Inorganic Nanostructured Anion-Exchange Materials Based on Aluminum Hydroxide

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Annotation
Inorganic sorbents, in comparison with ordinary organic ion exchangers, have higher selectivity, radiation, thermal, and chemical stability. Inorganic ion exchangers are universal materials exhibiting both cation exchange and anion exchange properties. In this work, using aluminum hydroxide (AHO) as an example, we study the possibility of expanding the range of metal oxyhydrates that can serve as the basis to produce inorganic anion-exchange materials. The properties of aluminum hydroxide largely depend on the method of its production. This phenomenon is associated with a different state of Al\(^{3+}\) ions in aqueous solutions during hydrolysis. Estimation of the size of the primary particles of hydrated alumina gives a value of 19 nm. The most potent effect on the structure and ion-exchange properties of aluminum hydroxide is exerted by the introduction of alloying elements into its composition. Isomorphic substitution of a part of Al(III) ions in the structure of aluminum hydroxide with ions with a higher charge (Ti(IV), Zr(IV), or W(VI)) leads to an increase in the content of exchangeable OH-groups in the resulting material. The synthesized materials are amorphous substances, to study their structure; the method of diffuse X-ray scattering was used. The Gibbsite structural motif is determined, and structural changes occurring under the influence of various factors, and synthesis conditions are analyzed. By optimizing the composition of the material, it is possible to improve its sorption characteristics significantly. AAW-0, AAZ-0, and AAT-0 anion exchangers synthesized based on hydrated aluminum oxide can be used to purify weakly acidic electrolyte solutions from anionic impurities in the dynamic mode of repeated sorption-desorption cycles. Materials based on mixed hydrated oxides of various elements can also be used as catalyst supports. Their anion exchange properties allow a wide range to vary the number of different anions introduced into the solid phase and, accordingly, to regulate the number and state of active catalytic sites.

Keywords: Inorganic Sorbents; Inorganic Anion Exchangers; Anion Exchange; Aluminum Hydroxide; Aluminum Complexes; Hydrolysis; Atomic Density Distribution Curves.

Introduction
The use of hydrometallurgical processes in non-ferrous metallurgy is often tricky due to the presence of impurities in industrial solutions that disrupt the ordinary course of methods, for example, during electrochemical deposition or cementation of metals, leaching of industrial products (Waelz oxides, slags, sublimes, lead dust, etc.) separation of liquid and solid phases [1]. For these purposes, such techniques as reducing the content of impurities in electrolytes, such as precipitation in the form of a poorly soluble compound, water-alkaline washing, or calcining industrial products before dissolution, are usually used. However, these techniques do not always allow us to obtain results that satisfy the requirements of modern technology. The main reason for this situation is the low selectivity of extraction, little cleaning depth, the occurrence of large amounts of hard filterable suspensions, and solid waste. The listed disadvantages are practically absent in sorption methods for the extraction of impurities from solutions [2]. However, concerning non-ferrous metallurgy, these methods are developed mainly for the separation of impurities from solutions that are in cationic rather than anionic form [3]. One of the reasons for this situation is the relatively narrow range of manufactured grades of anion exchangers suitable for the selective purification of anions of composite electrolytes. The possibilities of sorption methods for cleaning solutions are greatly expanded when inorganic sorbents are used along with ion-exchange resins [4]. Moreover, for the extraction of anions from solutions, the most promising is the use of materials based on hydrated metal oxides as sorbents [4, 5].

Inorganic sorbents, in comparison with conventional organic ion exchangers, have higher selectivity, radiation, thermal, and chemical stability [6-9]. However, the practice puts forward new requirements for a further increase in the stability of inorganic sorbents in solutions of acids and alkalis, in special hydrothermal conditions, for a further rise in their exchange capacity, for
Among the currently known inorganic sorbents, poorly soluble oxygen compounds of various elements occupy a significant place. Among them, the class of hydrated oxides of multivalent metals is of great theoretical interest and practical importance. Many works performed in Russia and abroad and devoted to the study of the sorption properties of hydrated oxides revealed their excellent ion-exchange features. At the same time, the research conducted allowed us to obtain the first evidence of the possibility of modifying their structure and properties under the influence of various factors. Thus, hydrated metal oxides can be considered as a universal basis for the synthesis of ion-exchange materials with a specific set of properties.

The decisive role of the structure of the solid phase in achieving the desired ion-exchange properties is shown for materials synthesized based on hydrated oxides of manganese (IV), antimony (V), and titanium (IV) \([4,87,88]\). But the limited circle of the studied objects does not yet allow us to formulate general provisions describing the relationship between the ion-exchange properties and the conditions for the preparation and structure of hydrated oxides. Additional difficulties along this path are due to the amorphous nature of hydrated oxides, which determines the disagreements in the structural models proposed by different authors, and most often, their complete absence.

One of the new ways to change the properties of hydrated oxides is to introduce foreign ions into their structure \([4]\). Nevertheless, in the published works, the efficiency of the introduction of metals with different valences as additives for a wide range of hydrated oxides was hardly evaluated. First, in the available works, the effect of additives on the structure of the substances used was not revealed. This situation does not allow reliable forecasts to be made on their impact on the ion-exchange properties of synthesized materials. An exception is only the work on the introduction of additives in inorganic ion-exchange materials with a spinel structure \([4]\). All this impedes the development of methods for the targeted synthesis of inorganic ion-exchange materials and does not allow the extensive use of doping to improve their properties further.

In connection with the solution of the problem, modified materials due to the introduction of additives of additional ions in their phase, it became necessary to develop methods for implementing this process.

However, a one-sided study of the effect of element additives on the ion-exchange properties of the synthesized materials alone does not provide all the information about the mechanism and patterns of their influence. Knowledge of the structure of the corresponding mixed materials and the state of the ions of the additives included in their structure will allow us to solve the problem of predicting the effect of various additives on the properties of hydrated oxides.

Following the outlined ways to solve this problem, the goal of this study was to develop the physical and chemical foundations of the method of directed synthesis of ion-exchange materials. Hydrated oxides and, in particular, hydrated alumina is selected as the basis for the synthesis of such materials. In this regard, one of the goals of this study was to establish the relationship between the structure and ion-exchange properties of the selected materials, including the application of methods for modifying their structure by introducing additives.

Inorganic ion exchangers are universal materials exhibiting both cation exchange and anion exchange properties. Many works in this area are devoted mainly to the synthesis and use of inorganic cation exchange materials. In this case, the knowledge of the processes of anion exchange and the synthesis of inorganic anion exchangers is significantly behind the development of research in the field of cation exchange materials.

Earlier, we discussed the results of the synthesis and production tests of an inorganic anion exchanger based on titanium oxyhydrate intended for purification of arsenic zinc-cadmium solutions \([6, 7]\). In this paper, using aluminum hydroxide (AHO) as an example, we study the possibility of expanding the range of metal oxyhydrates that can serve as the basis to produce inorganic anion-exchange materials. Earlier, we developed methods for producing inorganic anion exchangers based on aluminum hydroxide doped with W(VI), Zr(IV) and Ti(IV) ions. The synthesized materials were assigned conventional symbols, respectively, AAW-0, AAZ-0, and AAT-0 \([10-18]\). This work is devoted to the study of the influence of various factors on the structure and ion-exchange properties of the resulting materials.

