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Present state of research on the sorption of inorganic compounds by oxide hydroxides from aqueous solutions

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ABSTRACT. The general trends and methods of studying sorption from solutions on oxide hydroxide surfaces are discussed, including coprecipitation and sorption on previous activated sorbents. The models of the sorption mechanism and of the interrelation between different types of sorption are examined.

The bibliography contains 166 references.

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I. Introduction

Inorganic sorbents are used in all branches of industry and in the protection of the environment. They are used when aqueous solutions must not be contaminated with when the appropriate sorbents are cheap and simple to prepare and to regenerate, and stable towards radiation.[1] Oxide hydroxides (which are also known as oxyhydrates, hydroxides, and hydrated oxides†) come closest to these requirements, offering a high sorption activity in conjunction with a relatively simple synthesis (mainly the oxide hydroxides of iron, titanium, zirconium, aluminium, and tin[1]). Iron, aluminium, and titanium are widely distributed in nature, and their use is preferred on ecological grounds. The marked variation in the properties of oxide hydroxides prepared by different methods[2–8] has stimulated extensive studies of sorption on these materials. Workers who have synthesised oxide hydroxides by different methods have obtained results which are difficult or even impossible to reconcile. A search for regularities in this stream of data should help to assess the prospects of the various trends in research, to systematise and correlate existing data, and to identify bright spots in which fundamental studies of these topics could be developed. The aim of the present review is to outline some regularities in this field of study. The discussions will be confined to work published between 1976 and 1989.

A logical analysis of existing data requires first of all a clear definition of the concepts of sorption and coprecipitation. As has been pointed out,[2,9] sorption is a process in which a substance (the sorbate) is captured by previously synthesised sorbents, whereas in coprecipitation the capture takes place during the deposition of the sorbent from a solution containing the sorbate. It follows from these definitions that coprecipitation (as compared to sorption) is a process with time limitations set by the rate of formation of the precipitate of the macrocomponent (sorbent); subsequent processes in which the microcomponent (sorbate) is captured from the solution come under the definition of sorption, which has no time limits. During the contact between the sorbent and the sorbate the deposited sorbent can undergo transformations leading to the achievement of the most stable structure for the given conditions: this occurs in all the systems but is particularly important in systems with coprecipitation. A redistribution of the sorbate between the solid and the liquid phase could take place as a consequence. The initial picture can also be blurred by changes in the state of the sorbate in solution. Furthermore the time limitation, i.e. the instant when the true coprecipitation comes to an end, is poorly defined, and therefore it is often dismissed from the discussion consciously or unconsciously.

The result of the extraction by sorption depends on the time of sorption, and therefore a knowledge of the kinetics and mechanisms of all the changes taking place in the system is a necessary condition for a correct use of the sorbent, i.e. for the best results. Sorption processes are often used to remove microcomponents in solution in the presence of macrocomponents at a concentration 3–10 orders of magnitude higher. Therefore the ratios of the sorbent and the sorbate to the macrocomponents and the participation of the latter in the sorption process should be carefully monitored.

We shall review the principal directions of the experimental studies of the sorption of inorganic compounds from aqueous solutions on oxide hydroxides, which constitute (together with studies of the sorption on carbons from the gas phase and on organic sorbents from solutions) the largest group of studies in the modern science of reactions at a phase boundary (interface science). The writer does not claim to have reviewed the topic exhaustively: he has merely collected the most interesting (or typical) results of current research.

† Hydroxides, hydrated oxides, and oxide hydroxides are different chemical compounds,[2] but in the publications reviewed here the terms are applied indiscriminately to what are essentially oxide hydroxides: the products of the reaction of oxides with H_2O, both stoichiometric and nonstoichiometric.

II. Trends in the study of sorption processes on oxide hydroxides

Studies in which the adsorbate is coprecipitated with the sorbent occupy a major place in the current work on oxide hydroxides, but most of the authors fail to distinguish between the concepts of sorption and coprecipitation and discuss their results in terms of either concept, taken at random.[10–28] The experimental foundations of most of this work consist in determining the equilibrium sorption (or coprecipitation) of the microcomponents as a function of the nature of the macrocomponent (sorbent) and of the pH of the system for a fixed composition of the ionic medium. As we have already pointed out, these quantities should be treated as quasiequilibrium quantities.

Thus, the coprecipitation of the cations of the *s*, *p*, and *d* metals and of some anions with the oxide hydroxides of Fe, Ti, Zr, La, Y, Cd, Th, Be, Mg, Sc, and Nd has been studied at pH 4–14.[10–15]

The basic conclusion most often reached in that work is that the coprecipitation of the cations increases with the acidic properties of the collector, whereas (conversely) the coprecipitation of the anions decreases. The strength of the capture of the anion decreases as its aciditiy increases. We should stress that in the whole of this work the acid–base properties of the collectors are characterised only qualitatively, and the state of complex formation of the sorbates is ignored. The need to allow for the rate of establishment of equilibrium and for the forms in which the sorbate can exist in solution has been pointed out,[10] but even in later work this rate was not determined. Some reports[11,12,22,23] draw attention to the behaviour of the sorbate in solution, but the effect of the ionic strength and of the pH on the behaviour of the sorbent is ignored, in spite of the mention of gels of freshly precipitated oxide hydroxides which undergo uncontrolled spontaneous changes over long periods under the conditions of the experiment, especially in response to changes in the pH of the suspension (pH_s).[3–8]

The results of these studies of coprecipitation in combination with sorption[10–31] consist of tabulations of pH values at which various microcomponents can be removed from a solution of given macrocomposition by coprecipitation with a stated macrocomponent.

Another approach to the study of sorption processes, which is dominant among Russian scientists, is based on the theoretical model of classical ion exchange. The methodology of the study of sorption in inorganic sorbents is the same as in studies of organic ion-exchange resins, as is clearly shown in Belinskaya's review.[32] Many typical examples can be quoted:[33–51] in most cases granulated sorbents are preferred, in spite of the known fact that the drying and heat treatment needed during the granulation can seriously degrade the sorption properties.[1] Classical methods are used, like the limited volume[34,35] and the column dynamics method.[33,37–48] Studies of the sorption kinetics of both simple and complex ions in these systems show that the rate-limiting step is usually internal diffusion within the grain).[31–35] This approach is also being used to study problems of sorption selectivity, such as the sorption of SO_4^{2-} and NO_3^- on hydrated zirconium dioxide,[33] but it leads to partial, empirical results, whereas this type of problem is already basically solved (see below).

Unfortunately, the Soviet workers whose approach we are discussing seemed unaware (judging by their lists of references) of the immense amount of information on sorption problems obtained by foreign scientists, and made no attempt to interpret their own results in terms of alternative, more fully developed approaches.

Since complex formation is a phenomenon with universal ramifications we should pay special attention to studies of the sorption of complex ions of given compositions (classical complexes). The platinum metal complexes have been studied most widely. We can distinguish two groups of studies, each devoted to the same sorbates, carried out over approximately the same period, and containing much kinetic information: references 37–54 and 55–75. The compounds studied in this work included the complexes of composition MX_4^{2-} [where M = Pd(II), Pt(II) and X = Cl^-, Br^-, CN^-, CNS^-, NO_2^-], $M'Cl_6^{n-}$ [where M′ = Pt(IV), Ir(IV), Ir(III), Os(IV), Ru(IV), Ru(III), Rh(III)], and $Ir_3O(SO_4)_6Y_3$ (where Y = H_2O, SO_4^{2-}, and HSO_4^-). Abovskaya, et al. have studied the aquo complex of Pd(II)[48] and sulphate solutions of Rh(III) containing several complex forms.[49] The sorbents used in that work[37–54] included oxide hydroxides (hydrated oxides, or oxides, in the authors' terminology) of titanium (IV), zirconium(IV), tin(IV), and aluminium(III), whereas other workers[55–75] used crystalline oxide hydroxides (oxyhydrates in the authors' terminology) of the REE and many samples of amorphous oxide hydroxide of iron(III) (ferrogels), differing in the nature of the initial iron(III) salt and in the precipitation conditions (pH, oxidiser, temperature, time, etc.).

Both groups of papers discuss the kinetics of the process, including the temperature dependence of the rate, the influence of the nature and of the concentration of the ionic medium, and the effect of the composition of the products. Some papers[55,73–75] also discuss the interaction of the sorbents with the supporting electrolytes. That work leads to the following conclusions.

