isotopes on magnetite, haematite, and pyrolusite have been studied.[45] Data that confirmed the specific behavior of Co^{2+} and the similarity of the properties of Sr^{2+} and Cs^+, described previously, have been obtained.[42] Thus, cations that are highly susceptible to hydrolysis and prone to form aqua complexes are best sorbed in the pH region close to pH_{PZC}. Both the amount sorbed and the rate of sorption are maximum in this region. The rate of sorption of all three cations obeys approximately the first-order equation with respect to the sorbate concentration. The same dependences hold for heterogeneous hydrolysis[14,15,46] and heterogeneous photolysis,[17] whose mechanisms are substantially different. Unfortunately, the temperature dependence of the rate was not studied in the previous works[42,45]; this restricts the possibility of the analysis of the sorption mechanism. Even today, kinetic studies able to solve the problem of the mechanism are rare.[15]

Giacomelli *et al.*[13] studied chromium(III) hydroxide gel, which differed from that studied in our work[19] only in that the chromogel precipitated at pH 9 was aged in the mother liquor for 2 days at 85 °C and then either kept in a dilute solution of perchloric acid or dried to a constant weight. The curves for the surface charge *versus* the pH of the medium for various concentrations of the supporting electrolyte, KNO_3, found by potentiometric titration (as in several other studies) cross at one point, which was defined as[13] the point of zero salt effect (PZSE). In the opinion of the authors, chromogel has a loose structure consisting of polymer chains separated by interlayers of adsorbed water; therefore, sorption of protons and hydroxyl groups occurs inside chromogel particles[13] and, hence, in the case of gels, we deal with bulk charge rather than with surface charge. Therefore, PZSE is the point of zero bulk charge (PZBC). Apparently, it was actually the PZBC that we determined in our experiments with gel-like oxide hydroxides. However, the introduction of a new parameter, PZBC, is not reasonable, because the charge unit is expressed in $C\,g^{-1}$, which is acceptable for both surface charge and bulk charge, the more so because the amount sorbed is always expressed in either grams of the sorbate per gram of the sorbent or in moles of the sorbate per gram of the sorbent.

The specific surface area for metastable phases cannot be determined with sufficient reliability. However, knowledge of S_{sp} is not necessary in investigation of surface properties. Since the S_{sp} value is the surface area of unit weight of the sample, then all the quantities being determined should be related to unit weight of dry substance, which can be found knowing the amount of the initial material used for the preparation of the gel-like sorbent.

When discussing the importance of determination of the pH_{PZC} value for characterizing the state of the surface of oxide hydroxides, it should be noted that, among the recent studies on the surface chemistry of inorganic sorbents, works dealing with crystalline materials, studies of sorption equilibria, and verification of various sorption models still predominate. Studies related to the kinetic regularities and to nonequilibrium systems are few in number.

To elucidate the mechanisms of sorption of various types of ions, kinetics and the relationship between the conditions of synthesis of the samples and the pH_{PZC} and the surface complexation constant should be systematically studied. Taking into account the data published previously,[13,16–21] of particular interest is the study of pH_{PZC} and surface complexation constants as functions of the water content in oxide hydroxides.

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