**Hydrolysis of Aluminum Compounds**

The main stage of the synthesis of ion-exchange materials based on hydrated oxides is the hydrolysis of the corresponding metal salts \([19]\). The mechanism of the hydrolysis of metal salts is very complex and depends on many external factors, such as the composition of solutions, temperature, rate of interaction of the components, the nature of their mixing, etc. In our previous work, we examined in detail the synthesis of colloidal solutions of aluminum hydroxide \([20]\). Many factors that influence the process of synthesis of colloidal solutions are also relevant in the preparation of ion-exchange materials based on hydrated oxides. The synthesis is also carried out using sol-gel processes. In this regard, it is necessary to consider such an important issue as the state of aluminum in aqueous solutions at various stages of the hydrolysis process with the formation of hydrated aluminum oxide.
In the results of calculations of dissolution constants, strength constants, and Gibbs free energy for various hydrated aluminum complexes are presented [21-25]. The equilibrium constants of the reactions of the formation of the corresponding ions were calculated using the obtained values.

As indicated, the solubility of these oxide and hydroxide phases of aluminum is essential in the production of aluminum at elevated temperatures and various pH values including under conditions where the formation of anionic hydrolysis products, such as [Al(H₂O)(OH)]⁻ and [Al(OH)₃]⁻. It is also known that other hydrolyzed monomeric aluminum particles are formed, ranging from [Al(OH)]⁺ to Al(OH)₃(aq) [24]. In, in more concentrated solutions of aluminum salts, some polymer types of aluminum hydrolys products were identified, including [Al₂(OH)₆]³⁺, [Al₆(OH)₁₃]⁻ and [Al₂₁(OH)₃₄]⁷⁺ (or, more precisely, [Al₂₁(AlO₄)(OH)₁₃(H₂O)₁₂]⁷⁺) [99]. The formula gives the reaction describing the formation of these species:

\[
pAl^{3+} + qH₂O \leftrightarrow Al_p(OH)_{3-p-q} + qH^+ \quad (1)
\]

Based on these data, the dependence of the relative fraction of aluminum hydroxy complexes \( \beta_i \) on the pH of the solution is calculated, which is shown in (Figure 1).

An analysis of the data shows which hydroxide complexes of aluminum exist at a given pH value. So, for example, at pH = 12, the only ion \( Al(OH)_5^- \) is the most prevalent, and the other hydroxide complexes exhibiting minimal solubility will exist at approximately pH = 6 ÷ 8. It is more convenient to present the data from Figure 3 in the form of a Brown and Ekberg diagram [24], which shows the regions of existence of aluminum (III) ions of the form \( Al(OH)_n^{(3-n)-} \) depending on the pH and concentration of aluminum compounds (Figure 2).

For each reaction, the dependence of the logarithm of solubility on pH was calculated, and a total curve was obtained. These dependencies are presented in Figure 3.
The data obtained show that at pH = 6.7, there is minimal solubility. This pH value corresponds to the point of zero charge - pH_{pzc}, which corresponds to the absence of charge on the surface of Al_{2}O_{3} particles. At pH < pH_{pzc}, Al_{2}O_{3} particles have a positive charge, and at pH > pH_{pzc}, they have a negative charge. This charge is due to both the dissociation of OH– groups and the absorption of free OH– ions. The maximum rate of formation of the solid phase of aluminum hydroxide, respectively, will be observed at the point of zero charges (pH_{pzc}).

The obtained theoretical conclusions are generally in good agreement with experimental data. Thus, by lowering the pH of the solution by various methods (including electrodialysis), it is possible to achieve the complete precipitation of aluminum hydroxide. However, in some sources, there are conflicting data on the value of pH_{pzc} for aluminum hydroxides. This fact is associated with various methods for its preparation and, accordingly, with a different structure of its surface.

In, the Rayleigh turbidity of hydrolyzed aluminum solutions containing various amounts of bound hydroxide ions per aluminum ion was measured [19]. At the same time, the formation of multinuclear aluminum complexes is shown. It was found that before the deposition, the size of the formed multinuclear hydroxo complexes reaches at least eight or nine aluminum atoms per one isopolycation. It is unlikely that any solutions other than those with an OH/Al ratio of 1.0 correspond to equilibrium conditions.

Based on the presented data, it can be assumed that the method of its synthesis will have a significant influence on the properties of the resulting aluminum hydroxide. In particular, the features should depend on the order and rate of the merging of the reagents. So, when pouring an alkali solution into an aluminum salt solution (direct synthesis order), structures with an excess positive charge and, accordingly, more prone to anion exchange should preferably form. When an aluminum salt solution is infused into an alkali solution, anionic forms of hydrated aluminum oxide are preliminarily created, which lead to the formation of structures with an excess negative charge. Such structures should be more prone to cation exchange. An increase in the rate of interaction of reagent solutions should lead to the formation of metastable forms corresponding to the initial structure of aluminum oxyhydrate ions. Further aging of the formed sediments should change from the structure; however, this process can be complicated due to the slow rate of mass transfer processes in the formed solid phase.

This effect was confirmed in, where it was reported that a solution of 1 M aluminum salts at 1<OH/Al<2.5 requires about six months to balance the equilibrium at room temperature and about 1 hour at 70 °C [19-78]. Small-angle X-ray scattering data show the formation of [Al_{12}(AlO_{4})(OH)_{12}(H_{2}O)_{12}]^{7+}, cations, although the formation of a certain number and smaller units cannot be ruled out. Other types of solutes that have been proposed to explain the data are [Al_{12}(OH)_{24}]^{7+}; [Al_{12}(OH)_{3}]^{3+}; [Al_{12}(OH)_{3}]^{3+}; [Al_{12}(OH)_{3}]^{3+}, [Al_{10}(OH)_{24}]^{6+}, [Al_{8}(OH)_{24}]^{6+}; [Al_{12}(OH)_{3}]^{7+}; [Al_{7}(OH)_{16}]^{5+}, [Al_{10}(OH)_{24}]^{6+}, [Al_{3}(OH)_{32}]^{7+} [11]; [Al_{12}(OH)_{3}]^{7+}; [Al_{7}(OH)_{16}]^{5+}, [Al_{10}(OH)_{24}]^{6+}, [Al_{3}(OH)_{32}]^{7+} [22, 78]. It was also noted that the nature of the initial cation in the solution determines the form of aluminum hydroxide, which further crystallizes from the solution (hydrargillite or bayerite) [79].