The sorption of anionic complexes on the granulated oxide hydroxides of Ti, Zr, Sn, and Al is fast (equilibration time τ_{eq} = 10–60 min at 20 °C) and is characterised by diffusion-limited kinetics, i.e. the activation energy E_a of the process (kJ mol^{-1}) is 30–40 for MCl_6^{n-}, 19–25 for $PdCl_4^{2-}$,[37–48] and 22 for $PtCl_6^{2-}$ on γ-Al_2O_3.[54]. On the other hand the sorption of aquo complex is very slow (τ_{eq} = 4–20 h), E_a = 18.5 kJ mol^{-1} for rhodium(III).[49] Increasing the concentrations of the components and of the supporting electrolyte slows the sorption of the complexes on the oxide hydroxides of Ti, Zr, and Sn;[37–50] furthermore increasing the ionic stength suppresses the sorption, i.e. it lowers the degree of utilisation of the sorption capacity of the sorbents, which is not large for these oxide hydroxides, reaching a maximum (30 mg metal g^{-1} of sorbent) for ZrO_2. The SO_4^{2-} ions interfere most strongly with the sorption fo MCl_6^{n-} and $PdCl_4^{2-}$ on TiO_2 and ZrO_2. Ageing the solutions of the complexes (sorbates) increases the sorption from aqueous solutions but lowers the sorption from solutions in hydrochloric acid.[37–48]

The composition of the sorbed forms immediately after the establishment of the sorption quasiequilibrium is the following: $PdCl_4^{2-}$ [51,52] and $PtCl_6^{2-}$ [54] are sorbed on γ-Al_2O_3; $PtCl_3H_2O^-$ on ZrO_2; $PtCl_6^{2-}$, $OsCl_6^{2-}$, and $OsCl_5H_2O^-$, $RhCl_6^{3-}$, $IrCl_6^{3-}$, $IrCl_6^{2-}$, and $IrCl_5H_2O^-$, and $PdCl_4^{2-}$, are sorbed on ZrO_2, TiO_2, and SnO_2.[37–48] This means that the forms predominantly present in solution are sorbed without change in composition. Upon ageing the complexes in the sorbent phase undergo a slow aquation, giving $OsCl_5H_2O^-$ and $OsCl_4(H_2O)_2^0$, $RhCl_4(H_2O)_2^-$ and $RhCl_2(H_2O)_4^+$, $IrCl_3(H_2O)_3$, and $PdCl_3H_2O^-$.[37–50]

These complexes are also sorbed undecomposed and almost instantaneously at room temperature on ferrogels from solutions not containing a supporting electrolyte,[55,57,63] and the capacity of the ferrogel can reach 2×10^{-3} mol g^{-1} of $Fe(OH)_3$, i.e. more than 400 mg of Pt, Ir, and Os on 1 g of $Fe(OH)_3$.[55] However, in the presence of a supporting electrolyte (more than 0.05 mol dm^{-3}) the

chemistry of the sorption process is radically altered.[55,57] On the surface of the ferrogels (in the presence of a supporting electrolyte) and of the REE oxide hydroxides (whether or not on ionic background is present) we observed a process which has been described in detail[55,58] and called heterogeneous hydrolysis. The rate of this process is strongly dependent on the nature of the complex, the sorbent, and the ionic background, and also on the temperature (E_a = 60–130 kJ mol^{-1}); it usually corresponds to a first-order equation in the concentration of the complex-forming metal or of the sorbate [in the latter case, except $PdCl_4^{2-}$, $OsCl_6^{2-}$, and $Pt(CNS)_4^{2-}$]. The observed rate constants K_H vary with these factors from 10^{-5} ($PtCl_4^{2-}$ [64]) to 0.2–0.5 s^{-1} ($RuH_2OCl_5^{2-}$ at 80 °C[55,65]). Heterogeneous hydrolysis takes place gradually against a background of hindered transformations of the complex sorbate in the solution, spontaneously in the pH-static regime, and not associated with oxidation–reduction or photochemical changes in the complex.[55] The products of the heterogeneous hydrolysis are the amorphous hydroxides of the central atom (CA),[55,59] strongly bound to the surface of the sorbent: the rate of detachment of the ligands from the CA is equal to the rate of transfer of the latter from the bulk of the solution to the surface of the sorbent. The rate of this process is directly proportional to the basicity of the sorbent [characterised[55] by the pH at the point of zero charge (pH_{PZC} or pH^0)] and depending in a complicated way on the concentrations of NaCl and Na_2SO_4 in the system. This dependence can be represented by the linear equation

$$K_H = a \pm bC_{el},$$

where C_{el} is the concentration of NaCl or Na_2SO_4 and the sign of the second term is determined by the nature of the sorbent and of the electrolyte.[58,62,63] It has been shown[73–75] that this is the result of the interaction of the sorbent with the supporting electrolyte, which alters the basicity of the sorbent.

Ageing the solutions of complex sorbates accelerates the heterogeneous hydrolysis; increasing the ionic strength of an electrolyte ($NaClO_4$) inert towards the sorbate and the sorbent suppresses the reaction;[66] the rate is unaffected by the charge on the complex anion.[67] A correlation has been found between the stability (or the lability) of the complex sorbate and the rate of the heterogeneous hydrolysis: the rate increases with increasing lability and with decreasing stability of the complex, and *vice versa*. The possibility of heterogeneous hydrolysis itself is determined by the stability of the complex. Thus, complexes with β = 10^{36}–10^{40} [$Pt(Cn)_4^{2-}$, $Fe(Cn)_6^{3-}$, $Fe(CN)_6^{4-}$] do not undergo heterogeneous hydrolysis.[55] The process has a pseudoequilibrium character, with sorption isotherms of the high affinity type;[76] the pseudoequilibrium capacity can reach (0.5–3.0) × 10^{-3} mol of complex g^{-1} of sorbent for the ferrogels and Ln_2O_3.[72] The reactions of these complexes with MCO_3 (M = Ca, Sr, Ba) are of the heterogeneous hydrolysis type.[68] A complex dependence exists between the rate of heterogeneous hydrolysis and the concentrations of sorbate and sorbent.[55]

We should also mention a group of papers describing sorption on previously activated oxide hydroxide sorbents [goethite, magnetite, haematite, jarosite, and amorphous hydroxides of iron(III)] at high temperatures (100–190 °C) from sulphuric-acid solutions of iridium and ruthenium in the form of sulphato or aquo hydroxo complexes of indeterminate composition.[77–81] It was shown that in these cases the sorption is irreversible, as in heterogeneous hydrolysis, and slow, that the capcity of the sorbents is low, and that the complex sorbates are fully or partially decomposed during the sorption.[81]

Lastly, we cannot fail to mention the work of Nechaev,[82–85] distinguished by an original approach to the mechanism of sorption on oxide hydroxides [for example, the sorption of $AuCl_4^-$ on the crystalline oxides of iron (III)]. Nechaev tried to relate the sorption equilibrium constants to the ionisation potentials of the oxide surfaces at pH^0.[83] He determined the composition of the sorbed forms and established that the sorption is accompanied by partial aquation of the $AuCl_4^-$.[82,84] The sorption of $AuCl_4^-$ and of its aquo derivatives was found to be described by Langmuir isotherms; the surface charge is of secondary importance in the sorption process, whereas the electronic structure of the surface plays a dominant role and determines the sorption activity of the oxides [at least, in respect of Au(III)].[85] However, the traditional (deeply "equilibrium") approach to the study of sorption and the fact that all the conclusions apply only to a single, easily hydrolysed and reduced complex ($AuCl_4^-$) detract from the value of the results.

In the foreign literature the studies of direct sorption on previously prepared sorbents greatly outnumber the studies of coprecipitation.[86,87] The vast majority of publications is based on the concept of an electrically charged oxide hydroxide surface. When in contact with H_2O or with an aqueous solution of electrolyte (sorbate) this surface can be identified with an electrode surface in contact with a solution,[88] and the appropriate definition of a potential-determining ion can be applied to it. For the oxide hydroxides these ions are H_3O^+ and OH^-;[89,90] their distribution between the bulk of the solution and the sorbent surface creates a surface charge q and a potential $\Psi(x)$ at the interface. The concepts of specific and of nonspecific sorption are also used. When the sorption energy E_s is Coulombic,

$$E = q\Psi(x),$$

i.e. when the interaction is purely electrostatic, the sorption is treated as nonspecific; in the opposite case the sorption is specific, i.e. it is accompanied by the formation of new chemical bonds. Because of the difficulty of determining $\Psi(x)$ and E_s experimentally (whereas the surface charge is easily measured[89–91]) the type of sorption is determined by using the point of zero charge PZC and the pH_{PZC} (pH^0)‡. The symbol pH^0 defines the pH of the so-called zero solution, for which the electrode has an equilibrium potential $\Psi(x)$ = 0[88] and the surface charge of the sorbent is q = 0. In the absence of specific sorption of the electrolyte ions pH^0 is independent of the concentration of electrolyte.

Simple cations and anions are mostly used as sorbates in the work of foreign scientists. Studies of sorption equilibria also seem to be predominant. Measurements of pH^0 and studies of the dependence of q on the nature and concentration of the electrolyte are a major part of most of these investigations. A specific link between the magnitude and other characteristics of the sorption and of the surface charge of the oxide hydroxide is sought, defined by the relationship between the pH^0 values of the sorbent, the pH of the suspension (pH_s) in the sorption system, and the concentration and nature of the supporting electrolyte. Since the previous review of the pH^0 and pH_{IEP} values was published[93] in 1965 it seems useful to complement the existing[93] data with information extracted from work published during the last two decades (Table 1).

‡ pH_{PZC} should be distinguished from pH_{IEP} (the pH of the isoelectric point), defined[92] as the pH of a solution in which the potential of the solid (ζ) is zero, i.e. the charge at the boundary of the diffuse layer of solution is zero.

Table 1. ph of the point of zero charge (pH^0) of some oxide hydroxides.

Oxide hydroxides	Method of preparation	Electrolyte	Concentration of electrolyte mol dm^{-3}	pH^0	Refs.
α-Fe_2O_3	Boiling a solution of $Fe(NO_3)_3$ for 18 dyas	KCl		9.2	[112]
	Natural	KCl		5.4–6.0	[91]
	After Atkinson [112]	KCl		6.3	[114]
	Reagent	KCl		8.4	[101]
				8.4	[107, 109]
	After Atkinson [112]	KCl		8.5	[92]
		K_2SO_4, $Ca(NO_3)_2$	0.1	9.6 6.5	[92] [92]
	Heating γ-Fe_2O_3 at 550 °C for 2 h in air				
	washed with H_2O	KCl		3.2	[97]
	washed with KOH (pH 9)	KCL		6.7	[97]
	Precipitation from a solution of $Fe(NO_3)_3$ by adding	KNO_3		8.6 (20 °C)	[124]
	NaOH and ageing at 150 °C in an autoclave			7.6 (20 °C)	[124]
α-FeOOH	Precipitation from a solution of $Fe(NO_3)_3$ by KOH at pH 12 and ageing in the in the mother liquor at 60 °C for 24 days	KCl		7.6	[112]
	After Atkinson [112]	$NaNO_3$		7.6	[125]
		KNO_3		7.5	[108]
		$NaNO_3$	0.1	10.2	[126]
β-FeOOH	Crystallisation of ferrogel in a chloride medium	KCl		7.6	[113]
				8.5	[127, 128]
γ-Fe_2O_3	Dehydration of α-FeOOH at 350 °C and cooling in air for 1 h				
	washed with H_2O	KCl		3.3	[97]
	washed with KOH (pH 9)	KCl		5.5	[97]
Fe_3O_4	Natural	KCl		6.4	[119]
	ditto	KCl		6.5	[91]
	ditto after HCl treatment	KCl		3.8	[91]
Ferrogel	Precipitation from a solution of $Fe(NO_3)_3$ by sodium hydroxide at pH 8, freshly prepared	$NaNO_3$	0.1	7.9–8.0	[102]
	Precipitation from a solution of $FeCl_3$ at OH/Fe = 4	$NaNO_3$	0.1	8.1	[114]
	Precipitation from a solution of $Fe(NO_3)_3$ at OH/Fe = 4	$NaNO_3$	0.1	8.4	[114]
	Precipitation from a solution of $Fe(NO_3)_3$ at pH 7	$NaNO_3$	0.1	8.1	[109, 110]
	Precipitation from a solution of $FeCl_3$ by a saturated solution of NH_4OH	$NaNO_3$	0.1	8.5	[125]
	Precipitation from a solution of $Fe(NO_3)_3$ by sodium hydroxide at pH 7 and ageing in the mother liquor for 3 h	$NaNO_3$	0.1	7.9	[109]
Ferrogel, freshly prepared	Precipitation from a solution of $FeCl_3$ by sodium hydroxide at pH 7.5	NaCl	1.0	7.7	[55, 75]
		NaCl	0.01	6.3	[55, 75]
		Na_2SO_4	0.5	8.3	[55, 75]
Ferrogel	Precipitation from a solution of $Fe_2(SO_4)_3$ by sodium hydroxide at pH 7.5	NaCl	1.0	6.2	[55, 75]
		$NaClO_4$	0.01	5.8	[55, 75]
	Precipitation from a solution of $Fe_2(SO_4)_3$ by sodium hydroxide at pH 7.5	NaCl	1.0	8.7	[55, 75]
		$NaClO_4$	0.01	5.8	[55, 75]
	Precipitation from a solution of $FeCl_3$ by sodium hydroxide at pH 9	NaCl	1.0	8.7	[55, 75]
	Same gel, aged in a solution of 1 M NaCl for 1 h at 80 °C	NaCl	1.0	8.3	[55, 75]
Ferrogel	Same gel, aged in a solution of 0.5 M Na_2SO_4 for 1 h at 80 °C	NaCl	1.0	5.1	[55, 75]
Y_2O_3	Reagent, ItO-03, B form	$NaClO_4$		7.45	[73]
		NaCl		7.60	[73]
		Na_2SO_4	0.01	7.85	[73]
		Na_2SO_4	0.1	8.55	[73]
		Na_2SO_4	0.5	8.75	[73]
Sm_2O_3	Reagent, SmO-E, C form	NaCl		7.45	[73]
		Na_2SO_4	0.1	7.90	[73]
			0.5	8.80	[73]
Yb_2O_3	Reagent, ItbO-03, B form	NaCl		7.15	[73]
		Na_2SO_4	0.1	7.25	[73]
		Na_2SO_4	0.5	8.25	[73]
TiO_2	Hydrolysis of $TiCl_4$, ageing in mother liquor for 3 weeks, rutile	KNO_3		5.6 (20 °C) 5.1 (50 °C)	[124] [124]
	Precipitation from a solution of $Ti(SO_4)_2$ by 2 M NaOH, washed and dried at 50 °C, anatase	$NaNO_3$		6.0	[129]
	Rutile			5.8 ( )	[126]
ZrO_2	Prepared by a method similar to that described for TiO_2 [129]	$NaNO_3$		9–10	[129]
$ZrO_2.4H_2O$	Precipitation from a solution of $ZrOCl_2$ by sodium hydroxide at pH 3.8–4.1, dried, the precipitation conditions do not affect pH^0	NaCl		6.5	[130]
	Reagent	LiCl, NaCl		4.3	[131]
	Reagent	KCl, CsCl		5.1	[132]
CeO_2	Prepared like TiO_2 [129]	$NaNO_3$		7	[129]
ThO_2	Ditto			10–11	[129]
α-Cr_2O_3	Precipitated from a solution of $Cr(NO_3)_3$ by the slow hydrolysis of $CO(NH_2)_2$ at 95 °C	KNO_3		6.35	[108]
γ-Al_2O_3	Reagent	KNO_3		4.6 (15 °C) 5.25 (20 °C) 5.3 (25 °C)	[133] [133] [133]
$Al(OH)_3$	Synthetic gibbsite	NaCl	0.5	9.5	[126]
RuO_2	Heated at 400 °C	KNO_3		5.4	[96]
90% RuO_2 + +10% IrO_2	Heated at 500–700 °C for 6 h	KNO_3		5.45	[139]

Notes. 1. The concentration of the supporting electrolyte is shown in cases of specific sorption or when the pH^0 value is quoted for specified concentrations of electrolyte. 2. pH_{IEP} is 7.9 for α-Fe_2O_3 (washed with KOH) and 6.8 for γ-Fe_2O_3 (washed with KOH).