The stoichiometry of the complex [Al_{12}(AlO_{4}) (OH)_{12}(H_{2}O)_{12}]^{7+} ion was confirmed by X-ray studies [24]. This study showed that this complex ion has the formula [Al_{12}(AlO_{4}) (OH)_{24}(H_{2}O)_{12}]^{7+}, which is equivalent [Al_{12}(OH)_{3}]^{7+}. In this variety of complex ions, 12 aluminum atoms are in the centers of 12 oxygen octahedra AlO_{6}, and one aluminum atom is in the aluminum-oxygen tetrahedron AlO_{4}. In its structure, shown in Figure 4 A, there are also 12 water molecules bound to ions Al^{3+} [80-89]. A similar structure was identified for a very stable mixed metal hydroxide compound of the formula [GaO]_{6}[Al_{12}(OH)_{3}]^{7+} [90]. This mixed compound demonstrates the same structure as ions containing only aluminum. In [100], the formation of an even more abundant cation with the Keggin structural motif [Al_{12}O_{3}(OH)_{26}(H_{2}O)_{26}]^{8+} was found. The structure of such a cation is shown in (Figure 4b).

Aluminum hydroxide Al(OH)₃, often found in the form of a gel-like material. In crystalline form, it is obtained by supplying CO₂ to an alkaline solution of an alkali metal aluminate at 80 °C. In nature, aluminum hydroxide is most often found in the form of gibbsite, as well as in the form of other structures [26]. Various modifications of aluminum three hydroxide Al(OH)₃, are described in the literature. Of these, the most common are gibbsite (hydrargillite), bayerite, and nordstrandite. Aluminum monohydroxide AIOOH is known in the form of two modifications: diaspores and boehmite [27]. In addition to these crystalline phases, the literature contains information on a few other aluminum hydroxides. However, these forms are not well understood. Therefore, let us dwell on the crystal structure of only gibbsite, bayerite, nordstrandite, diaspore, and boehmite.

The neutralization of a sodium aluminate solution with carbon dioxide is recommended to obtain pure phases of aluminum hydroxide. The mechanism of this process is expressed by the following scheme [27]:

\[
\text{Sodium Aluminate Solution} + \text{CO}_2 \rightarrow \text{Amorphous Aluminum Hydroxide} \xrightarrow{20\,\text{°C}, \, pH<} \text{Gel - shaped boehmite} \xrightarrow{50\,\text{°C}, \, pH>7} \text{Bayerite} \xrightarrow{20\,\text{°C}, \, pH>12} \text{Well Crystalized Boehmite}
\]
It was also established that Al(OH) could be obtained in the form of boehmite by adding ammonia to a boiling solution of aluminum salt or from a suspension of gibbsite in water in an autoclave at a temperature of 300 °C [28].

In several works, it was found that natural and synthetic gibbsite always contains Na⁺ ions in an amount of 0.2–0.3%. Washing with acids does not reduce the amount of sodium in the solid phase. Although many authors argue that without alkali metal ions, the structure of gibbsite cannot exist at all, but this effect has not yet been rigorously proved [10, 27].

In contrast to gibbsite, there is no question for bayerite about the possibility of stabilization of its structure by alkali metal ions. In crystalline boehmite, AlO(OH) → Al—O—Al group chains combine with the oxygen atoms of the OH groups of the neighboring chain. According to, bayerite has a triclinic structure [27]. As a result of such a distortion of the structure, it turns out that the minimum O-O distance between oxygen atoms in two adjacent layers in bayerite is more significant (313 pm) than in gibbsite (282 pm).

An exciting pattern linking the acid-base properties and the structure of hydrated oxides in the solid-state was discovered by Megaw H.D [29]. With a small polarizing effect of the cation, OH-groups are packed as neutral groups, and a significant distance remains between the centers of oxygen atoms. In another extreme case, with a significant polarizing effect of the cation, a strong attraction arises between the OH-groups, as a result of which they approach each other. Table 1 below shows the distances between oxygen atoms illustrating this effect [29].

### Table 1: Comparison of the distance between oxygen atoms (pm) in the structures of various hydrated oxides

| Material | O—H...O Bond Length (pm) |
|----------|--------------------------|
| LiOH     | 265                      |
| NaOH     | 282                      |
| Ca(OH)₂  | 281                      |
| Mg(OH)₂  | 281                      |
| Al(OH)₃  | 283                      |
| B(OH)₃   | 281                      |

The O—H...O bond length in hydrated oxides with acidic properties averages 265 pm. Thus, bayerite should exhibit more basic properties than gibbsite. Therefore, hydrated alumina with a bayerite structure will be easier to peptize under the influence of acids, and gibbsite - under the action of alkalis.

Alum earth Al₃O₃, is obtained by dehydration of Al₂O₃(OH) or Al(OH)₃ into at least six types, of which α-Al₂O₃ (corundum) is a form formed only at high temperature. α-Al₂O₃ is unlimited metastable at ordinary temperatures [24,30]. In α-Al₂O₃, oxygen ions form a hexagonal close-packed array in which Al³⁺ ions are distributed symmetrically among octahedral sites [31]. Gibbsite crystals give a sheet structure based on a double layer of closely packed hydroxyl ions, with Al³⁺ being in two-thirds of the octahedral positions [32]. Less commonly, the form of Al(OH)₃, nordstrandite, is obtained by controlling the crystallization of a gel-like hydroxide by the addition of a chelating agent, ethylene glycol.

There are various forms of mixed oxides; aluminum and different metals are available. Al³⁺ in octahedral positions or occupy empty tetrahedral positions. A classic example of such a mixed oxide is the MgAl₂O₄ spinel. The spinel structure was studied by photoelectron spectroscopy [33]. Vibrational and solid-state NMR methods are also useful for studying the structure of aluminate compounds [34-36].

The simplest mixed alumina containing alkali metals is sodium aluminate NaAlO₂. It is obtained by heating Al₂O₃ with sodium oxalate, sodium carbonate, or caustic soda at 800 ÷ 1000 °C. Sodium aluminate forms white crystals of rhombic crystal system, cell parameters a = 537 pm, b = 521 pm, c = 707 pm, α = 4. Several more compounds of the sodium aluminate type are known in the Na₃O-Al₂O₃ system. So, sodium aluminate Na₃AlO₃ forms a rhombic structure: it contains a discrete chain of tetrahedra AlO₄ in which R Al-O = 176.1+178.9 pm. The triclinic sodium aluminate Na₃AlO₂ contains a ring structure obtained from six tetrahedral AlO₄ groups connected by oxygen bridges in an infinite chain, while Na₃AlO₃ contains discrete chains of five AlO₄ tetrahedra distributed at the angles [22, 37, 38]. NMR spectroscopy of Al atoms, as applied to polycrystalline aluminates, shows characteristic chemical shifts for AlO₄, AlO₃, and AlO₂ polyhedra [36]. The study of aluminosilicate solutions carried out in, showed that technological processes also ensure the formation of Si–O–Al bonds in Al₂O₃ groups [23]. In the structure of Cs₂Al₂O₄(OH)₈, the anion consists of two AlO₄ tetrahedra separated by one oxygen atom [39]. The complex anions [AlO(OH)]₃⁺ and [Al₂O(OH)₃]⁻, are composed of tetrahedral groups distributed uniformly, their structures were determined by X-ray diffraction in the study of barium aluminates [40, 41]. The basic aluminum sulfate,
The hydrated aluminum cation \([\text{Al(OH}_2\text{)}_6]^{3+}\) has an octahedral shape. Below are some crystals in which it occurs (the average Al-O distance is indicated in parentheses): NaAl(SO\(_4\))\(_2\)\(\cdot\)12H\(_2\)O (187.8 pm); Mellite, also called “Honey Stone”, which is an aluminum salt from mellitic acid, with the chemical formula Al\(_2\)C\(_6\)(COO)\(_6\)\(\cdot\)16H\(_2\)O [45] (187.2 pm); Al\(_2\)CuCl(SO\(_4\))\(\cdot\)14H\(_2\)O (187.8 pm) [46]. These crystals were also studied by neutron diffraction and 1H NMR, which confirm the presence of \([\text{Al(OH}_2\text{)}_6]^{3+}\) and allow the localization of hydrogen atoms of water molecules in the coordination sphere [47]. According to Raman scattering data, the vibrational regimes of the \([\text{Al(OH}_2\text{)}_6]^{3+}\) ion in crystals of various alum were determined as follows \(\nu_1 = 542\), \(\nu_2 = 473\), \(\nu = 347\) cm\(^{-1}\) [48]. In the Raman spectra of single crystals of the [Al(OH\(_2\))\(_2\)]Cl\(_3\) salt, the \(\nu_\text{int}(\text{Al-O})\) vibrational mode takes place at a frequency of 524 cm\(^{-1}\) [49]. The aluminum cations \(\text{AlO}^+\) isolated from HF solutions, in the form of BF\(_4^-\) or SbF\(_6^-\) salts, show \(\nu(\text{Al-O})\) near 1050 cm\(^{-1}\) [50].