The factual material thus obtained can be summarised as follows. In the absence (and only in the absence) of specific sorption pH^0 occurs at the intersection of all the $q = f(pH_s)$ curves for different concentrations of electrolyte,[88–92,94] and this quantity alone fully characterises the oxide (or oxide hydroxide).[94] In many cases (the oxides and oxide hydroxides of Cu, Fe, Al, Ru[95,96]) the oxide hydroxides have lower pH^0 values than the corresponding "dry" oxides, but opposite examples can also be seen in Table 1 (for Zr, Ti, and Al). The K^+, NO_3^-, and ClO_4^- ions are usually sorbed nonspecifically,[97–99] whereas the ions Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Li^+,

Zn^{2+}, Ga^{3+}, Eu^{3+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, SO_4^{2-}, PO_4^{3-}, SeO_3^{2-}, $P_3O_{10}^{5-}$, and F^- are specifically sorbed.[89,90,92,99,100–111]. Cl^- can be sorbed both specifically and nonspecifically.[91,112–114]

The specific sorption of cations produces a shift in pH^0 of the oxide hydroxide sorbent towards lower values, and the sorption of anions has the opposite effect. Specifically sorbed ions can displace nonspecifically sorbed ions, but not *vice versa*.[98,99] The sorption of M^{2+} and M^{3+} cations produces a change in pH_s, and is strongly dependent on this parameter if the latter is fixed and controlled. The dependence on pH_s of the equilibrium and (or) pseudo-equilibrium sorption of the cations, and the abiity of the cations to form hydroxo complexes, have a dome-like or near-exponential shape (stretched S) leading to a plateau.[29,101–106,115–117,119,120]

The first shape of this dependence is characteristic of cations which easily form stable and readily soluble hydroxo complexes, for example Zn^{2+}, Cr^{3+}, and Al^{3+}; the second is found for cations which do not possess this property, for example Co^{2+}.[115–117] The sorption of cations on oxide hydroxides is accompanied by the removal of one or two protons from one sorpton centre. At low adsorptions the sorption of M^{2+} is described by the Langmuir isotherm,[116,117] and at high adsorptions by the Freundlich[106] and Frumkin isotherms:[115] this is attributed to the energy nonuniformity of the sorption centres on the surface of oxide hydroxides.

IR spectroscopy identifies three types of surface hydroxyl groups, containing oxygen attached to the surface in mono-, bi-, and tridentate configurations.[105] At low coverages the first (and most active) type is used, and when these are occupied the energetically less favourable positions come into play. The same effect is seen in the kinetics of the process:[106] on increasing the sorbent/sorbate ratio the rate of sorption of cations (Cd^{2+}) increases because of the increased proportion of the more active centres, and *vice versa*. As reported[105,106] the rate of sorption of M^{2+} cations is quite high, and the sorption quasiequilibrium is established in 10–30 min at room temperature.

The isotherms for the sorption of anions (for example, PO_4^{3-}) on highly active oxide hydroxide sorbent samples (for example, ferrogels[109–111]) belong to the high affinity type of isotherm (H type[76]). At pH = const the sorption of the anions increases with the ionic strength of the solution. Three regions can be observed in the sorption isotherms. Ageing the ferrogels lowers their capacity towards PO_4^{3-} ions and their rate of sorption.[109–111] The sorption of PO_4^{3-} ions decreases the pH^0 value of the ferrogel.[109] Comparing data from different laboratories[55,109,111,121] shows that the properties of ferrogel surfaces are unstable and sensitive to influences from the sorbate and from the ionic medium. The sorbability of the anions increases with their acidity[122] and with decreasing pH_s.[123]

A few (but very important) studies of the effect of temperature and composition of the oxide hydroxide on its surface properties have been reported.[94,96,99,124,126,133–137] In the case of magnetite[135] and of haematite and rutile[124] it has been shown that pH^0 decreases with increase in temperature and increases when the temperature is lowered: for example, pH^0 for α-Fe_2O_3 in KNO_3 solutions is 9.5 at 5 °C, 8.6 at 20 °C, and 7.6 at 60 °C.[124] An increase in temperature also increases the slope of the $\partial q/\partial pH$ curves slightly, and makes the branches of the $q = f(pH_s)$ curves lying in the acidic and the alkaline region respectively more asymmetric. The sorption equilibrium constants increase with temperature,[135] and the $\Delta G^0_{ads\,H^+}$ values correspondingly increase somewhat; the effect of the ionic strength on the surface charge also increases only slightly with temperature.[124] On the other hand for γ-al_2O_3 pH^0 increases from 4.45 to 8.95 (even in solutions of KNO_3) when the temperature is increased from 10 to 50 °C.

Thus the response of pH^0 for an oxide hydroxide to a change in temperature depends first and foremost on its chemical nature. It is found that in the mixed oxide hydroxides $RuO_2 + IrO_2$ [134] and $TiO_2 + Al_2O_3$ [137] pH^0 is the mean of the pH^0 values of the components.[134,137] Heat treatment of the oxides also produces different effects on pH^0, depending on their chemical nature and method of preparation.[96,134] It has been established that homo- and heterodispersed sols of α-Fe_2O_3 have identical pH^0 values.[94] This is consistent with the report[134] that pH^0 is unrelated to the specific surface S_{sp} of the oxide hydroxide. Lastly we shall mention a study[138] of the kinetics of charge transfer (electrons and protons) through the interface in suspensions of α-Fe_2O_3 and α-FeOOH by the pulse radiolysis method. It was shown that the rate of charge transfer is strongly dependent on pH_s: the rate constants vary between 10^{-1} and 10^4 s^{-1} in the pH_s range 3–11.

III. Models of the sorption mechanism on oxide hydroxides

The model of the sorption mechanism should describe the distribution of the sorbate (and preferably also of the components of the supporting electrolyte) near the reactive surface (or interface) as well as the thermodynamics and the kinetics of the process. The criteria for evaluating the quality of the model were clearly formulated by Barrow and Bowden:[139] it could be useful to re-state them in their entirety. An ideal model should be effective, comprehensive, realistic, and predictive. An **effective** model should offer a detailed description of the observations: otherwise, its fundamental hypothesis is incorrect. Effectiveness is a necessary but not a sufficient quality of the model. A **comprehensive** model can be used unmodified in a wide range of conditions. A **realistic** model is consistent with generally accepted theories of the behaviour of the components of the system. A predictive model leads to a new understanding of the phenomena and offers wider prospects of exploiting them in different circumstances.

Studies of sorption processes are divided mainly into two streams, which we can call simply the western and the eastern stream. The western stream consists mainly of the Dutch–American school, to which we owe a systematic and "well equipped" theory of the sorption of ions in an electrical double layer.[89–92,94–96,100–115,119,120,124,126] This group of studies is distinguished by a very precise formulation of the problem, a strictly methodical approach, and high-grade processing of the experimental data. It is noteworthy that the research problems are considered from the standpont of preconceived ideas. While this is one of the main strengths of the approach it also introduces a certain weakness by lowering the probability of unexpectedly discovering interesting new results.

The eastern stream consists of the work of Indian and Soviet scientists (mainly the latter). It is characterised by the absence of firm preconceptions experimental results are interpreted by any suitable theory or theoretical fragment capable of explaining the experimental facts. Of course this classification of the two streams is not absolute, and a mutual "diffusion" of the two approaches and conceptions can be detected.[55,73,75,97,99,116,117,129,132]

Before proceeding to a detailed discussion of the models we should make the following comments. Whatever the actual compounds used as the sorbents (hydroxides, oxides, or even

carbonates) the effects observed in studies of sorption from aqueous solutions in real experimental systems relate to sorption on oxide hydroxides. This is suggested both by numerous studies of structure formation in oxide hydroxides[3–8,140–142] and by studies of the interaction of H_2O with oxides,[131,143–146] and has been repeatedly confirmed by the work of western scientists.

Let us begin our examination of the sorption models with the most fully developed theories. The foundations of the coordination chemical theory of sorption on oxide surfaces were laid in the 1980's.[95,147,148] The basic hypothesis of this theory is that H_2O molecules are dissociatively sorbed on the oxide surface during its contact with an aqueous solution or with a moist atmosphere: as a result the surface is covered with a layer of hydroxyl groups having a density of 2–10 OH nm^{-2},[148] which undergo fast protolytic reactions with the solution. This establishes an equilibrium distribution of the charges in advance of the other sorption processes. On a neutral surface (at the point of zero charge) the numbers of positively and of negatively charged centres are equal. At the contact with a solution of $pH < pH^0$ the surface (now in the oxide hydroxide form) becomes positively charged, whereas at pH > the surface charge is negative. As was stated above pH^0 is determined experimentally: attempts to calculate it on theoretical grounds have proved unsuccessful.[95] The sorption process is primarily electrostatic.

On a given oxide hydroxide cations are sorbed at $pH_s > pH^0$ and anions at $pH_s < pH^0$.[120,123] However, cation sorption takes place (in part) in the region of positive surface charge,[129,149] and therefore simple electrostatic models are inappropriate. A deeper understanding of the sorption can be gained from considerations of the complex formation between the cations and the OH^- groups of the boundary layer and of the replacement of these groups by anions:[148] the site binding model.[105,120] The possibility of these processes and their special features are related to the stucture of the electrical double layer (EDL) at the interface. The characteristics of the EDL are the equilibrium constants of the surface ionisation and of the surface complex formation K, the surface charge q, the capacity, and the potential $\Psi(x)$.

Barrow and Bowden[139] have constructed three models of the sorption in the EDL, composed of one, three, and four planes of ions respectively (Fig. 1). All three models give expressions for the sorption equilibrium constants.

According to the one-plane model all the adsorbed ions are accommodated in a single plane and have the same potential: the neutral $-S-OH$ surface, which joins the centres of the $-SO_3^-$, $-S-OH$, and $-S-OH_2^+$ groups. The expressions for the equilibrium constants contain the term $\exp(nF\Psi/RT)$, where n is the valency of the sorbed ion, F and F are well known constants, and T is the temperature. The surface complex is written as $-SA$.

According to the three-plane model H^+ and OH^- are located in a separate internal plane s, the electrolyte ions and the sorbate ions are in the next layer, and the expression for the equilibrium constant contains the term $\exp[-F(\Psi_\beta-\Psi_0/RT)$; the surface complex is written as $-SOH_2^+-A^-$ or $-SOH_2^+-HA$.

According to the four-plane model[150] H^+ and OH^- are again located on the innermost potential plane while the next plane contains the sorbed ions and the next the ions of electrolyte (see Fig. 1). The sorption centre is described as $-S\begin{matrix}OH\\OH_2\end{matrix}$, and the sorption complex as $-S\begin{matrix}OH\\A_1\end{matrix}$ or $-S\begin{matrix}A_1\\OH_2\end{matrix}$; the expression for the equilibrium constant contains the term $\exp(-nF\Psi_\alpha/RT)$. The sorbate can replace both the $-OH$ and the $-OH_2$ group, i.e. it can react with the surface irrespectively of its charge. From this pont of view all the surface centres are vacant, so that the sorbate reacts with centres caryring an average charge. In the case of a polyvalent sorbate this model allows interaction with all forms of ions in solution (though some are known to be preferred), i.e. it offers a choice between the particles in solution but not between the surface centres. However, even in the sorption of the PO_4^{3-}, F^-, SO_4^{2-}, and SiO_3^{2-} anions on goethite[139] none of these models is ideal. Many arbitrary assumptions are needed to produce a satisfactory agreement between calculation and experiment. Special attention must be paid to the concentration of the sorbate, the pH of the medium, and the contact time of the phases.

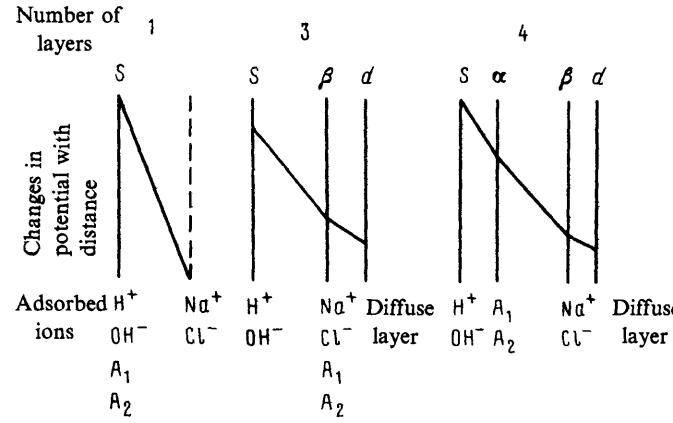


Figure 1. Three models of the interaction between the solution and the adsorption surface of the ions.[139] The bulk of the adsorbent is on the left, that of the solution is on the right; the diagrams show the proposed localisation planes of the individual classes of ions and the changes in electrical potential with distance.

These models ignore the steric factor (the size of the sorbate ions) and they treat the surface of the sorbent as uniform and nonporous, and therefore they cannot be applied to gels.[151] However, as shown by Perram,[146] a layer of oxide hydroxide gels can readily be formed on oxide surfaces in contact with water, and this observation led to the development of the EDL theory.

There have been attempts[105,106,120] to treat the surface of the oxide hydroxide sorbent as energtically nonuniform (heterogeneous) to account for the difference in sorption at low and at high coverages. The simplest two-position model[106] stipulates the formation of $-S-M(OH)_n(-Cd(OH)_2)$ from uniform $-S-OH$ centres at low coverages (i.e. low adsorption densities) through reversible reactions of the first order in the sorbate, and the use of other centres (of various types) in the region of high coverges. A more general solution of this problem is proposed by van Riemsdijk, et al.:[120] the heterogeneous surface is represented as an assembly of uniform subsurfaces, and the sorption on each of these is

described by a standard (Langmuir or Freundlich) isotherm. The heterogeneous surface is described by the symbol $-S\begin{vmatrix} O^- \\ OH^0 \\ OH_2^+ \end{vmatrix}$, and and centres with different energies are treated as subsurfaces. Models similar to the four-plane model[139] are used, and it is assumed that the form of the energy distribution function of the adsorption centres is retained when the ions are adsorbed.

Hiemstra, et al.[152] proposed a many-centre model of the adsorption on the oxide hydroxide–solution interface (multisite complexation, MUSIC) in which different OH groups are coordinated by one, two, or three metal ions; the model was thought to account for the microheterogeneity of oxide surfaces. It was tested on gibbsite, goethite, haematite, rutile, and silicon dioxide:[126] different crystallographic faces were found to make different contributions to the formation of the surface charge and to the PZC. Faces which (in general) remain uncharged over a wide range of pH were identified, and it was shown that in a crystalline oxide pH^0 is determined by the behaviour and by the presence of faces containing the greatest number of OH groups coordinated by only one metal atom from the lattice. Successful attempts to calculate the pH^0 were made.[152,126] It was shown that the binding centres model is a special case of the multisite complexation model.

Westall and Hohl[153] pointed out that the sorption energy is very difficult to divide into an electrostatic and a chemical component, though this procedure could lead to a rational choice between many possible models relying on similar law of mass action (LMA) and material balance equations but different descriptions of the EDL. Attempts to formulate a strictly quantitative description of the sorption of electrolytes on oxide hydroxide surface have also met other problems. Thus, the maximum sorption always exceeds the possible monolayer sorption,[154] and furthermore all the surface models are based on the conception of the EDL of a single particle is a large volume of electrolyte solution, though the presence in solution of a large number of dispersed particles (as is always found in real systems) shoud have a profound effect on the parameters of the EDL. The mathematical description of the EDL is very complicated even for a single particle, and for a more complex system it is quite impossible at present.[151]

Recent reports (for example, by Spitz, et al.[155]) have stressed that no quantitative descriptions of the surface–sorbate interaction based on the concept of acid–base interactions have so far been put forward. One contributor to a recent monograph,[76] Lyklema, described the sorption of ions on solid surface by rejecting all mathematical procedures and relying wholly on qualitative relationships. He defended his approach by the following argument: it is impossible at present to determine the sorption of an electrolyte, since different methods give different results; furthermore the sorption in the EDL of ions of a single type can also not be determined, and therefore it is reasonable to describe the process in terms of uncharged particles; lastly, the problem of potential-determining ions is far from clear. Evidently, a comprehensive mathematical description of sorption from solutions of electrolytes on oxide hydroxides is not likely to be available in the near future. Nevertheless it does not follow that all current attempts to produce such a description are meaningless.

Let us consider, as a typical example of the work of the eastern stream, a group of Indian and Japanese publications.[143,156–158] Venkataramani and Gupta[143] studied the sorption of H_2O on the oxides of titanium(IV), bismuth(III), and thorium(IV), and on magnetite: they measured the sorption isotherms and made pH-metric titrations of the oxide samples in a medium of $NaNO_3$. The reversibility of the sorption of H_2O was demonstrated, the effect of the preparative conditions (method of precipitation, and ageing) was studied, and the content of $-OH$ and $-ONa$ surface groups in the samples was determined. However, the results[143] cannot be used to predict the adsorption behaviour of the oxides because there is no link between the results and information on pH^0 and on the structure of the EDL, and also because no attempt has been made to determine pH^0.

Other publications in this group[156,157] discuss data on the sorption of M^{2+} and M^{3+} cations on magnetite and an amorphous iron(III) oxide from the standpoint of a typical ion exchange model. Inoue, et al.[158] treat the oxide hydroxides of tin(IV) and niobium(V) as ion exchangers with weakly acidic functional groups, interpreting the functional groups and the liquid layers near the solid surface as an exchange phase in which the electrostatic bond and the LMA have the same significance as in solutions. They correctly point out that the simplified approach in which the sorption is treated as a typical ion exchange phenomenon cannot be applied to oxide hydroxides, i.e. it does not correctly explain the effect of the experimental conditions on the sorption capacity and on the distribution coefficient. Nevertheless they make a sharp distinction between ions bound by Coulombic forces (free ions in the bulk phase) and ions attached to the functional groups by a coordinate bond ("undissociated" ions in the ion exchanger phase). They use the pH_{TEP} concept, but in fact they are operating with pH^0 since they use a nonspecifically sorbed electrolyte (NaCl) to determine this parameter. The failure to distinguish between these quantities detracts from the universality of the method, though not from its effectiveness.