Raman bands of highly concentrated solutions of Al(NO\(_3\))\(_3\) are consistent with \([\text{Al(OH}_2\text{)}_6]^{3+}\) and NO\(_3^-\) in the form of solvent-separated ion pairs [51]. \(^{1}H\) NMR can distinguish the protons of the hydration shell and the mass of water. \(^{27}Al\) NMR signals distinguish between \([\text{Al(OH}_2\text{)}_6]^{3+}\) ions from other species such as \([\text{Al(OH}_2\text{)}_3\text{(SO}_4\text{)}_3]^{3+}\) in sulfate solutions, or \([\text{Al}_2\text{(OH)}_2\text{(OH}_2\text{)}_4]^{4+}\) and more highly polymerized complexes, which are formed during aging of aqueous solutions of aluminates [52]. According to Raman scattering data [53] and NMR data [54-64] for the cation \([\text{Al}_2\text{(OH)}_2\text{(OH}_2\text{)}_4]^{4+}\), formed soluble sulfate and chloride, and is stored in an aqueous solution. In the presence of HC\(_1\), it decomposes into smaller particles, but with the addition of alkalis, particles with higher molecular weight can be formed. In highly alkaline solutions of aluminum compounds, the predominant species are mononuclear ions \([\text{Al(H}_2\text{O)}_2\text{(OH)}]^{+}\), \([\text{Al(OH)}_2]^{+}\), and binuclear ions \([\text{Al}_2\text{(OH)}_2\text{(OH)}_2]^{3+}\) [65-68].

The UV spectra of aqueous solutions of AlCl\(_3\), Al(CIO\(_4\))\(_3\), Al(NO\(_3\))\(_3\), and Al(SO\(_4\))\(_3\) also confirm the predominance of hexa-aqua-aluminum cation in their structure. The presence of an absorption band at 240 nm is due to charge transfer between the internal coordination sphere and the solvent: \([\text{Al(H}_2\text{O)}_2]^{3+}\) → \([\text{Al(OH)(H}_2\text{O)}_2]^{2+} + \text{H}^+\)

It was also found that chloride and perchlorate anions do not replace the intrasphere aqua groups in hexa-aqua aluminum ions. In this case, the sulfate anion, entering the internal coordination sphere, caused a decrease in this line, up to its complete disappearance. Equivalent conductivity measurements showed that the sulfate anion at concentrations above 0.50 M exhibits stronger ion-pairing than chloride, nitrate, and perchlorate. This effect confirmed the conclusion that the sulfate anion can enter the internal coordination sphere of Al\(^{3+}\) [69].

To elucidate the stereochemical limitations associated with the structures of aluminum hydrates, the energies were calculated using the molecular orbitals method for complex ions of the composition \([\text{Al(OH}_2\text{)}_n]^{3+}\) (n=1÷7), and hydroxo complexes \([\text{Al(OH)}_n]^{3+}\), \([\text{Al(OH)}_2]^{3+}\) or \([\text{Al(OH)}_3]^{3+}\) [70, 71]. Calculations were performed for H\(_2\)AlOH\(_2\) and (H\(_2\)AlOH)\(_2\) molecules using the molecular orbitals method [72]. No confirmation of the existence of such molecules has been obtained. However, small molecules of this kind can sometimes be detected using matrix isolation techniques. For example, in the interaction of aluminum atoms with H\(_2\)O molecules under extreme conditions, the formation of a compound of the type HAIOH occurs, while heavier metals of group III form M · H\(_2\)O\(_2\) adducts [73].

There are several different modifications of hydrated alumina. The most widely used form is pseudo-boehmite. Pseudo boehmite is one of the most mobile types of hydrated aluminum oxides in terms of its interaction with acids and alkalis. The primary way to obtain pseudo-boehmite in existing plants is the reprecipitation of aluminum hydroxide, which consists in dissolving hydargillite in acid or alkali, followed by neutralization and precipitation of a hydrated gel (hydrogel). The obtained hydrated gel, under certain aging conditions, at a pH of 7.5–9.0 and a temperature of 20–70 °C, turns into pseudo-boehmite [74]. The aging process of a hydrogel consists of gradual dehydration. In this case, the formation of bridging bonds through the hydroxo group, with the participation of free electronic oxygen pairs. These processes are called olation, and the resulting groups are called in groups –O\(^{\\text{OH}}\). The reaction of the formation of olic compounds from hydroxo- or aqua complexes is sometimes called olation, and the process of producing oxo compounds from hydroxo-, aqua, or olic compounds is called oxidation [75]. The formation of olic compounds (olation) and their transformation into oxo compounds (oxolation) is facilitated by an increase in temperature and concentration of the solution, as well as its long-term exposure. The reverse processes of the conversion of olic compounds to moneric ions proceed very slowly, while the transformation of oxo groups to olic is almost impossible [76].

The processes of oxolation, with the formation of bridging o xo bonds or o xo groups, occur in parallel. The aging process is completed by subsequent crystallization, with a change in the structure of molecules according to the following scheme:

\[\text{Al}(\text{H}_2\text{O})_2^{3+} \rightarrow \text{Al(\text{OH})(H}_2\text{O})_2^{2+} + \text{H}^+\]
The transition rate of each step is determined by the pH of the medium, temperature, and time [74]. The formation of pseudo-boehmite occurs through crystallization in the volume of amorphous spherical particles, the basis of which are mono- and binuclear hydroxo complexes of aluminum, followed by the formation of fibers or needles by the mechanism of “oriented growth” [77]. Moreover, to start crystallization, it is enough that dehydration of 20–40% of amorphous hydroxide occurs, which explains the phase inhomogeneity of pseudo-boehmite.