We should stress the fact that complex cases are known in which none of the existing sorption models can offer a suitable explanation. For example, the sorption of UO_2 ions on the surface of the oxides of Ti(IV), Th(IV), Zr(IV), Ce(IV), and others[129,149] in the region of positive surface charge produces a shift of pH^0 towards the right. The authors put forward the concept of attack of the OH surface group by the sorbate ions without previous deprotonation: this process is energetically most favourable for dimeric and trimeric sorbate cations and their neutral molecules, and is called electrical sorption by the authors. Under these conditions the sorbate in the sorbent phase forms bridges between pairs of neighbouring surface on groups. Another example is heterogeneous hydrolysis,[55] discussed below.

The ion exchange model of this process is very widely used in the Soviet publications. It is based on the oxyacid theory of amphotericity,[159,160] according to which amphoteric oxides (hydroxides, oxide hydroxides, oxide hydrates) show cation or anion exchange properties according to the pH_s. The cation exchange properties (selectivity, capacity) of an oxide hydroxide decrease and its anion exchange properties increase. The rate of ions exchange is limited by diffusion in the boundary layer or in the sorbent grain (outer and inner diffusion), and the sorbability of the ions depends on their charge and size. The attraction towards exploiting the analogy with organic ion exchangers, which is obvious for this approach, can be seen in a group of mainly Soviet publications.[31–54] Thus, in Belinskaya's review[32] the inorganic sorbents are treated as polymeric ion exchangers with functional goroups which dissociate at the $-M-O^-$, $-M-OH$, and $-M-O-H$ bonds, though some experimental facts are admittedly incompatible with this scheme.

The discrepancy is avoided by assuming compensation of the charge on the polymeric ion exchanger skeleton (usually assumed to be negative) by mobile cations. The mathematical description of ion exchange is a well known process which can be applied to inorganic sorbents without special difficulties. In many resports[26–54] the discussion is limited to a qualitative explanation of the results in terms of the ion exchange model.

A group of papers[10–25] develops the interpretation of the sorption process (coprecipitation) as an acid–base interaction between the sorbate and the sorbent. This model is based only on static (pseudoequilibrium) experiments on the sorption of metal cations. The mechanism assumes the adsorption of hydrolysed forms of the cations with a minimum charge, i.e. $M(OH)_n^0$. It is suggested that the sorbate is attached to the sorbent by forming tin bridges between $M(OH)_n$ and the oxide hydroxide sorbent (collector).

The coprecipitation of cations begins at pH values of the system which define the onset of hydrolysis and of the formation of simple or polynuclear products in solutions of the elements being coprecipitated. The formation of coordinationally saturated complexes of the sorbate suppresses the sorption (coprecipitation) by this mechanism. Coprecipitation takes place at a pH of the medium lower than the pH for the deposition of the sorbate, suggesting a shift in the hydrolysis equilibrium of the sorbate.[16] The acid–base interaction model is qualitative and does not provide a basis for the mathematical description of the sorption equilibrium or for any prediction. The process is examined exclusively from the point of view of the behaviour of the sorbate: the behaviour of the sorbent, including the presence of charge and of an EDL on its surface, is totally ignored. As the authors themselves point out,[10–25] the observed phenomena could equally be described in terms of ion exchange, but this means using a different model to discuss the results.

An interesting analysis of this group of papers was published by Artyukhin,[30] whose conclusions are still valid. The great diversity of the points of view on the sorption mechanism and the failure to allow for the linked hydrolytic equilibria in the formulation of the sorption equilibria are stressed. It is pointed out there there is no direct proof of the sorption of both neutral and charged forms of the sorbate, and that data on the equilibrium (or quasiequilibrium) limited to pH-metric measurements are an insufficient basis for the construction of a model of the mechanism of the process. In the processing of the experimental results[29,30] an attempt was made to demonstrate the sorption of metal cations in the uncharged hydroxo form over the whole range of pH; the preferential sorption of uncharged forms implies the absence of an electrostatic barrier (which is a reasonable assumption when discussing the sorption of cations on a positively charged surface). It is concluded that all the sorptions lead to the formation of an uncharged compound in the sorbent phase. We consider this to be a special case, applicable to the aquo cations of metals, as shown by many published results.[37–54] It is assumed that any form of the sorbate, including forms present in solution in negligibly small amounts, can be responsible for the distribtion of the sorbate. Clearly, this is a problem of major importance for constructing a mechanism of the sorption on oxide hydroxides. To complete the picture we should mention (without going into details) the use of the isomorphous coprecipitation[28] and of the coordination model.[24,27]

Let us now consider the heterogeneous hydrolysis mechanism, proposed by the present writer. This is a kinetic model of a nonequilibrium process, unlike any other model used in adsorption studies. As was shown in section II, heterogeneous hydrolysis takes place with formation of uncharged hydroxo complexes as the reaction product, as in the sorption of M^{n+} cations.[10–30] The high rate of formation of these products for metals such as zinc, cobalt, nickel, and copper in noncomplexing ionic media allowed the construction of a model[16–25,29,30] of sorption involving the uncharged form $M(OH)_n^0$ as the sorbed species. However, a study of the process with sorbate in the form of stable complex ions (as in heterogeneous hydrolysis) shows that in reality the mechanism is more complex.

We should stress that not one of the sorption models previously suggested (electrostatic, ion-exchange, coordination, complex formation with the functional groups of the sorbent, acid–base, isomorphous coprecipitation) can effectively describe heterogeneous hydrolysis. The rate of the heterogeneous hydrolysis and its temperature dependence suggest first and foremost that the rate-determining step of the process is a relatively slow chemical reaction. The established participation of the electrolyte and of H_2O in the heterogeneous hydrolysis,[64,66,73,74] its uncontrollable pH-static regime,[55,60–62] the localisation of the process on the sorbent surface,[72] and its progress against a background of hindered reactions of the sorbate and of the sorbent[55] show that heterogeneous hydrolysis is a multistage chemical reaction which includes, however, an adsorption step. The uncharged form of the sorbate in heterogeneous hydrolysis is the last, and does not react. We have proposed[55] a three-stage model of the mechanism, including the fast reversible adsorption of the dominant form of the sorbate complex, the slow reversible aquation of the complex on the sorbent surface, and the fast partially reversible dissociation of the aquo complex formed on the surface of the oxide hydroxide sorbent with compensation of the additional surface charge, which defines the condition of the spontaneous pH-static regime. The observed rate constant of the heterogeneous hydrolysis can be expressed as the rate constant of a heterogeneous reaction:[161,162]

$$K_{\text{H}} = K_x k_{a_x}^{-1} k_{\partial_x}^{-1} C_x C_{\text{M}}^{-1} \left(1 + \sum_i k_{a_i} k_{\partial_i}^{-1} C_i\right)^{-1},$$

where K_d is the rate constant of the aquation of the i-th form of the complex reacting on the sorbent surface; k_{a_x}, k_{∂_x}, k_{a_i}, κ_{∂_i} are the rate constants of the adsorption and of the desorption of the reacting and of any other i form of the sorbate complex present in solution; C is the concentration of the forms; C_{M} is the total concentration of the complex-forming metal.

The rate of aquation, characterised by K_x, is several orders of magnitude greater than the rate of aquation of the sorbate complex in solution,[55] which also produces sparingly soluble uncharged hydroxo forms. Heterogeneous hydrolysis shows a similarity to the processes described in various papers,[37–54] since it includes stages of adsorption and of chemical reaction of the sorbed substances, but it differs from them in the high rate of the second stage and in the fact that the sorbate is not held on the sorbent surface in the form of the initial component. The model is effective, realistic, and comprehensive for the platinum metal group, and it has a predictive value in conjunction with quantitative data on the stability and the lability of the complex sorbates and on the basic properties of the sorbent.[55]

Data[55,58,72,75] on the pseudoequilibrium properties of the heterogeneous hydrolysis and on the interactions of the sorbents with the supporting electrolytes show that the strongly basic OH groups of the sorbent take part in the heterogeneous hydrolysis reactions, and that the presence and concentration of these groups are determined by the pH^0 value of the sorbent.

The weakness of the model lies in the impossibility of mathematically relating the rate of the process to the concentration of the basic centres of the sorbent furthermore the rate of the process cannot be calculated theoretically, since the calculation would require a knowledge of the stability constants and of the rates of aquation of the sorbate complexes, of the acid–base equilibria of the OH groups on the sorbent surface, of the rates of protolysis of the aquo forms of the sorbate in the sorbent phase, of the rate of the phase transformations of the sorbent, and of all the activity coefficients. Most of these quantities are unknown, and furthermore the form of the mathematical equations linking them to the rate is also unknown. The model also offers no information on the character of the bond between the sorbate and the sorbent during the intermediate and the final stages of the process, when the assumption of a combination of van der Waals and electrostatic bonds is not incompatible with observations.

IV. Interrelation between the properties of the sorbate, of the sorbent, and of the ionic medium and the sorption mechanism

In his analysis of the status of research on sorption by inorganic compounds and of coprecipitation Melikhov[9] observed that very little published information is available on the relationship between the sorption and the states of the surface region of the sorbent and of the sorbate in this region and (we add) in the solvent, and that insufficient attention is being paid to this problem. Workers in the eastern stream are specially prone to ignore the interrelation of three aspects of the sorption process: the structure formation in the sorbents (in our case, the oxide hydroxides), their surface properties (which depend directly on the previous aspect), and the sorption itself. On the other hand, as was shown by Khvostova and Pichugina[163] (for the platinum metals, though their conclusions apply also to other metals), the real composition, i.e. the nature and the relative amounts of the complex forms in solution, determine the degree of removal of an element by extraction, electrode position, cementation, etc., and obviously also by sorption. The addition of any other reagent, including the solvent, produces a shift of the equilibrium aquation, hydrolysis, and of other reactions (substitution, polymerisation, complexation of the ions, etc.) in the solution, and thus affects the sorption process to the extent of inducing a change in the mechanism.[37–75] However, this obvious consideration is often ignored, and in many cases even the initial complex forms of the sorbed element are not established.[15,25,27,28]

Let us now examine the few disconnected data on this topic and establish possible interrelationships between the three aspects of the sorption process defined above.

The following propositions can be considered to be established beyond dispute. I. Crystalline oxides (and oxide hydroxides) have a much lower sorption activity than their corresponding amorphous phases; their capacity is lower,[55,72,78,82–84,99,106,156] their kinetics are more sluggish,[60,65,77–80] and their selectivity is lower, i.e. they have sorption isotherms of the Langmuir or Freundlich type instead of "high affinity" isotherms.[72,106,116,117,156] 2. The presence of ligands in the solution, and their nature, have a strong influence on the magnitude and on the kinetics of the sorption;[22,23,25,47–49,55,77,87,164] metal ions bound in complexes are much less sorbable than unbound ions. 3. Ions in the sorbed state undergo chemical reactions, especially hydrolysis, much more readily than free ions in solution.[55,101–106,115–118] 4. The supporting electrolyte interacts with the sorbent[73–75,90–92] (see also Table 1) and with the sorbate,[55] strongly influencing both the kinetic and the (pseudo)equilibrium characteristics of the sorption process.

We shall consider, as a specific example of the establishment of interrelations between the properties of the sorbate, of the sorbent, and of the ionic medium and the sorption mechanism, a group of papers on the sorption of complex anions of the platinum metals on the oxide hydroxides of titanium(IV) and zirconium(IV),[37–50] on ferrogels, and on the oxide hydroxides of the REE.[55–75] These studies are specially suitable for our analysis because they include kinetic data, which allow various effects of the properties of the components to be displayed though they remain constant during equilibrium measurements.

The analysis of these studies[37–50,55–75] shows first of all that at least two stages are needed for the sorption process; the adsorption stage itself and a preliminary chemical interaction of the sorbate with H_2O, the supporting electrolyte, and the sorbent surface. The composition of the sorption complex and the rate of transformation of the sorbate in the sorbent phase depend on the nature of the sorbate and of the sorbent, but the participation of the ionic medium is very substantial in both cases. In the first stage this effect is seen as a competing interraction between the sorbate and the background ions, which lowers the extent of sorption (say) of the complex anions when the concentration of NaCl or of Na_2SO_4 is increased.[37–50] In the second stage the effect is seen in the form of the interaction of the supporting ions with the sorbate and the sorbent, as shown most clearly by the dependence of the rate of heterogeneous hydrolysis on the concentration of the ligand in solution and by the change in the sorption properties of the REE oxide hydroxides and of the ferrogels[55–75] under the influence of the ionic medium.

Obviously, the slow changes in the chloro complexes sorbed on the surface of the titanium(IV) and zirconium(IV) oxides[37–47] bear some similarity to heterogeneous hydrolysis, but the rates of these reactions are so small that the authors[37–47,50] could not detect the complete detachment of the ligands. This process can be represented as the second stage of the heterogeneous hydrolysis infinitely stretched out in time, whereas the sorption of the complexes on the surface of the titanium(IV) and zirconium(IV) oxide hydroxide surfaces is interpreted as the fixed first stage of the proposed[55] three-stage mechanism of heterogeneous hydrolysis. The difference in mechanism between the first[37–50] and the second group of studies[55–75] is due to a difference in the characteristic properties of the sorbent surface: its size and its energy nonuniformity, but the property of the sorbent mainly responsible for the change from the ion exchange to the heterogeneous hydrolysis mechanism is probably its basicity.[55]

The basicity of the sorbents has been characterised[55] by the pH^0 values, which are well correlated with other quantities determined by the basicity (the Cartledge ionic potential and the pH of the saturated solutions of hydroxides, calculated from the solubility products,[165] Fig. 2). This allows us to compare oxide hydroxides of different structure groups, arbitrarily assuming them to have equal basicities. The correlation can also be made in terms of data obtained[166] by characterising the acid–base properties of oxides through the heats and the isotherms of the sorption of NH_3 and CO_2 from the gas phase. According to that work[166] the basicity of the oxides increases in the series

$$BeO, TiO_2, ZrO_2, Nb_2O_5, Ga_2O_3 < ThO_2,$$

$$MgO, ZnO, Al_2O_3 << CaO, Nd_2O_3, La_2O_3,$$

whereas by using the Table 1 we obtain

$Al_2O_3, TiO_2,$

$ZrO_2 < \alpha\text{-}Cr_2O_3 < Fe_3O_4 < CeO_2 < Yb_2O_3 < Sm_2O_3 < ThO_2.$

The two sequences are satisfactorily consistent.

It is also clear that pH^0 is strongly dependent on the method of preparation of the oxide hydroxide. According to the pH^0 values (see Table 1) the bulk (or surface) positive charge of the metal oxide hydroxides produced at the contact with aqueous solutions of electrolytes decreases in the sequence

Fe^{3+} hydrogels (with $pH_{bas} > 8-9$)$Ln_2O_3.nH_2O > Cr_2O_3 > Al_2O_3 >$

$>$ FeOOH(goethite, akaganeite, lepidocrocite) $> ZrO_2 > TiO_2$.

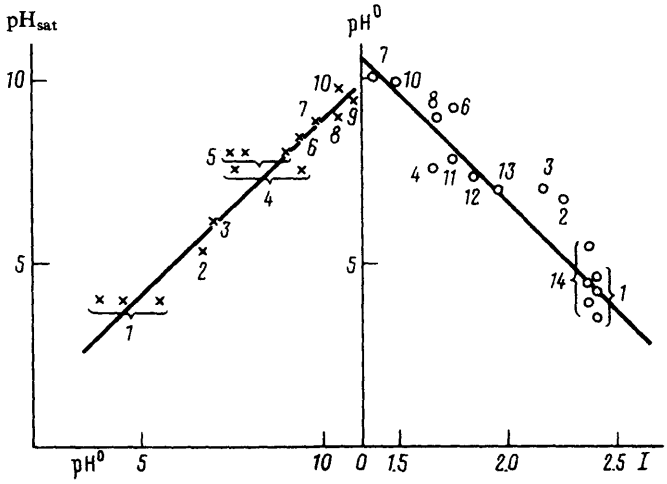


Figure 2. Correlation between pH^0, the ionic potential *i*, and the pH of a saturated solution of oxide hydroxides:[55] *1*, $TiO(OH)_2$; *2*, $ZrO(OH)_2$; *3*, $Cr(OH)_3$; *4*, $Cu(OH)_2$; *5*, $Y(OH)_3$; *6*, $Zn(OH)_2$; *7*, $Pb(OH)_2$; *8*, $La(OH)_3$; *9*, $Ni(OH)_2$; *10*, $Cd(OH)_2$; *11*, $Sn_2O_3.nH_2O$; *12*, $Y_2O_3.nH_2O$; *13*, $Yb_2O_3.nH_2O$; *14*, $Sn(OH)_4$.