With aging, the fraction of hydroxosalts decreases, and the content of structural water decreases to 1.5–1.7 mol $H_2O$ / mol $Al_2O_3$. The presence in a pseudo-boehmite of a mixture of two or more morphological forms (amorphous fibrous, finely dispersed, needle-shaped) greatly complicates, and sometimes distorts, the results of studying the formation of the porous structure of active alumina.

The work is devoted to a theoretical study of the chemistry of the phenomena of solvation of aluminum salts [81]. It discussed such fundamental aspects as the structural characteristics of complex aluminum ions, hydrolysis, acidity, the structure of solvates, the effect of countercations, and chemical stability. Static calculations, supplemented by a shielding model, were used to study a few possible planar and cyclic configurations of binuclear, trinuclear, tetranuclear, and pentahedral aluminum complexes. Molecular dynamics calculations have been performed to study their behavior in aqueous media. Structural analysis of the hydrolysis products of $AlCl_3$∙$6H_2O$ was carried out. Binuclear, trinuclear, and tetranuclear aluminum hydroxo-chlorine complexes have been studied in both the gas and liquid phases. The chemistry of aluminum sulfate complexes was studied. The hydrolysis products of $AlCl_3$∙$6H_2O$ in the presence of sulfates were revealed. The structural characteristics of the hydrolysis products of $Al_2(SO_4)_3$∙$18H_2O$ were also studied. Additional structural information was obtained from the results of mass spectroscopy and using computational methods. The discovered cationic structures turned out to be like those formed during the hydrolysis of aluminum chlorohydrate. The hydrolysis, stability, and dynamics of binuclear and pentahedral aluminum hydroxo-chloro-complexes in aqueous media were studied. During the simulation, several spontaneous associative hydration reactions were detected in the first hydration shell of the complexes. It was found that binuclear aluminum hydrochlorides are stable in solution, while penta-nuclear aluminum complexes underwent significant topological changes. The calculations performed by the author made it possible to explain some anomalies found in the experiments. Our analysis made it possible to develop methods for the synthesis of inorganic ion-exchange materials based on hydrated aluminum oxides with predominantly anion-exchange properties.

The Experimental Part

Methods of Synthesis and Research of Ion-Exchange Properties of Materials

Precipitation of hydrated alumina samples was carried out at fixed pH values. Two variants of the reaction of the interaction of reagents were implemented: direct and reverse order of reagent draining. A direct procedure for draining solutions was provided by adding a 0.1 M $NaOH$ solution to a 0.1 M aluminum sulfate solution. The reverse order of draining the solutions involved adding 0.1 M solution of $H_2SO_4$ to 0.1 M sodium aluminate solution. The resulting precipitates were washed with water and granulated using the method of drying in air at room temperature, followed by dehydration. Decrystallization is the destruction of large xerogel particles after soaking in water, due to capillary forces. Samples with additives of various ions were prepared as follows. Additives of tungsten ions $W(VI)$ were introduced into a solution of sodium aluminate or $NaOH$ in the form of a $NaWO_4$ salt. Additives of Ti(IV) and Zr(IV) ions were introduced into solutions of $AlCl_3$∙$6H_2O$ or $Al_2(SO_4)_3$∙$18H_2O$, respectively, in the form of their sulfates or chlorides. Further precipitation of the mixed hydroxides was carried out by adding a $NaOH$ solution. The study of the ion-exchange properties of materials in static conditions was carried out using sealed vessels that were placed in a rotating cassette (60 rpm) for mixing. In all experiments during the synthesis of sorbents, constant pH value was maintained using a system of automatic control of the flow of reagents based on an automatic titrator. For granulation of sorbents based on mixed hydroxides, a drying method with subsequent dehydration was also used. To obtain monoionic forms of sorbents, they were treated with 0.1 N $NaOH$ solution and then with water to remove $Na^+$ ions.

The acid-base properties of the synthesized materials were studied both in static and dynamic conditions. In the static version, sealed vessels were used, which were placed in a rotating cassette (60 rpm) for mixing. Mixing was carried out until equilibrium was established between the solid and liquid phases. In dynamic conditions, the methods usual for the column method were used. In all experiments, when studying the ion-exchange properties of synthesized materials, special measures were taken to prevent the absorption of $CO_2$ solutions from the air.

The ion-exchange properties of the synthesized materials were studied by potentiometric titration using 0.1 M HCl or $NaOH$ solutions while stabilizing the ionic strength of the solutions ($I = 0.1$, $NaCl$ correction. The calculation of dissociation constants of exchange centers was carried out according to the method described in [82]. To calculate the dissociation constants, we used the equation of the titration curve, which had the following form:
This expression describes an ion exchanger with a discrete set of exchange centers. As noted in [82], equations (2) possess the property of charge symmetry. It is valid both for proton donors and for proton acceptor centers. For proton-acceptor centers, the comparison of the sorption isotherm is similar. In this regard, equation (2) can be applied both to cases of cation exchange and to anion exchangers. For calculations, the method of minimizing the mean-square residual functional was used [82]. Root mean square functional is a function that has several local extrema. For this system, we used an algorithm for coordinate-wise scanning of the functional on a given number of points with the choice of the best point for a sequence of values.

Based on the exchange capacity and the size of the absorbed ions, the specific surface area \( S \) can be calculated, and from it, the average diameter \( d \) of a hydrated aluminum oxide particle:

\[
d = \frac{6}{\rho S} = \frac{C}{E_g N_A \pi R^2_{An^-}}
\]

(3)

Where: \( d \) - diameter, \( nm \); \( C \) - is a constant equal under these conditions to \( C = 2500 \text{ nm}^2/\text{g} \); \( E_g \) - total anion exchange capacity; \( N_A \) - Avogadro’s number; \( R_{An^-} \) - radius of anions involved in ion exchange.

When calculating the particle diameter \( d \) of aluminum hydroxide, it is assumed that the forming particles of aluminum hydroxide are monodisperse, close to a spherical shape, and have a density \( \rho \) of gibbsite.

**A technique for studying the structure of amorphous materials by diffuse x-ray scattering**

The structure of the obtained samples of hydrated alumina was studied by diffuse X-ray scattering [86]. Diffuse X-ray scattering was studied on amorphous samples by reflection from the sample, on a DRON-4-07 X-ray diffractometer using CuKa, CoKa, FeKa radiation with a monochromator on the primary beam. The fluorescence radiation was filtered out by an amplitude differential discriminator. The value of incoherent scattering was calculated theoretically by the formula \([83,86]\):

\[
I_{IS}(s) = \frac{1}{B^2} \left[ B^2 - \sum_j f_j(s) \right]
\]

\[
B = 1 + \frac{2\hbar l}{mc} \left( \frac{\sin \Theta}{\lambda} \right)
\]

\[
s = \frac{4\pi \sin \Theta}{\lambda}
\]

(1)

Results and Discussion

The amphoteric properties of aluminum hydroxide limit the pH range of its deposition to approximately 5.0–9.5 [85]. It was experimentally established that the total exchange capacity (TEC) of hydrated alumina concerning the Cl\(^-\) ion in this interval weakly depends on the pH of the deposition (pH\(_{se} \)):[86]; for different samples, its values are in the range 1.6–2.1 mol/kg.