The easy replacement of sorbed complex anions by simple anions (for example, SO_4^{2-}) [37–48] is characteristic of nonspecific, electrostatic bonds (see Section III). The strength of the electrostatic bond to a protonated oxide hydroxide surface is determined by the density of surface charge. At low surface charges the electrostatically bound sorbed groups experience negligibly small interactions from the weakly electrophilic sorbent surface (TiO_2, ZrO_2), and therefore the rate and the extent of transformation of the sorbed complex ions on the crystalline oxide hydroxides of Ti, Zr, Sn, and Fe are small, the sorption is reversible,[37–50] and these sorbents are not suitable for removing metals (typical complex formers) from media containing complexing salts.

As the density of surface charge and the basicity of the surface are increased the ratio of the rates of the adsorption stage and of the transformation of the sorbate in the sorbent phase is altered: though the rates of adsorption and desorption remain high, the rate of the second stage increases. Thus, in the hydration and protonation of the dry REE oxides the surface becomes saturated with basic hydroxyl groups which are not removed from the surface into the bulk of the solution when the acid content of the system is limited. Therefore the matrix of the Ln_2O_3 oxide has a decreased affinity for electrons and for hydroxyl groups, even when the surface has a positive charge. This nucleophilicity weakens the metal–anionic ligand bonds in the sorbed complex, and facilitates its transformations (aquation, in the case of heterogeneous hydrolysis). The ferrogels and the carbonates of the alkaline-earth metals show a similar behaviour.[55]

Thus the basicity of the oxide hydroxide sorbent determines the sorption mechanism and the changes in basicity define the boundary between "ion exchange" and heterogeneous hydrolysis. These considerations are convincingly confirmed by the observation that lowering the basicity of a ferrogel by removing the excess of OH groups during cryogranulation while retaining its large specific surface and amorphous structure alters the character of the sorption process and converts the heterogeneous hydrolysis into "ion exchange".[55]

By using the pH^0 as a characteristic of the basicity of the oxide hydroxide, the stability constants of the complex sorbate, and data on the interaction of the ionic medium with the sorbate and the sorbent we have formulated the group of principles which should guide the choice of conditions for the sorption extraction of complex-forming metals from complex-forming media.[55]

1. The complete sorptional removal of complex-forming metals form complex-forming media containing high concentrations of electrolytes without changing the composition of the solution is possible only under conditions of fast and exhaustive transformations of the sorbate in the sorbent phase.

2. The process which ensures this condition is heterogeneous hydrolysis.

3. Metals can be effectively precipitated from complex-forming media by heterogeneous hydrolysis if the stability constant of the complex does not exceed $10^{38}-10^{40}$; the process is completed in practically convenient times if the half-life of the ligand in the sorbate complex is less than 2–3 days at temperatures between 20 and 100 °C.

4. Sorbents suitable for heterogeneous hydrolysis in salt media include the crystalline (or gel) oxide hydroxides with $pH^0 \geqslant 6.5$ [i.e. the oxide hydroxides and the carbonates of Cu(II), Ni(II), Cd, Pb(II), Zn, etc.].

5. To remove metals which form labile but stable complexes in the presence of high concentrations of ligand we must use neutral or weakly alkaline gel sorbents; for systems with low concentrations of ligand and (or) inert complexes in salt media the most effective sorbents are crystalline oxide hydroxides of the Ln_2O_3 type.

V. Conclusions

The great majority of studies of sorption on oxide hydroxides deals with sorption equilibria (or pseudoequilibria): little attention has been paid to its kinetics, in spite of the reported observation[106] of very strong energy nonuniformity of the sorbent surface. Fairly simple cases of sorption of aquo cations and acid anions are usually considered; the mathematical description of the sorption is very complex, and is based on many more or less arbitrary assumptions. The treatment of the results often reduces to the traditional models of Langmuir sorption and ion exchange. Most of the publications are aimed primarily at the behaviour of either the sorbent or the

sorbate. Sorption experiments are carried out either in the absence of an ionic background or in solutions of electrolytes indifferent to the sorbate. Crystalline phases are predominant among the sorbents. Studies of the EDL do not resolve the contradiction in the effects of pH_s on the sorption process. There is no information on the effect of interactions of the electrolyte with oxide hydroxide gels on the sorption properties of the latter (except the ferrogels[55]), and very little has been published on the composition and distribution of the sorption products on the sorbent surfaces, on the changes in structure and properties of the sorbent during the sorption, and on the effect of the temperature, composition, and concentration of the ionic medium on the rate and the mechanism of the sorption process. Very diverse partial models of the sorption mechanism have been put forward. We are therefore unable to formulate the general principles to be followed in the selection of practical sorption conditions and to propose a comprehensive predictive model.

Unfortunately, work based on the so-called equilibrium measurements of sorption during coprecipitation contains little information and is non-predictive because the coprecipitation with metal oxide hydroxides [usually of Fe(III), Ti(IV), Zn(IV), Sn(IV), Al(III), etc.] usually produces gel-like deposits with a very high sorption capacity (the corresponding crystalline phases have a much lower activity[72,75,78,79]). Flynn[6] has stressed that gel phases are nonequilibrium systems containing an excess of free energy. Therefore equilibrium measurements during coprecipitation are, in reality, nonequilibrium measurements, and in the case of complex sorbates they depart from equilibrium in respect of both the sorbent and the sorbate. These data are points on a kinetic curve of very long duration. An important contribution to the understanding of the behaviour of these sytems was made by Egorov,[2] but unfortunately his book has not received the attention which it deserved. Only by combining data on the phase formation in gels, which are plentifully available,[3–8,141,142] with data on the interactions between gels and electrolytes, of which very few are available at present, will a convincing explanation be found for the results of a large group of investigations.[10–30,86,87,101,103]

Concerning the potential application of sorptional extraction in practice we note that the prejudice of many workers in favour of crystalline granulated oxide hydroxide sorbents (in preference to gel sorbents) is based on the widespread belief that the former are more convenient and can be use repeatedly (see, for example, Simanova and Boichinova[50]), whereas the latter cannot, and also on considerations of cost and ecological effects. Both arguments are largely misconceptions. As regards convenience, one thinks of the use of sorbents in columns in automated industrial processes, ignoring the stringent requirements of stable dynamic regimes and absence of impurities in the solution, which do not apply to the use of gel-like sorbents in a static regime. The gel sorbents can be used with simpler apparatus. As regards cost and ecological considerations we should consider the whole cycle of operations involved in the synthesis of granulated oxide hydroxides; precipitation from a salt solution, washing formation, drying, and heat treatment. Though the cost of this overall process is lower than the cost of synthesising organic sorbents (resins) it is quite considerable. The volume of water needed to wash the precipitated gel should also be compared with the volume of water which can be purified by the sorbent thus produced. The synthesis of the gel sorbents includes only the first (or the first and second) stage of this synthetic cycle. In view of the much higher sorption activity of the gels we recommend their use in many practical applications.

The capacity and the selectivity of a sorbent do not vary in the same sense; repeated use of the sorbent assumes a stable structure and stable properties. A careful analysis shows that these advantages of the sorbents always occur in pairs, i.e. two of them exclude the third. But are all three always required?

The following situations are met in practical cases of sorptional concentration.

1. The extraction (recovery) of a valuable microcomponent from a very large volume of solution (for example, gold from sea water). This requires stability of the sorption properties and a high capacity, whereas the selectivity (extent of removal) is less important since the process is repeated until the sorbent is saturated. In this case the granulated sorbent is definitely preferable.

2. The intensive purification of large volumes of very dilute solutions from trace impurities (for example, the purification of drinking water from heavy metals). Here selectivity is important, a high capacity is desirable, but the possibility of repeated use is less important. A gel sorbent could be preferred.

3. The extraction (recovery) of valuable microcomponents from small volumes of solutions, usually technological and containing high concentrations of electrolytes (for example, platinum metals from electrochemical production solutions) in order to minimise the loss of valuable materials in the technological cycle. In this case selectivity is important; the use of the total capacity and the repeated use of the sorbent are effectively excluded. A gel sorbent is preferred.

4. The concentration of trace components in analytical chemistry: in this case selectivity is the only requirement.

We should also note that in the second and the third case the kinetics of the sorption are very important, whereas in the first and the fourth case they are of secondary importance.

Thus the crystalline, granular, and gel sorbents all have a place in the practical exploitation of the method, but for different purposes.

This analysis of published data on sorption on oxide hydroxides has identified the main gaps in this area and has shown the need to fill these gaps, to systematise experimental facts more fully, and to unify the procedures and the terminology used in the research. The range of materials under study must be expanded further, and relationships between the properties of the sorbates and of the sorbents and between the sorption mechanism and the prospects of practical application of the sorption methods of concentrating components must be established.

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