It can be assumed that during precipitation from a solution of aluminate, where aluminum is predominantly in the form of \([Al(H_2O)_n(OH)_4]^{-}\) ions, the formation of a sorbent containing a certain amount of aluminum with a coordination number of 4 is possible [90]. When precipitating from an \(Al_2(SO_4)_3\) solution, where aluminum is in a state with a coordination number of 6, a sorbent is formed containing Al\(^{3+}\) ions in an octahedral configuration; this situation corresponds to the facts described in [61, 63, 89, 90]. Based on the classification of inorganic acids, according to Ricci, we can conclude that aluminum exhibiting coordination number of 4 should produce acids with a lower pK\(_a\) value, unlike aluminum with a coordination number of 6 [88].

Since the synthesized materials are amorphous substances, the diffuse X-ray scattering method was used to study their structure. A study of diffuse X-ray scattering by these samples indicates the proximity of their structural motive. The results of structural studies are presented in Figure 5.
The crystal structures of gibbsite, bayerite, and nordstrandite are like each other and are based on a double layer of hydroxyl ions packed in an approximately densest manner. Aluminum atoms are in octahedral coordination, occupying, however, only 2/3 of the possible positions [29]. The crystal lattice structure of gibbsite Al(OH)$_3$ is shown in Figure 6.

The layers are held together by hydrogen bonds arising between the ions OH$^-$. Moreover, each hydroxyl group of one layer is located against the OH$^-$ group of the next layer. The result is a monoclinic structure with the following lattice parameters $a = 862.4$ pm, $b = 506.0$ pm, $c = 972.0$ pm, $\beta = 94^\circ 34'$, $z = 8$ [10].

The OH---OH distances calculated from the curves of the radial distribution of atomic density (RDAD) are 300–340 pm and the population of the first coordination sphere of aluminum is close to 6. These values, as well as the interplanar distances for materials, determined from the curves of the radial distribution of atomic density, in the best way, correspond to gibbsite [10]. The calculation of the unit cell parameters of aluminum hydroxide samples according to the model with the atomic packing in the lattice characteristic of gibbsite shows that the synthesized materials have a more amorphized structure than that of individual gibbsite (Table 2).

These data once again confirm the assumption of the maximum loosening of the structure of aluminum hydroxide upon receipt in the pH range close to 8.

A change in the order of draining of solutions during the deposition of hydrated alumina has a weak effect on the structure of the products formed. The pK values of their OH exchange groups and the total exchange capacity (Figure 7).
Table 2: Parameters of unit cells of gibbsite gratings and aluminum hydroxide samples obtained at pH = 9.0

| Material                               | Space group | z  | a, pm | b, pm | c, pm | β  |
|----------------------------------------|-------------|----|-------|-------|-------|----|
| Gibbsite [10]                          | P2_1/n      | 8  | 868   | 507   | 972   | 94.5°|
| Aluminum hydroxide, pHs=9.1            | P2_1/n      | 8  | 887   | 567   | 911   | ~90° |
| Aluminum hydroxide, pHs=7.8            | P2_1/n      | 8  | 922   | 606   | 1001  | ~90° |
| Aluminum hydroxide, +9.1 at.% Ti(IV)   | P2_1/n      | 8  | 908   | 581   | 986   | ~90° |
| Aluminum hydroxide, +20.0 at.% Ti(IV)  | P2_1/n      | 8  | 915   | 588   | 1002  | ~90° |

One of the reasons for the difference in the acid-base properties of the synthesized materials is the different packing density of atoms in the solid phase. As noted in [29,93], the O–H...O distance in hydrated oxides with acidic properties is 255 pm in alkaline from 330 to 360 pm (see Table 1). In crystalline aluminum hydroxide, this distance is 279 pm [29]. The O–H...O distance in the materials synthesized by us is 300±20 pm for hydrated alumina obtained at pH = 9.1 and 320±30 pm at pH = 7.8. From these data, it follows that amorphous hydrated alumina should exhibit more basic properties than crystalline. A comparison of the pKa values for the dissociation of OH-groups of crystalline Al(OH)₃ - pKₐ = 8.86 [94] and aluminum hydroxide obtained at pH = 7.8 - pKₐ = 9.75±0.08 confirms the correctness of the above assumption.

When studying the effect of pH deposition on the anion exchange properties of hydrated alumina, it was found that this dependence has a maximum (Figure 8). This phenomenon, as shown by structural studies (Figure 5), is associated with different ordering of the structure of hydrated alumina arising from precipitation from solutions with different pH. The maximum exchange capacity corresponds to the minimum duration of the short-range order zone.

Potentiometric titration curves of aluminum hydroxide samples obtained at pHₐ = 7.8 using the “direct” and “inverse” methods indicate that they have mainly the main function: the total exchange capacity of the precipitates obtained for Cl⁻ and Na⁺ ions is 2, respectively. 2.0±0.2 and 0.33±0.05 mol/kg (see Fig. 7). However, in the hydrated alumina sample obtained by the “direct” method, the fraction of more basic OH groups with pKₐ = 5.97 ± 0.04 and pK₉₁ = 5.14 ± 0.06 increases. Also, the acidity of OH groups participating in the exchange of cations pK₉₁ = 9.75 ± 0.08 and pK₉₁ = 9.30 ± 0.07, respectively, decreases slightly. For this reason, the anion-exchange capacity of the sample reaches 0.5–0.8 mol Cl⁻/kg already in solutions with a reaction of the medium close to neutral. In accordance with formula (3) and based on the obtained anion exchange capacity, it is possible to estimate the size of aluminum hydroxide particles that form its nanostructured motif. This estimate gives a value of 19 nm.

Figure 7: Potentiometric titration curves of aluminum hydroxide samples obtained with the “direct” (1) and “reverse” (2) order of solution draining.

1 exp b and 2 exp b — experimental data for the anion-exchange part of the curve; 2 exp a and 2 exp b — experimental data for the cation exchange part of the curve; 1a and 2a are the calculated data for the cation exchange part of the curve; 1b and 2b are the calculated data for the anion-exchange part of the curve. The calculated values of the constants of acid (a) and basic (b) dissociation: 1 - pKₑ =9.75±0.08; 2 - pKₑ = 9.30±0.07; 1 - pK₉₁ = 5.97±0.04; pK₉₂ = 8.79±0.06; 2 - pK₉₁ = 5.14±0.06; pK₉₂ = 8.69±0.07; The corresponding values of the ion-exchange capacity of the material: 1 - Eₑ =0.40±0.01; 2 - Eₑ = 0.37±0.01; 1 - E₉₁ = 0.59±0.02; E₉₂ = 1.56±0.04; 2 - E₉₁ = 0.123±0.008; E₉₂ = 2.16±0.06. Indices 1 and 2 refer to the corresponding types of ion exchange centers.

Figure 8: The effect of pH deposition of hydrated alumina on its anion exchange capacity for Cl⁻ ions.

The well-known phenomenon can also be associated with a different course of the deposition of hydrated alumina with a change in the order of the merging of solutions. The hydrolysis of acidic solutions of aluminum salts (the “direct” method for the synthesis of hydrated aluminum oxide) leads to the formation of polycationic forms of aluminum, and the hydrolysis of solutions

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of alkali metal aluminates—polyanionic [11, 12, 21]. The conditions of the “direct” method for the synthesis of hydrated alumina contribute to the inclusion of an additional number of anions present in the solution, which probably enhances the anion-exchange function of hydrated alumina but does not significantly change its structural motive.

The experiments show that it is more appropriate to use hydrated alumina as an anion exchanger. For its synthesis, it is preferable to use the “direct” order of draining the solutions, providing pHs = 8.5±0.5. Also, attention should be paid to the fact that an increase in the precipitation pH leads to an increase in short-range order—curves 2 and 3 in Figure 5. Comparing these data with the composition of the liquid phase of aluminum salt solutions depending on pH (Figure 1), it is fashionable to conclude that more alkaline media during the precipitation of hydrated alumina, predominantly polyanionic forms are formed. It can be assumed that they are more prone to ordering during precipitation. Also, it was previously noted that the presence of sodium ions in the solid phase helps to stabilize the Gibbsite phase [10, 27]. However, these effects have almost no effect on the ion-exchange properties of the synthesized samples of hydrated alumina.

A more pronounced effect on the ion-exchange properties of hydrated alumina is the introduction of doping ions into its composition. The ions Ti(IV), Zr(IV), and W(VI) were chosen as alloying ions after analysis of their crystal-chemical properties [13, 84]. Their introduction into the hydrated alumina was carried out at the stage of precipitation by adding the corresponding salts to an aluminum chloride solution (TiCl₄, ZrOCl₂) or a NaOH solution (Na₂WO₄). The “direct” method of draining solutions was used, pH₁=8.5±0.5. Granulation of sediments was carried out by drying them in the air at room temperature.

We consider the effect of ion additives on the structure of hydrated alumina using the example of Ti⁺ ions since the latter have led to the maximum effect in terms of increasing the exchange capacity. When analyzing the curves of the radial distribution of atomic density in these materials (Figure 5), a trend of increasing disorder in the structure attracts attention, with the amount of additive increased.

The curves reflecting the dependence of the total exchange capacity of hydrated alumina for ion Cl⁻ (sorbiv - 0.1 M HCl) on the content of the dopant in it are extreme (Figure 9). For each additive, there is an optimal concentration range in which the material has a maximum value of the total exchange capacity, which can be used to improve the sorption properties of hydrated alumina. The best results are achieved by doping hydrated alumina with Ti(IV) ions. For this reason, these materials have been investigated in more detail.

To assess the effect of the addition of Ti(IV) ions on the acid-base properties of the synthesized materials, potentiometric titration curves of the synthesized aluminum hydroxide samples containing 20 at.% Ti (IV). An analysis of the data indicated an increase in the content of OH exchange groups in this material compared to the initial aluminum hydroxide (Figure 10). The presence of a Ti(IV) ions in the precipitate, which has a higher electronegativity than Al(III), is likely to cause a slight increase in their values pKₐ₁ = 7.30±0.02, pKₐ₂ = 9.25±0.01, compared with similar values for hydrated alumina - pKₐ₁ = 5.97±0.04; pKₐ₂ = 8.79±0.06. However, in solutions with pH<6, the anion exchange capacity of the doped sample remains 2-4 times higher than the first hydrated alumina, which makes it more promising for practical use. It should be especially noted that in this case, the model of an ion exchanger with a discrete set of exchange centers does not quite correctly describe the experimentally obtained potentiometric titration curves.

Figure 10 shows that the calculated curve and experimental points in some areas deviate quite strongly from each other. Also, at the point of maximum inflection, the experimental dependence has a steeper slope than the calculated one. As noted in [82], the broadening of the distribution function of exchange centers over the exchange constant leads only to a decrease in the slope of the titration curve at the point of maximum inflection. The deviation obtained can only be explained by the effect of sorbed ions on neighboring exchange centers due to the induction effect resulting from significant electron delocalization and the formation of (p→d) conjugations [95]. As is known, the delocalization of electrons leads to significant induction effects [96] and an increase in the radius of action of impurity centers [97], which can be fully justified as ions absorbed by the sorbent as a result of the ion exchange process.

Figure 9: The dependence of the total exchange capacity (E, mol Cl⁻/kg) of hydrated alumina on the content of doping additives Ti(IV) (1), Zr(IV) (2) and W(VI) (3) in the composition of the solid phase sorbent.

α is the concentration of doping ions, at. %.
Figure 10: Potentiometric titration curve of a sample of hydrated alumina with additive 20 at. % Ti(IV). $pK_{b1}=7.30\pm0.02$, $pK_{b2}=9.25\pm0.01$.

Non-binding lone pairs have high energies (they correspond to significant diagonal elements of the Fock operator), especially if they are pure π-orbitals, while the charge transfer energy to valence was loosening molecular orbitals increases. In this case, the coefficient for charge transfer becomes large in magnitude, which leads to significant “tails” of self-consistent molecular orbitals of unshared pairs on loosening vicinal molecular orbitals, that is, to any paired functional groups or atoms attached to two adjacent atoms. The “tails” of the molecular orbitals of such molecules have substantial weights and lead to bonds comprising three or four atoms. In connection with this effect, one can expect a change in the acid-base properties of the active exchange centers of hydrated oxides upon the introduction of heavy sorbed ions into their structure. In this case, it can be assumed that the incorporation of the sorbed ions into the structure of aluminum hydroxide leads to an increase in the basicity of exchange OH-groups adjacent to the sorbed ion, and, accordingly, to the rise in the steepness of the potentiometric titration curve as compared to its classical form.

A study of the structure of hydrated alumina samples doped with Ti(IV) ions shows that an increase in the content of doping ions in hydrated alumina leads to a decrease in short-range order (see Figure 5) and to the rise in the size of its unit cell parameters (see Table 2). Particularly sensitive to changes in the concentration of the additive is parameter $c$, which is related to the distance between the layers in the structure of gibbsite [10]. As can be seen from Figure 5 and Table 2, the disordering of the structure of materials is accompanied by an increase in interlayer distances. Introduction to the composition of hydrated alumina more than 25÷30 at. % of Ti(IV) ions generally lead to a change in its structural motive.

These dependencies in all the samples studied are like each other, and only a slight shift in the position of the maxima is observed. Consequently, significant structural changes when varying their composition does not occur. Therefore, based on the proposed model of the structure of hydrated alumina, the unit cell parameters can be calculated using the curves of the radial distribution of atomic density in the corresponding samples. The calculated parameters are presented in Figure 11 for additions of Ti$^{4+}$ ions to the structure of hydrated alumina.

The data obtained indicate an increase in the unit cell parameters with an increase in the amount of Ti$^{4+}$ ion addition, which is usually observed during the formation of solid solutions [92]. The parameter “$c$” is particularly sensitive to changes in the amount of additive (Table 2). The detected effect indicates an increase in the distance between the layers in the formed materials, which should lead to a rise in the accessibility of sorption centers for exchange ions. With the introduction of Ti$^{4+}$ additives, in addition to increasing the availability of sorption centers, a tendency toward an increase in their quantity due to a violation of the charge balance in the sorbent matrix may appear. Based on the data obtained, it can be concluded that the addition of Ti$^{4+}$ ions to hydrated alumina leads, firstly, to an increase in disorder, and secondly, to a rise in interlayer distances in the structure of synthesized materials.

The obtained results allow us to propose the following mechanism of the action of dopants, which explains the behavior of the curves in Figure 5. During the isomorphic substitution of part of Al(III) ions in the structure of hydrated alumina with higher valence ions, an excess positive charge arises in the matrix, which is compensated by the appearance of an additional amount of OH-groups capable of participating in ion exchange. An increase in the concentration of doping ions increases the content of OH-groups and the total exchange capacity of aluminum hydroxide but weakens the bond between the layers in its structure. At a particular stage, the structural motive characteristic of hydrated aluminum oxide is destroyed and, consequently, the ion-exchange properties of the material associated with it change. The action of these factors leads to the appearance of extrema on the curves depicted in Figure 9.
Another problem that arises when studying the processes of anion exchange on oxyhydrate sorbents is to elucidate the nature of the interaction of sorbed anions with an oxyhydrate matrix. These whole experiments were conducted on the sorption of acid anions of various strengths (Figure 12). Sorption was carried out against a background of 0.1 H₂SO₄, the concentration of the adsorbed anion was maintained at 0.01 M.

Figure 12: The dependence of the sorption of anions of various acids on aluminum hydroxide with the addition of 20 at.% Ti⁴⁺ ions on pKₐ dissociation of the last stage of the corresponding acids.

The exponential nature of the dependence of capacity on pKₐ, the last stage of dissociation of the corresponding acid, indicates the formation of a stronger bond between the sorbent and the sorbent ion than electrostatic interaction. The strength of this bond increases with decreasing acid strength, the anions of which are sorbed. This effect additionally confirms our assumption regarding the effects of electron delocalization during sorption of anions on an inorganic anion exchanger. The exceptions are: tetraboric acid (pK = 9), ascorbic acid (pK = 11.8), phenol (pK = 10.0) and ethylene glycol (pK = 14.1). This deviation is associated with great kinetic difficulties in the sorption of these substances by anion exchange due to the influence of the steric factor and the small constants of their dissociation.

A similar effect of an increase in the sorption of anions with a decrease in the strength of their acids was found during the sorption of anions of the chromium subgroup on iron hydroxide [91]. The authors attribute this effect to the different state of sorbed ions in an aqueous solution, namely, to the presence of the forms: \( \text{MeO}_2^{2-} \), \( \text{HMeO}_2^- \) and \( \text{MeO}_2^+ \). Moreover, they believe that the partially protonated \( \text{HMeO}_2^- \) ion has the most significant tendency to sorption on iron hydroxide. However, this model does not explain the excellent sorption of anions of simple, monobasic acids, such as formic, acetic, phenol, etc.

To explain the observed effects, we can assume the following. As is known, an increase in the pK value of acid dissociation is associated with an increase in the interaction energy of the proton and the acid residue, which is due to an increase in the electron density at the H–O bond. Therefore, a completely logical assumption is an increase in the degree of covalency of the bond of such anions with the sorbent matrix. Besides, the vacant d-sublevels of cations forming the sorbent matrix can make an additional contribution to the energy of the resulting covalent bond.

Based on these summer cottages, it can be concluded that hydrated alumina with Ti⁴⁺ ions can be used for the synthesis of anion exchangers selective for anions for which the corresponding acids have high pK values of the last stage of dissociation. These provisions were practically used in the synthesis of inorganic anion exchangers based on mixed hydrated aluminum and titanium oxides.

The results of the experiments were used to develop methods for producing inorganic anion exchangers based on hydrated alumina doped with W(VI), Zr(IV) and Ti(IV) ions, which are assigned the symbols AAW-0, AAZ-0, and AAT-0, respectively [14-18]. Table 3 shows the comparative characteristics of these sorbents obtained by the results of 5 cycles of sorption of anions from solutions of 0.1 M HCl and 0.05 M H₂SO₄. The desorption of absorbed ions was carried out with 0.1 M NaOH solution. Table 3 shows the exchange capacity of anion exchangers for Cl⁻ and SO₄²⁻ ions, respectively \( (E_{\text{Cl}}^-, E_{\text{SO}_4^{2-}}^-, \text{Mol/kg}) \) and the average loss of sorbent for one cycle of operation \( (\Delta m, \text{wt.%}) \).

Table 3: Comparative characteristics of anion exchangers based on aluminum hydroxide

| Anion exchanger | \( E_{\text{Cl}}^- \) | \( E_{\text{SO}_4^{2-}}^- \) | \( \Delta m, \% \) |
|-----------------|-----------------|-----------------|-----------------|
| Aluminum hydroxide | 2.0±0.1 | 1.0±0.1 | 2.2±0.3 |
| AAW-0 | 4.3±0.2 | 2.1±0.1 | 1.6±0.2 |
| AAZ-0 | 6.0±0.3 | 3.1±0.2 | 1.3±0.1 |
| AAT-0 | 7.8±0.4 | 3.9±0.2 | 1.1±0.1 |

The data presented in table 2 show that, compared with the initial hydrated alumina, doped sorbents have a higher total exchange capacity and better chemical stability. The findings are not limited to anion exchangers. Materials based on mixed hydrated oxides of various elements can also be used as catalyst supports. Their anion exchange properties allow a wide range to vary the number of different anions introduced into the solid phase, and, accordingly, to regulate the number and state of active centers.

Conclusions

The introduction of alloying elements exerts the most potent effect on the structure and ion-exchange properties of hydrated alumina into its composition during the deposition of ions. Isomorphic substitution of a part of Al (III) ions in the structure of hydrated alumina with ions with a higher charge (Ti(IV), Zr(IV), or W(VI)) leads to an increase in the content of OH exchange groups in the resulting material. The addition of Ti(IV) ions to hydrated alumina leads to an increase in disorder and an increase in interlayer distances in the structure of synthesized materials. By optimizing the composition of the material, it is possible to improve its sorption characteristics significantly. The AAW-0, AAZ-0, and AAT-0 anion exchanger synthesized based on hydrated aluminum...
oxide can be used to purify weakly acidic electrolyte solutions from anionic impurities in the dynamic mode of repeated sorption-desorption cycles. Estimation of the size of the primary particles of hydrated alumina gives a value of 19 nm.

The presented results allow us to draw quite far-reaching conclusions that are not limited to the synthesis of inorganic anion exchangers. Materials based on mixed hydrated oxides of various elements can also be used as catalyst supports. Their anion exchange properties allow a wide range to vary the number of different anions introduced into the solid phase and, accordingly, to regulate the number and state of active catalytic sites.

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